THE
CHEMICAL ELEMENTS
AND THEIR COMPOUNDS

BY

N. V. SIDGWICK
FELLOW OF LINCOLN COLLEGE
HON. STUDENT OF CHRIST CHURCH
FORMERLY PROFESSOR OF CHEMISTRY
IN THE UNIVERSITY OF OXFORD

VOLUME I

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PREFACE

THIS book is an attempt to discuss in detail the properties of the elements and their compounds in the light of modern ideas of atomic and molecular structure. The development of these ideas in the last thirty years has made it possible to transform 'Inorganic' Chemistry from a mass of disconnected facts into an ordered system of relations. Inorganic textbooks are, however, usually so over-burdened with the details of mineralogy, metallurgy, technical chemistry, and analysis that hardly any space is left for the considerations of the theoretical relations; while the customary exclusion of all but the simplest compounds of carbon deprives us of the help of the best-known and most important of the elements. I have tried to avoid these errors both of excess and of defect, and to give an account of the compounds of all the elements, with special reference to the general relations between them. The basis of classification is, of course, the Periodic Table, the simplest arrangement for exhibiting the relations of the elements.

Among my many obligations I must first express my indebtedness to the great Handbooks of Abegg and of Gmelin (8th edition), as well as to the Abstracts published by the British and the American Chemical Societies: to Professor Linus Pauling's *Chemical Bond* (Cornell University Press, 2nd edition, 1942): and to the *Structural Inorganic Chemistry* of A. F. Wells (Clarendon Press, 1945). The numerous valuable monographs on particular branches of the subject that I have consulted are acknowledged in their places. But I would particularly mention the *Thermochemistry* of F. R. Bichowski and F. D. Rossini (Reinhold, New York, 1936): G. W. Wheland's *Theory of Resonance and its Application to Organic Chemistry* (Wiley, New York, 1944): and the *Chemie der metall-organischen Verbindungen* of E. Krause and A. v. Grosse (Borntraeger, Berlin, 1937).

Among those from whom I have received personal help I must in the first place express my deep gratitude to Professor Linus Pauling, who, in addition to publishing a book of the first importance on molecular structure, has, especially during his residence in Oxford as Eastman Professor, given up much time to answering my questions on a whole series of points large and small, and has read and criticized in detail my introductory section. To my colleagues in Oxford, and especially to Dr. L. E. Sutton of Magdalen College, and to Mr. H. M. Powell, University Reader in Chemical Crystallography, I am very grateful for help and advice on many points. I owe more than I can say to the late Dr. R. V. G. Ewens, formerly Scholar of this College, and Reader in Chemistry at Guy's Hospital Medical School, who up to his untimely death had read nearly the whole of my manuscript, and made numerous corrections and modifications of the greatest value to me. Dr. M. W. Lister of Harwell, now Assistant Professor of Chemistry at Toronto University, has read the whole book in proof and detected many errors. I have been greatly helped by him and by Dr. Charles Coryell of the

Massachusetts Institute of Technology in my account of the uranide elements. In the laborious checking of the numerous references I have had the assistance of Mr. W. T. L. Neal of Exeter College, Mr. B. B. Goalby of New College, Mr. M. F. Hoare of The Queen's College, and Mr. A. Mackay of this College. The indexes were compiled with the help of Mr. C. P. Horgan of Trinity College.

The references I have tried to bring up to the summer of 1948; but the delays in the publication of original papers and abstracts, and in some subjects the restrictions of military secrecy, make it peculiarly difficult to assign an exact term to this in the immediate post-war years. Many of the statements in this book already need correction and amplification, but that is inevitable in so rapidly advancing a subject.

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May 1949

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VOLUME II

ABBREVIATIONS

Journals

Ann. Liebig's *Annalen der Chemie.*

Ann. Rep. Chem. Soc. *Annual Reports of the Chemical Society.*

Atti R. *Atti della Reale Accademia dei Lincei.*

Ber. *Berichte der Deutschen Chemischen Gesellschaft.*

Bull. Soc. *Bulletin de la Société Chimique de France.*

C. or **Chem. Centr.** *Chemisches Centralblatt.*

C.E.N. *Chemical and Engineering News* (Washington).

C.R. *Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.*

Gaz. *Gazzetta Chimica Italiana.*

J.A.C.S. *Journal of the American Chemical Society.*

J.C.S. *Journal of the Chemical Society.*

J.S.C.I. *Journal of the Society of Chemical Industry.*

Mon. *Monatshefte für Chemie.*

Trans. Far. Soc. *Transactions of the Faraday Society.*

Books

Abegg. R. Abegg *et al.* *Handbuch der anorganischen Chemie.* Hirzel, Leipzig, 1905– .

Gmelin. *Gmelin's Handbuch der anorganischen Chemie.* Verlag Chemie, Berlin, 8th edition, 1924– .

Chem. Bond. L. Pauling, *The Nature of the Chemical Bond.* Cornell Press, 1939, 2nd edition, 1942.

E.T.V. N. V. Sidgwick, *Electronic Theory of Valency.* Clarendon Press, 1927.

Krause and v. Grosse. E. Krause and A. v. Grosse, *Die Chemie der metallorganischen Verbindungen.* Borntraeger, Berlin, 1837.

M.I. C. Willgerodt, *Organische Verbindungen mit mehrwertigem Iod.* Enke, Stuttgart, 1914.

N. Ansch. A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie.* Vieweg, Brunswick (1st edition, 1905; 3rd, 1913; 5th, revised by P. Pfeiffer, 1923).

NN. I. and W. Noddack, *Das Rhenium.* Voss, Leipzig, 1933.

S.I.C. A. F. Wells, *Structural Inorganic Chemistry.* Clarendon Press, 1945.

Wheland, Resonance. *G. W. Wheland, The Theory of Resonance and its Application to Organic Chemistry.* New York and London, 1944.

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c = Velocity of light } see p. xii.
h = Planck's Constant }
ν = Frequency (vibrations per second).
E.A.N. Effective Atomic Number (see p. xvii).
Polar should be used only in the strict sense, meaning 'having a dipole moment'.
Sol^v: grs. anhydrous substance dissolving in 100 grs. solvent.

Square brackets [ ]: (1) in reaction kinetics mean concentrations (usually in moles per litre); (2) in formulae indicate ions.

et al. = and others (authors).

Greek and Latin numerical prefixes (*uni* = mono; *ter* = tri; *sexa* = hexa, &c.) are used indifferently; the supposed objection to 'hybrid' words, of which the first part is derived from Greek and the second from Latin, if it were valid would require us to say quadrifluoride but tetrachloride, would reject 'metastable', and would condemn the Church of England for speaking of the Pananglican Synod. Note that ennea = 9 and dodeca = 12. Symbols like al, hg, mean atom/valency (al = $\frac{1}{3}$ Al : hg = $\frac{1}{2}$ Hg).

In types of formulae A is as a rule put for the central atom and B for the covalently attached atoms. R is used for alkyls or aryls, X for halogens and other monovalent radicals (ionized or not), and Am for NH_3 and similar amines. Other abbreviations are Alk = alkyl; Ar = aryl; Me, Et, Pr, Bu, &c. = methyl, ethyl, propyl, butyl, &c.; Φ = phenyl (C_6H_5); Bz = benzyl ($C_6H_5 \cdot CH_2$); py = pyridine; en or *en* ethylenediamine; Ox = oxalato-group (C_2O_4); Cy = CN. A is sometimes used for the monovalent radical of a diketone or keto-ester (as $C_5H_7O_2$ from $C_5H_8O_2$, acetyl acetone).

SOME USEFUL PHYSICAL CONSTANTS

Lengths: $1\ \mu = 10^{-4}$; $1\ \mu\mu = 10^{-7}$; 1 A or A.U. = 10^{-8} cm. 1 X unit for X-rays = 1/1000 A (strictly 1/1002 A).

Velocity of light, $c = 2{\cdot}99776 \times 10^{10}$ cm./sec.

Quantum Theory: Energy $E = h\nu$, where ν = frequency (vibrations/second) and h (Planck's constant) = $6{\cdot}620 \times 10^{-27}$ erg-seconds.

Absolute zero = 0° K. = −273·16° C.

1 calorie = $4{\cdot}183 \times 10^7$ ergs = 4·183 joules.

1 electron-volt (e.v., energy acquired by an electron in moving through a potential drop of 1 volt) is equal to $1{\cdot}591 \times 10^{-12}$ erg, or 23·07 k.cals. per g.-molecule.

1 Faraday = 96,500 coulombs.

Light Quanta

Wave-number = waves per cm. = frequency/c.

Quantum of wave-length 7,000 A (red end of visible) = 40·8 k.cals./g.-mol.: of wave-length 4,000 A (violet end) = 71·4 k.cals./g.-mol.

Factors for Absorption and Emission Spectra

Transition	*Energy*		*Wave-length*	*Wave number, cm.*$^{-1}$
	E. volts	*Ht/g.-mol.*		
Electronic	1–10	23–230 k.cals.	12,350 to 1,235 A	8,100 to 81,000
Oscillational or Vibrational	1/10	2·3 k.cals.	123,500 A = 12·35 μ	810
Rotational . . .	1/1000	23 cals.	1,235 μ = 0·1235 cm.	8·1

Einstein's Equivalence of Mass and Energy

$E = mc^2$. Hence the mass of one hydrogen atom corresponds to 940 million e.v., or of 1 gramme to $2{\cdot}2 \times 10^{10}$ k.cals.

Gas constant $R = 1{\cdot}9885$ cals./degree C.

Avogadro Number N (molecules in 1 g.-molecule) $= 6{\cdot}025 \times 10^{23}$.

Mean translational energy of N gas molecules at $T°$ is RT, = *ca.* 600 k.cals. at 25° C.

The fraction N_1/N of the molecules of a gas that have energies of nE or above (where E is the mean energy) is for

$n =$	5	10	50
$N_1/N =$	$6{\cdot}8 \times 10^{-3}$	$4{\cdot}5 \times 10^{-5}$	$3{\cdot}7 \times 10^{-22}$

There are two scales of atomic weights in use, one physical and the other chemical. On the physical scale the unit is $\frac{1}{16}$th of the mass of the commonest isotope of oxygen ($^{16}O = 16{\cdot}000$); on the chemical scale it is $\frac{1}{16}$th of the mean atomic mass of the ordinary mixture of oxygen isotopes ($O = 16{\cdot}000$). According to Aston (1942) the ratio

$$\frac{\text{Unit of Chemical Atomic Weight}}{\text{Unit of Physical Atomic Weight}} = 1{\cdot}000275.$$

INTRODUCTION

FUNDAMENTAL PARTICLES[1,2]

THE fundamental particles of which the universe is now believed to be composed are given in the following table, with their dates of discovery, electric charges ($e = 4{\cdot}802 \times 10^{-10}$ E.S.U.),[3] masses (on the physical scale, where $^{16}O = 16{\cdot}000$), and their average lives.

Particle	*Date of discovery*	*Charge*	*Mass*	*Life*
Proton	..	$+e$	1·00758	Infinite
Neutron	1932	0	1·00894[a,b]	Infinite
Electron	1897	$-e$	0·000548[c] (H/1838)	Infinite
Positron	1932	$+e$	0·000548	*ca.* 10^{-9} sec.
Meson*	1935	$-e$, $+e$ (? also 0)	*ca.* H/9 and H/6	*ca.* 10^{-6} sec.
Neutrino	1934	0	? 10^{-18}	..

a = [4], *b* = [5], *c* = [6].

Of these the first three alone are of primary importance for chemistry. The proton is, of course, the hydrogen nucleus or positive hydrogen ion (see I. 26).

The neutron[9,10] with a mass number of 1 and an atomic number of zero may be called the first element of the Periodic Table, but as it can hold no electrons it has no chemical properties. Owing to the absence of charge it has an enormous penetrating power; while a proton of velocity 30,000 km./sec. (c/10) will travel only one foot in air, a neutron may go several miles in air before it loses all its energy, making only a few collisions on the way. The absence of charge also makes the neutron a very effective projectile for nuclear disruption, since it is not repelled by the nuclear charge as an α-particle would be. If neutrons could be concentrated they would

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* There probably[7,8] are at least two kinds of mesons, one with a mass equal to about 200 electrons, and the other about 320. The heavier kind were made artificially in the big Berkeley cyclotron, by passing 380 m.e.v. α-particles through thin plates of beryllium, carbon, or copper.[8]

[1] R. E. Peierls, *Nature*, 1946, **158**, 773.

[2] L. Pauling, *General Chemistry*, S. Francisco, 1947, p. 570.

[3] V. D. Hopper and T. H. Laby, *Proc. Roy. Soc.* 1941, **178**, 243; T. H. Laby, *Nature*, 1942, **150**, 648.

[4] D. J. Hughes, *Phys. Rev.* 1946, ii. **70**, 219.

[5] W. E. Stephens, *Rev. Mod. Phys.* 1947, **19**, 19.

[6] R. T. Birge, *Phys. Rev.* 1941, ii. **60**, 766.

[7] J. Ruling and R. Steinmauer, *Experientia*, 1946, **2**, 108.

[8] See *Chem. and Eng. News*, 22 Mar. 1948 (p. 850).

[9] J. Chadwick, *Nature*, 1932, **129**, 312; *Proc. Roy. Soc.* 1932, **136**, 692; ib. 1933, **142**, 1 (Bakerian Lecture).

[10] See also P. B. Moon, *Ann. Rep. Chem. Soc.* for **1938**, **35**, 21.

form a gas half as dense as hydrogen; the idea that liquid neutrons would have an enormous density (with a radius of 2×10^{-13} cm. one c.c. would weigh 25 million tons) is fallacious; the half quantum of zero-point energy (see under helium p. 7) would bring its effective radius nearly up to that of an ordinary atom.

A list of the International Atomic Weights of the elements is given in Table I (p. xxiii).

ATOMIC STRUCTURES

The nucleus of every atom except hydrogen is made up of protons and neutrons; if the mass number is N and the atomic number Z it consists of Z protons and N—Z neutrons; two isotopes have the same Z but different Ns. In a β-ray change we must suppose that a neutron changes into a proton with the emission of an electron. In the neutral atom the nucleus is surrounded by as many electrons as it contains protons; the atomic number is (1) the ordinal number of the element in the periodic system, (2) the number of protons in, and hence the positive charge of, its nucleus, and (3) the number of electrons surrounding the nucleus in the neutral isolated atom.

The electrons are arranged* in groups or shells according to their principal quantum numbers 1, 2, 3, &c. (K, L, M, N, O, P, Q, . . .); the electrons of each group are further divided into subgroups (*s*, *p*, *d*, *f*, . . .); the maximum number of subgroups is equal to the principal quantum number, and the largest number of electrons that each subgroup can contain is:

Subgroup . . .	*s*	*p*	*d*	*f*
Max. No. . . .	2	6	10	14

Hence the maximum size of the groups of principal quantum numbers 1, 2, 3, 4, . . . n is 2, 8, 18, 32, . . . $2n^2$.

A list of the structures of the elements is given in Table II, p. xxiv.

THE PERIODIC CLASSIFICATION

The periodic relations of the elements (Newlands, 1864; Mendeleeff, 1869; Lothar Meyer, 1870) can be expressed in two ways, each of which has its advantages. The form adopted by Bohr (Table III), in which each period, beginning and ending with an inert gas, is written in one line, shows most clearly the development of the atomic structures. The elements in brackets are those with an incomplete (between 8 and 18) electronic group in the core (i.e. as well as the outermost valency group); those within double brackets (the lanthanide and uranide elements) have two such groups, the second being between 18 and 32.

The second form of the table, due originally to Mendeleeff (Table IV), is more useful for bringing out the chemical similarities (which are so

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* For an explanation of the atomic structures see L. Pauling and E. Bright Wilson, Jr., *Introduction to Quantum Mechanics*, McGraw-Hill, New York, 1935.

dependent on the valencies), and is the one adopted in the following chapters. There are nine groups, each except the first and the last with two subgroups. The elements of the *N*th group are (with an obvious modification for Group VIII and for the lanthanides and the uranides) those which have either *N* electrons more than the preceding, or 8—*N* less than the following inert gas; in the first two (typical and sub-typical) periods one element satisfies both conditions; in the later periods there are two, the elements of the first kind forming subgroup A, and those of the second subgroup B.

MOLECULAR STRUCTURE

The atoms in a molecule are held together through their electrons, and essentially in two ways: (1) by the transfer of electrons from one atom to another, giving rise to an electrostatic (Coulomb) attraction (electrovalency, Kossel, 1916), and (2) by the sharing of pairs of electrons between two atoms, so that in a sense they belong to both (covalency: G. N. Lewis, 1916); the pair may either come one from each atom (normal) or both from one of them (co-ordinate or dative). The conditions which favour the passage of an electrovalency into a covalency are (Fajans, 1923-5) (1) a large charge on the ion, (2) a small size of the cation, (3) a large size of the anion, (4) the possession by the cation of a structure which is not that of an inert gas.

The effective atomic number (E.A.N.) of an atom in a molecule is the number of electrons which it has after these changes, and so is the atomic number plus 1 for each anionic charge, and for every electron from another atom which it shares, and minus 1 for each electron which it loses in becoming a cation. The valency of the atom is the difference between the number of unshared electrons in the isolated atom (the atomic number) and the number in the combined atom (Grimm and Sommerfeld, 1926); its covalency is the number of pairs of shared electrons that it holds. The maximum value of the covalency is limited (save under exceptional circumstances) in accordance with the period of the atom in the table, being 4 for the first short period (Li—F), 6 for the second short and first long periods (Na—Cl, K—Br), and 8 for the heavier elements.

RESONANCE[11]

This crude picture of atomic linkages is considerably modified in practice. Covalent links can sometimes be formed by one or by three electrons, and the links in molecules are often (perhaps usually) of an intermediate or mixed character, owing to the phenomenon of resonance. The equations of wave mechanics show that if a molecule can be represented, on the ordinary structural theory, by two different structures, then under certain

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[11] See Pauling, especially *Chemical Bond*, ed. 2, pp. 124–59; G. W. Wheland, *Theory of Resonance and its Application to Organic Chemistry* (New York, 1944), pp. 1–28.

conditions its actual state is not given by either, nor by a mixture of the two in chemical (tautomeric) equilibrium, but is a hybrid between them, and has to some extent the properties of both. The conditions which must be satisfied for this resonance to be possible are three: (1) the positions of the atoms in the two structures must be nearly the same, (2) the energy contents of the two (their relative stabilities) must not differ too greatly, the state of the hybrid being nearer to the more stable form, and (3) the number of unpaired (not of unshared) electrons must be the same in both; this last condition is almost always fulfilled. The resonance produces two important effects: (A) the energy content of the molecule is less, and its stability greater, than in either form, and hence the resonance must always occur when the conditions 1–3 are satisfied; (B) the linked atoms are rather closer together than in either separate form, owing to the greater strength of the link; this result is of great diagnostic importance in giving evidence of resonance.[12]

A typical example is that of carbon dioxide; the possible forms, with their distances and heats of formation from the atoms, are given below, and are compared with the observed values:

	$O{=}C{=}O$	$O\underset{\rightarrow}{\equiv}C\rightarrow O$	$O\leftarrow C\underset{\leftarrow}{\equiv}O$	*Observed*
Distance . . .	1·22+1·22 2·44	1·37+1·10 2·47	1·10+1·37 2·47	2·30 A
Heat of formation from atoms . . .	173+173 346	81·5+256 337·5	256+81·5 337·5	380 k.cals.

Often, as here, the resonance formulae differ only in the multiplicity of the links. But a very important form of resonance is that between a single covalency and an electrovalency, as in H—F and $H^+ F^-$; this will depend on the relative attractions of the atoms for the shared electrons. Pauling has shown[13] that we can assign electronegativity values to the elements, largely on the basis of their heats of linkage, as follows:

Electronegativities

H	2·1								
Li	1·0	Na	0·9	K	0·8	Rb	0·8	Cs	0·7
Be	1·5	Mg	1·2	Ca	1·0	Sr	1·0	Ba	0·9
B	2·0	Al	1·5	Sc	1·3	Y	1·3	La—Ln *ca.* 1·3	
	V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga *ca.* 1·6								
C	2·5	Si	1·8	Ge	1·7	Sn	1·7	Zr	1·6
N	3·0	P	2·1	As	2·0	Sb	1·8		
O	3·5	S	2·5	Se	2·4	Te	2·1		
F	4·0	Cl	3·0	Br	2·8	I	2·4		

The greater the difference in electronegativity between the two linked atoms the stronger the bond that unites them, and the greater its partial

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[12] For lists of the resonance energies and the resonance shortening see Wheland, op. cit., pp. 69, 286.

[13] *Chemical Bond*, eds. 1 and 2, pp. 58–75; *General Chemistry*, 1947, pp. 160, 543.

ionic character. If x_1 and x_2 are the values, the extra energy due to the partial ionic character is about $23(x_1 - x_2)^2$ k.cals./mole. With a difference of 1·7 units the link is about 50 per cent. ionic.

It should be noticed that these mixed ionic-covalent links have in some important respects the properties of covalent but not of ionic links. Two of the principal properties by which ionic links are recognized are (1) the independent motions of the ions (conductivity, low molecular weight in solution), and (2) their freedom of position in the molecule, leading to close-packing and the absence of isomers. Neither of these properties is to be found with the ionic-covalent bond; it is a condition of resonance that the atoms must occupy nearly the same places in both forms, so that the ions cannot separate; and as the positions are fixed in the covalent structure but adaptable in the electrovalent, the positions in the hybrid must be those of the covalent form. Thus for many purposes molecules with these mixed links must be regarded as covalent and not ionized.

STEREOCHEMISTRY[14]

The arrangements in space of the covalencies of poly-covalent atoms, while they are subject to small variations seldom exceeding 5° or 10°, tend to conform to one or other of quite a limited number of types. These are very simply related to the size of the valency group of electrons (in Lewis's sense, the shared electrons counting for both atoms) if the imaginary positions of the electronic pairs are taken to be the same whether they are occupied (shared) or not.

I. When the valency group is 4 we have with a covalency of 2 a linear structure (180°) as in Cl—Hg—Cl.

II. When the valency group is 6, if they are all shared we have three covalencies and these are at 120° in a plane with the central atom, as has been shown in boron trifluoride. Where only 4 of the 6 are shared the valency angle is still about 120° (as in stannous chloride).

III. With a complete valency octet (apart from the transitional elements, which require special treatment) the arrangement is tetrahedral; if some pairs are unshared the positions of the rest are only slightly affected (the angles being usually reduced from 109·5° in the direction of 90°) and are for a covalency of 3 (2, $\underline{6}$*) pyramidal, as in NH_3, and for 2 (4, $\underline{4}$) triangular, as in H_2O.

With the transitional elements the size of the valency group is uncertain, as it may include any or all of the electrons above 8 of the previous (penultimate) group. It is found that when this maximum size (n) is not much more than 8, the structure of a 4-covalent atom is tetrahedral, and we may assume that there the valency group is a shared octet, all the

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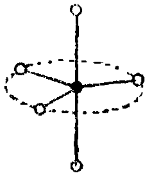
* Shared electrons are underlined.

[14] N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc.* 1940, 176, 153.

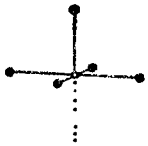
unshared electrons being in the previous group. When, however, *n* is not much less than 18, the 4-covalent structure is found to be planar; a reason for this is suggested later under V.

IV. When there are 10 valency electrons (the so-called inert pair (see p. 287) if present being counted in), the arrangement is that of a trigonal bipyramid, with two points at the poles of a sphere and the other three symmetrically disposed (at 120°) on the equator (Fig. 1).



Trigonal Bipyramid

FIG. 1



IF_5 Structure

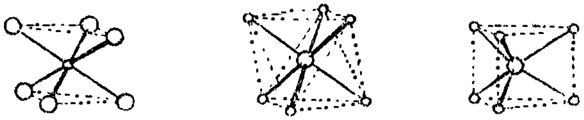
FIG. 2

With 5-covalent decets ($\underline{10}$) this has been established in every case examined, for example, with PF_5, $TaCl_5$, $Fe(CO)_5$, and $Sb(CH_3)_2(hal)_3$.

The 4-covalent decet (2, $\underline{8}$) has the structure derived from this with one of the five points empty. This has been established with $K[IO_2F_2]$[15] and with $TeCl_4$[16] (Fig. 2).

The 3-covalent decet occurs in the aryl iodide-chlorides $Ar \cdot ICl_2$, but their structure is unknown. The 2-covalent decet ($\underline{4}$, 6) occurs in the trihalide ions, as in $M[ICl_2]$ and $M[I_3]$, which are known to be linear (2 polar points).

V. Duodecet. In its fully shared form AB_6 this gives the octahedron established by Werner. On theoretical grounds[17] the three structures below are all possible: of these II is really a form of I in which the B · · B distances and the valency angles are all equal. Experimentally all AB_6 molecules are found to have the octahedral structure II except a few giant molecules (for instance, MoS_2 III, and nickel arsenide I and III). The reason, no doubt, is that the octahedron gives for a fixed A—B length the greatest distance from one B to another, and so is favoured, owing to the mutual repulsion of the B's, wherever the attraction of neighbouring atoms does not interfere, as it does in the giant molecules.



I. Trigonal Antiprism. II. Octahedron. III. Trigonal Prism.

FIG. 3

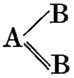
[15] L. Helmholz and M. T. Rogers, *J.A.C.S.* 1940, 62, 1537.
[16] D. P. Stevenson and V. Schomaker, ib. 1967.
[17] G. E. Kimball, *J. Chem. Phys.* 1940, 8, 188.

The 5-covalent duodecet (2, $\underline{10}$) must occur in IF_5 (Fig. 2), but the structure of this cannot be determined by electron diffraction because of the great difference (53 to 9) between the atomic numbers of iodine and fluorine.

The 4-covalent duodecet is found in the unusual type of $M[ICl_4]$, where the anion has been shown to have a planar square structure, i.e. an octahedron with two trans positions empty. It may be supposed that the same 4, $\underline{8}$ electronic arrangement occurs in the planar 4-covalent derivatives of the later transitional elements, such as $M_2[Ni(CN)_4]$; the nickel here has the atomic composition 2, 8 (16, $\underline{8}$), which presumably should be written 2, 8, 12 (4, $\underline{8}$), giving the same type of duodecet as in $M_2[ICl_4]$.

VI. 14-group. The very few examples of this rare condition that have been measured show two types of structure, one (in $K_3[ZrF_7]$) derived from an octahedron by adding a fluorine atom to the centre of one face,[18] and the other (in $K_2[NbF_7]$ and $K_2[TaF_7]$) from a trigonal prism by adding a fluorine atom at the centre of a prism face,[19] the strain in both cases being eased by distortion.

VII. 16-group: covalency 8. Only one compound of this rare kind has been examined, the very stable octacyanide $K_4[Mo(CN)_8]$; the anion of this salt has been shown[20] to have neither the cubic nor the antiprismatic (twisted cube) form, but that of a dodecahedron.

Multiple Links. With the octet the stereochemistry of these is well known; the angles are  $A\begin{smallmatrix}\diagup B\\ \diagdown B\end{smallmatrix}$ 125·15° and both B═A═B and B—A≡B 180°. The positions of multiple links with larger valency groups are scarcely known theoretically, and not at all practically.

ATOMIC RADII

By X-ray and electron diffraction, from the spectra, and in other ways, the lengths (distances between the nuclei) of a large number of covalent links have been measured, and it has been found that they can be approximately expressed as the sum of two values, one for each of the linked atoms, which are known as the atomic radii (a similar additivity is found to hold for ions, though the values are, of course, different). The observed lengths are, however, subject to small variations, of which the most important are those due to the multiplicities: in general the ratios of the links A—B, A═B, A≡B are roughly 1:0·9:0·8.[21] Resonance shortens the distances by introducing an element of multiplicity into single links, and in addition by the shortening which resonance itself involves.[22] There are

[18] G. C. Hampson and L. Pauling, *J.A.C.S.* 1938, **60**, 2702.

[19] J. L. Hoard, ib. 1939, **61**, 1252.

[20] J. L. Hoard and H. H. Nordsieck, ib. 1939, **61**, 2853.

[21] J. L. Kavanau, *J. Chem. Phys.* 1944, **12**, 467.

[22] H. A. Skinner, *Trans. Far. Soc.* 1945, **41**, 645.

other modifying influences as well, which are not yet fully understood.[23-5] Where the distances in a molecule have been measured, it is useful to be able to compare them with those derived from some standard series of values of the atomic radii. A list (Table V) is therefore given (p. xxix) of the most probable radii of the atoms in covalent and electrovalent links, and values taken from this are appended (as 'theory') to the measurements quoted in the text. This is merely to facilitate comparison, and the 'theoretical' values must not be supposed to have any special validity.

HEATS OF LINKAGE

The heat of formation H_f of a molecule from its elements in their (specified) standard states—for example, graphite, hydrogen gas, solid iodine—can be ascertained thermochemically. If the heat of volatilization or sublimation of the substance is known, and further the heats of atomization of the component elements from their standard states, the algebraic sum of all these quantities gives H_a, the heat of formation of the gaseous compound from its atoms; this is expressed in k.cals. per g.-molecule. The deduction from this of the heats of formation of individual links is (except with diatomic molecules) to some extent a matter of convention. Thus with water we have the following values (all, of course, for the gas)

(1) $2\,\mathrm{H}+\mathrm{O} = \mathrm{H{-}O{-}H} + 2\times 110{\cdot}2$ k.cals./mol.

(2) $\mathrm{H}+\mathrm{O{-}H} = \mathrm{H{-}O{-}H} + 103{\cdot}5$ „

(3) $\mathrm{H}+\mathrm{O} = \mathrm{H{-}O} + 116{\cdot}9$ „

Here we have three different values for the H—O link. The values (2) and (3) depend on the stability of the radical O—H; we are not concerned with this but only with the relation between H_2O molecule and its constituent atoms, i.e. with (1); our object is to get values such that their sum for all the links in a molecule gives its H_a as nearly as possible. Hence the value used for the heat of linkage is got by dividing the H_a of the normal molecule AB_x by x, the number of links that it contains (here H—O = 110·2 k.cals.). With such values the additivity for molecules with several kinds of links is found to hold very nearly, if allowance is made for the resonance energy when this is to be expected; the value of the resonance energy is, in fact, usually obtained by subtracting from the H_a of the substance the sum of the normal ('theoretical') values for the links that it contains. There are other influences which cause small changes in H_a, seldom amounting to 5 k.cals.; these will be discussed as they occur (see, for example, pp. 501-5).

The Tables VI A—D which follow give the most probable values for A (p. xxx) the heats of atomization of the elements from their standard states B (p. xxxi), the heats of formation H_a of single links C (p. xxxii), those of multiple links, and D (p. xxxii), the effects (where known) of change of valency on the heat of formation of the link.

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[23] V. Schomaker and D. P. Stevenson, *J.A.C.S.* 1941, 63, 37.

[24] W. Gordy, *J. Chem. Phys.* 1947, 15, 81, 305.

[25] L. Pauling, *J.A.C.S.* 1947, 69, 542 (for metals).

Table I

International Atomic weights 1948

	Symbol	*At. No.*	*At. Wt.*		*Symbol*	*At. No.*	*At. Wt.*
Aluminium	Al	13	26·97	Molybdenum	Mo	42	95·95
Antimony	Sb	51	121·76	Neodymium	Nd	60	144·27
Argon	A	18	39·944	Neon	Ne	10	20·183
Arsenic	As	33	74·91	Nickel	Ni	28	58·69
Barium	Ba	56	137·36	Niobium	Nb	41	92·91
Beryllium	Be	4	9·02	Nitrogen	N	7	14·008
Bismuth	Bi	83	209·00	Osmium	Os	76	190·2
Boron	B	5	10·82	Oxygen	O	8	16·0000
Bromine	Br	35	79·916	Palladium	Pd	46	106·7
Cadmium	Cd	48	112·41	Phosphorus	P	15	30·98
Caesium	Cs	55	132·91	Platinum	Pt	78	195·23
Calcium	Ca	20	40·08	Potassium	K	19	39·096
Carbon	C	6	12·010	Praseodymium	Pr	59	140·92
[Cassiopaeum = Lutecium]				Protoactinium	Pa	91	231
Cerium	Ce	58	140·13	Radium	Ra	88	226·05
Chlorine	Cl	17	35·457	Radon	Rn	86	222
Chromium	Cr	24	52·01	Rhenium	Re	75	186·31
Cobalt	Co	27	58·94	Rhodium	Rh	45	102·91
[Columbium = Niobium]				Rubidium	Rb	37	85·48
Copper	Cu	29	63·54	Ruthenium	Ru	44	101·7
Dysprosium	Dy	66	162·46	Samarium	Sm	62	150·43
Erbium	Er	68	167·2	Scandium	Sc	21	45·10
Europium	Eu	63	152·0	Selenium	Se	34	78·96
Fluorine	F	9	19·00	Silicon	Si	14	28·06
Gadolinium	Gd	64	156·9	Silver	Ag	47	107·880
Gallium	Ga	31	69·72	Sodium	Na	11	22·997
Germanium	Ge	32	72·60	Strontium	Sr	38	87·63
Gold	Au	79	197·2	Sulphur	S	16	32·066
Hafnium	Hf	72	178·6	Tantalum	Ta	73	180·88
Helium	He	2	4·003	Tellurium	Te	52	127·61
Holmium	Ho	67	164·94	Terbium	Tb	65	159·2
Hydrogen	H	1	1·0080	Thallium	Tl	81	204·39
Indium	In	49	114·76	Thorium	Th	90	232·12
Iodine	I	53	126·92	Thulium	Tm	69	169·4
Iridium	Ir	77	193·1	Tin	Sn	50	118·70
Iron	Fe	26	55·85	Titanium	Ti	22	47·90
Krypton	Kr	36	83·7	Tungsten	W	74	183·92
Lanthanum	La	57	138·92	Uranium	U	92	238·07
Lead	Pb	82	207·21	Vanadium	V	23	50·95
Lithium	Li	3	6·940	Xenon	Xe	54	131·3
Lutecium	Lu	71	174·99	Ytterbium	Yb	70	173·04
Magnesium	Mg	12	24·32	Yttrium	Y	39	88·92
Manganese	Mn	25	54·93	Zinc	Zn	30	65·38
Mercury	Hg	80	200·61	Zirconium	Zr	40	91·22

Group	1	2	3	4				5			6	
Subgp.	*s*	*s*, *p*	*s*, *p*, *d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	*p*
37 Rb	2	8	18	2	6			1				
38 Sr	2	8	18	2	6			2				
39 Y	2	8	18	2	6	1		2				
40 Zr	2	8	18	2	6	2		2				
41 Nb	2	8	18	2	6	4		1				
42 Mo	2	8	18	2	6	5		1				
43 Tc	2	8	18	2	6	6		1				
44 Ru	2	8	18	2	6	7		1				
45 Rh	2	8	18	2	6	8		1				
46 Pd	2	8	18	2	6	10		—				
47 Ag	2	8	18	2	6	10		1				
48 Cd	2	8	18	2	6	10		2				
49 In	2	8	18	2	6	10		2	1			
50 Sn	2	8	18	2	6	10		2	2			
51 Sb	2	8	18	2	6	10		2	3			
52 Te	2	8	18	2	6	10		2	4			
53 I	2	8	18	2	6	10		2	5			
54 Xe	2	8	18	2	6	10		2	6			
55 Cs	2	8	18	2	6	10		2	6		1	
56 Ba	2	8	18	2	6	10		2	6		2	
57 La	2	8	18	2	6	10		2	6	1	2	
58 Ce	2	8	18	2	6	10	1	2	6	1	2	
59 Pr	2	8	18	2	6	10	2	2	6	1	2	
60 Nd	2	8	18	2	6	10	3	2	6	1	2	
61 Il	2	8	18	2	6	10	4	2	6	1	2	
62 Sm	2	8	18	2	6	10	5	2	6	1	2	
63 Eu	2	8	18	2	6	10	6	2	6	1	2	
64 Gd	2	8	18	2	6	10	7	2	6	1	2	
65 Tb	2	8	18	2	6	10	8	2	6	1	2	
66 Dy	2	8	18	2	6	10	9	2	6	1	2	
67 Ho	2	8	18	2	6	10	10	2	6	1	2	
68 Er	2	8	18	2	6	10	11	2	6	1	2	
69 Tm	2	8	18	2	6	10	12	2	6	1	2	
70 Yb	2	8	18	2	6	10	13	2	6	1	2	
71 Lu	2	8	18	2	6	10	14	2	6	1	2	
72 Hf	2	8	18	2	6	10	14	2	6	2	2	

TABLE II

Atomic Structures

Group	**1**	**2**		**3**			**4**				**5**			
Subgp.	*s*	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*f*
1 H	1													
2 He	2													
3 Li	2	1												
4 Be	2	2												
5 B	2	2	1											
6 C	2	2	2											
7 N	2	2	3											
8 O	2	2	4											
9 F	2	2	5											
10 Ne	2	2	6											
11 Na	2	2	6	1										
12 Mg	2	2	6	2										
13 Al	2	2	6	2	1									
14 Si	2	2	6	2	2									
15 P	2	2	6	2	3									
16 S	2	2	6	2	4									
17 Cl	2	2	6	2	5									
18 A	2	2	6	2	6									
19 K	2	2	6	2	6		1							
20 Ca	2	2	6	2	6		2							
21 Sc	2	2	6	2	6	1	2							
22 Ti	2	2	6	2	6	2	2							
23 V	2	2	6	2	6	3	2							
24 Cr	2	2	6	2	6	5	1							
25 Mn	2	2	6	2	6	5	2							
26 Fe	2	2	6	2	6	6	2							
27 Co	2	2	6	2	6	7	2							
28 Ni	2	2	6	2	6	8	2							
29 Cu	2	2	6	2	6	10	1							
30 Zn	2	2	6	2	6	10	2							
31 Ga	2	2	6	2	6	10	2	1						
32 Ge	2	2	6	2	6	10	2	2						
33 As	2	2	6	2	6	10	2	3						
34 Se	2	2	6	2	6	10	2	4						
35 Br	2	2	6	2	6	10	2	5						
36 Kr	2	2	6	2	6	10	2	6						

TABLE II

Atomic Structures (*cont.*)

Group	1	2	3	4	5				6				7
Subgp.	*s*	*s*, *p*	*s*, *p*, *d*	*s*, *p*, *d*, *f*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*f*	*s*
73 Ta	2	8	18	32	2	6	3		2				
74 W	2	8	18	32	2	6	4		2				
75 Re	2	8	18	32	2	6	5		2				
76 Os	2	8	18	32	2	6	6		2				
77 Ir	2	8	18	32	2	6	7		2				
78 Pt	2	8	18	32	2	6	8		2				
79 Au	2	8	18	32	2	6	10		1				
80 Hg	2	8	18	32	2	6	10		2				
81 Tl	2	8	18	32	2	6	10		2	1			
82 Pb	2	8	18	32	2	6	10		2	2			
83 Bi	2	8	18	32	2	6	10		2	3			
84 Po	2	8	18	32	2	6	10		2	4			
85 At	2	8	18	32	2	6	10		2	5			
86 Em	2	8	18	32	2	6	10		2	6			
87 Fr	2	8	18	32	2	6	10		2	6			1
88 Ra	2	8	18	32	2	6	10		2	6			2
89 Ac	2	8	18	32	2	6	10		2	6	1		2
90 Th	2	8	18	32	2	6	10		2	6	3		1
91 Pa	2	8	18	32	2	6	10		2	6	4		1
92 U	2	8	18	32	2	6	10	3	2	6	2		1
93 Np	2	8	18	32	2	6	10	4	2	6	2		1
94 Pu	2	8	18	32	2	6	10	5	2	6	2		1
95 Am	2	8	18	32	2	6	10	6	2	6	2		1
96 Cm	2	8	18	32	2	6	10	7	2	6	2		1

The structures assigned to the last few elements are speculative; the distribution of the electrons between the 5*f* and the 6*d* orbits is uncertain; see W. F. Meggers, *Science*, 1947, **105**, 514. In these elements the quantum groups of the electrons are less important than the energies of the orbits, which are often very similar.

TABLE III

Periodic Classification (Thomsen-Bohr)

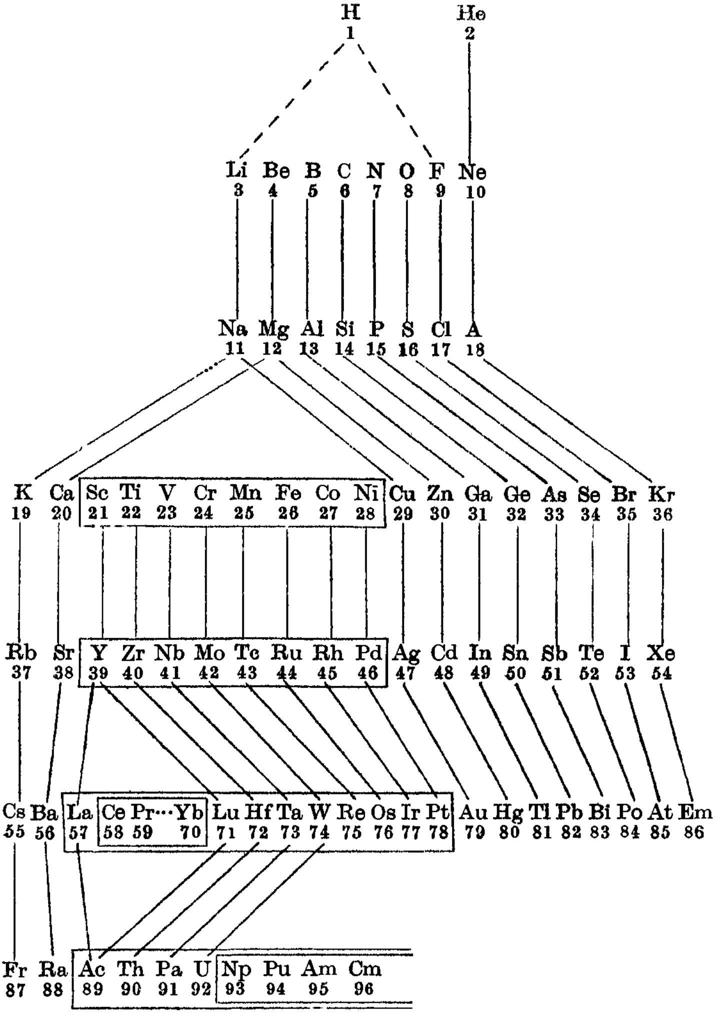

TABLE V

Atomic and Ionic Radii in A.U.

(Atomic for single links unless otherwise stated)

Atomic		*Ionic*		*Atomic*		*Ionic*	
H	0·30	H^-	1·3	Yb	1·56	Yb^{+++}	1·00
He	1·79			[Yb	1·70]		
Ne	1·60			Lu	1·56	Lu^{+++}	0·99
A	1·91						
Kr	1·97			Ga	1·26	Ga^{+++}	0·62
Xe	2·18			In	1·44	In^{+++}	0·92
				Tl	1·47	Tl^{+++}	1·05
Li	1·33	Li^+	0·78			Tl^+	1·49
Na	1·57	Na^+	0·98				
K	2·03	K^+	1·33	C—	0·771		
Rb	2·16	Rb^+	1·49	C=	0·665		
Cs	2·35	Cs^+	1·65	C≡	0·602		
				Si—	1·17		
Cu	1·35	Cu^+ *ca.*	1·0	Si=	1·07		
Ag	1·53	Ag^+	1·13	Si≡	1·00		
Au	1·50	..		Ge—	1·22		
				Ge=	1·12		
Be	0·90	Be^{++}	0·34	Sn—	1·40		
Mg	1·36	Mg^{++}	0·78	Sn=	1·30	Sn^{4+}	0·74
Ca	1·74	Ca^{++}	1·06	Pb—	1·46	Pb^{4+}	0·84
Sr	1·92	Sr^{++}	1·27			Pb^{2+}	1·32
Ba	1·98	Ba^{++}	1·43	Ti	1·36	Ti^{4+}	0·64
Ra		Ra^{++}	1·52	Zr	1·48	Zr^{4+}	0·87
				Hf	1·48	..	
Zn	1·31	Zn^{++}	0·83	Th	1·65	Th^{4+}	1·10
Cd	1·48	Cd^{++}	1·03				
Hg	1·48	Hg^{++}	1·12	N—	0·70	N^{3-}	1·7
				N=	0·60		
B—	0·88			N≡	0·55		
B=	0·76			P—	1·10	P^{3-}	2·1
B≡	0·68			P=	1·00		
Al	1·26	Al^{+++}	0·83	P≡	0·93		
Sc	1·44	Sc^{+++}	0·78	As—	1·21	As^{3-}	2·2
Y	1·62	Y^{+++}	0·93	As=	1·11		
La	1·69	La^{+++}	1·22	Sb—	1·41	Sb^{3-}	2·4
Ce	1·65	Ce^{+++}	1·18	Bi—	1·46		
Pr	1·65	Pr^{+++}	1·16				
Nd	1·64	Nd^{+++}	1·15	V	1·23		
				Nb	1·34		
Sm	1·64	Sm^{+++}	1·13	Ta	1·34		
Eu	1·63	Eu^{+++}	1·13				
[Eu″	1·85]			O—	0·66	O^{--}	1·32
Gd	1·61	Gd^{+++}	1·11	O=	0·55		
Tb	1·59	Tb^{+++}	1·09	O≡	0·50		
Dy	1·59	Dy^{+++}	1·07	S—	1·04	S^{--}	1·74
Ho	1·58	Ho^{+++}	1·05	S=	0·94		
Er	1·57	Er^{+++}	1·04	S≡	0·87		
Tm	1·56	Tm^{+++}	1·04	Se—	1·17	Se^{--}	1·91

TABLE IV

Periodic Classification (Mendeleeff)

Group	I		II		III		IV		V		VI		VII		VIII	0
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.		
Period 1.	H 1															He 2
2.	Li 3		Be 4		B 5		C 6		N 7		O 8		F 9			Ne 10
3.	Na 11		Mg 12		Al 13		Si 14		P 15		S 16		Cl 17			A 18
4.	K 19	Cu 29	Ca 20	Zn 30	Sc 21	Ga 31	Ti 22	Ge 32	V 23	As 33	Cr 24	Se 34	Mn 25	Br 35	Fe 26 Co 27 Ni 28	Kr 36
5.	Rb 37	Ag 47	Sr 38	Cd 48	Y 39	In 49	Zr 40	Sn 50	Nb 41	Sb 51	Mo 42	Te 52	Tc 43	I 53	Ru 44 Rh 45 Pd 46	Xe 54
6.	Cs 55	Au 79	Ba 56	Hg 80	La 57 Ce 58 Pr 59 Nd 60 Il 61 Sm 62 Eu 63 Gd 64 Tb 65 Dy 66 Ho 67 Er 68 Tm 69 Yb 70 Lu 71	Tl 81	(Ce 58) Hf 72	Pb 82	Ta 73	Bi 83	W 74	Po 84	Re 75	At 85	Os 76 Ir 77 Pt 78	Em 86
7.	Fr 87		Ra 88		Ac 89		Th 90		Pa 91		U 92 Np 93 Pu 94 Am 95 Cm 96					

TABLE V (*cont.*)

Atomic		*Ionic*		*Atomic*		*Ionic*	
Se=	1·07			I=	1·23		
Te—	1·37	Te^{--}	2·11				
Te=	1·27	Te^{4+}	0·89	Mn	1·25		
Po—	1·70			Re	1·37		
Cr	1·25	Cr^{3+}	0·65				
Mo	1·36	Mo^{4+}	0·68	Fe''	1·23	Fe^{++}	0·83
W	1·37	W^{4+}	0·68	Fe'''	1·22	Fe^{+++}	0·67
U	1·49	U^{4+}	1·05	Co''	1·32	Co^{++}	0·82
				Co'''	1·22		
F—	0·64	F^-	1·33	Ni''	1·39	Ni^{++}	0·78
F=	0·54						
Cl—	0·99	Cl^-	1·81	Ru''	1·33	Ru^{4+}	0·65
Cl=	0·89			Rh'''	1·32	Rh^{+++}	0·69
Br—	1·14	Br^-	1·96	Pd''	1·31		
Br=	1·04			Os''	1·33	Os^{4+}	0·67
I—	1·33	I^-	2·20	Ir'''	1·32	Ir^{4+}	0·66

TABLE VI A

Heats of Atomization from Standard States; k.cals per g.-atom

H	51·7	Be	75	B	115	C	170·4[a]	N	112·6[b]
Li	39·0			Al	55	Si	85·0	P	74·6[c]
Na	25·9					Ge	85·0	As	58·6
K	19·8					Sn	78·0		
Rb	18·9					Pb	47·5		
		Zn	27·4			Ti	100	V	85
		Cd	—			Zr	110		
		Hg	14·6	Tl	40				
		O	59·1			F	16·7[d]	Fe	94
		S	66·3			Cl	28·9		
		Se	61·0			Br	26·9[e]		
						I	25·6[f]		

[a] See IV. 923.

[b] See A. G. Gaydon and W. G. Penney, *Proc. Roy. Soc.* 1945, **183**, 374; see also Gaydon, *Dissociation Energies*, Chapman & Hall, London, 1947.

[c] Solid white phosphorus.

[d] The evidence for this low value is mainly spectroscopic, from the heat of dissociation of ClF as compared with Cl_2 and F_2; see especially P. H. Broderson and H. J. Schumacher, *Z. Naturforsch.* 1947, 2*a*, 358.

[e] Liquid bromine.

[f] Solid iodine.

TABLE VI B

Heats of Formation of Links from Atoms (H_a)

	H	*C*	*N*	*O*	*S*	*F*	*Cl*	*Br*	*I*
H	103·4	98·8	92·9	110·2	87·5	132·4	102·7	87·3	71·4
C	98·8	81·6	69·3	81·5	66·0	103·4	78·0	65·5	57·0
N	92·9	69·3	38·4			62·9	47·6		
O	110·2	81·5		34·9		43·5	49·3		
S	87·5	66·0			63·8	71·4	66·1	57·2	
F	132·4	103·4	62·9	43·5	71·4	33·3	71·3		
Cl	102·7	78·0	47·6	49·3	66·1	71·3	57·8	52·7	51·0
Br	87·3	65·5			57·2		52·7	46·1	42·9
I	71·4	57·0					51·0	42·9	36·2
Ag							70·4	67·7	60·1
Be				60·8			107·9	88·4	68·6
Zn		34·5							
Hg		*ca.* 15					52·9	45·0	35·4
B						140·6	96·7	76·9	
Al				91·2			91·6		
Tl							85·3	76·4	66·3
Si	75·1	69·1		89·3	60·9	127·9	85·8	69·3	51·1
Ge							104·1		
Sn							78·0	66·2	
Pb″						89·9	77·4	53·2	44·4
Ti							97·0		
Zr							116·9		
P	77·3						77·1	63·5	49·5
As	56·7						69·7	57·4	42·5
V							88·7		
Se	73·0	—C 70·7 =C 165·6				67·1	66·8		
Te	62·3					78·3			
Fe				65·1					
As				110·4 (OsO_4)					

Si—Si 42·5 Ge—Ge 42·5 P—P 149·2 As—As 117·2 Se—Se 57·6

TABLE VI C

Multiple Links

	Abs.	*Rel.*		*Abs.*	*Rel.*		*Abs.*	*Rel.*
$C—C$	81·6	1·00	$S—S$	63·8	1·00	$C—N$	69·3	1·00
$C=C$	146·1	1·79	$S=S$	103·4	1·62	$C=N$	135·0	1·95
$C\equiv C$	192·1	2·35	$Se—Se$	57·6	1·00	$C\equiv N$	212·0	3·06
$N—N$	38·4	1·00	$Se=Se$	92·5	1·63	$C—O$	81·5	1·00
$N=N$	97·6	2·54	$P—P$[b]	47·5	1·00	$C=O$	173·0	2·12
$N\equiv N$	225·0	5·86	$P\equiv P$	117·0	2·46	$C\equiv O$	256·0	3·14
$O—O$	34·9	1·00	$As—As$[b]	34·3	1·00	$C—S$	66·0	1·00
$O=O$[a]	96·0	2·75	$As\equiv As$	91·3	2·69	$C=S$	126·0	1·91

[a] For the ^1D state.

[b] See H. A. Skinner, *Trans. Far. Soc.* 1945, **41**, 645; F. S. Dainton, ibid. 1947, **43**, 244.

TABLE VI D

Effect of Valency

$P—Cl$ in PCl_3	77·1	$I—Cl$ in ICl	51·0	$Al—Cl$ in $AlCl_3$	91·6
,, in PCl_5	62·0	,, in ICl_3	42·0	,, in Al_2Cl_6	73·7
Ratio	0·80		0·82		0·80

$Sb—Cl$ in $SbCl_3$	68·0
,, in $SbCl_5$	58·6
Ratio	0·82

GROUP 0

INERT GASES

THE inert gases occupy a peculiar position in Chemistry. They are practically devoid of chemical properties, and yet for that very reason they have provided the key to the whole problem of valency and the interpretation of the Periodic Classification.

Further, their physical behaviour, largely owing to this inertness, is of great interest. Helium in particular shows physical properties to which there is no parallel elsewhere, and it has opened up quite a new field of physical investigation, that of extremely low temperature—the 'uncharted infinity' that lies between 1° K. and the absolute zero.

The more important physical properties of the inert gases are given in the following table.

TABLE

	He	Ne	A	Kr	Xe	Em
B.-pt. °K.	4·216°[a]	27·17°	87·92°	120·9°[d]	165·1°	208°
°C.	−268·94°	−245·99°	−185·24°	−152·3°	−108·1°	−65°
M.-pt. °K.	. .	24·5°[b]	83·8°[b]	105·9°[e]	161·3°[c]	160°
°C.	. .	−248·7°	−189·4°	−157·3°	−111·9°	−113°
Crit.T. °K.	5·23°[b]	44·7°[b]	150·69°	209·4°[b]	289·9°[b]	377·6°
°C.	−267·93°	−228·5°	−122·47°	−63·8°	+16·7°	+104·4°
Vol. in c.c. in 1 m.³ air[f]	5·24[g]	18·21	9,300	1	0·1	6×10^{-14}
Ht. of evapn.	0·0196	0·42	1·59	2·138[e]	3·020	
,, fusion	0·00435	0·801	0·2808	0·3907[i]	0·5485[c]	
(k.cals./g.at.)[c]	(3° K.)					
M.-pt./Crit.T.[b]	. .	0·548	0·556	0·554	0·557	
Trouton	4·64	19·8	18·1	17·7	18·3	
At. Diam. in Crystal (A)	3·57[h]	3·20	3·82	3·94	4·36	

a = [1], *b* = [2], *c* = [3], *d* = [4], *e* = [5], *f* = [6], *g* = [7], *h* = [8], *i* = [9]

HELIUM

This element was discovered spectroscopically in the chromosphere of the sun in 1868 by Lockyer and Frankland, who therefore called it helium. In 1895, after the discovery of argon, Ramsay found that the inactive gas which Hillebrand had obtained in 1890 from cleveite and other uranium minerals by heating or solution gave the same spectrum, and so must be helium.

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[1] G. Schmidt and W. H. Keesom, *Physica*, 1937, **4**, 963.

[2] K. Clusius and K. Weigand, *Z. physikal. Chem.* 1939, B **42**, 111.

[3] K. Clusius and L. Riccoboni, ib. 1938, B **38**, 81.

[4] E. Justi, *Phys. Z.* 1935, **36**, 571.

[5] K. Clusius, A. Kruis, and F. Konnertz, *Ann. Phys.* 1938, [v] **33**, 642.

[6] F. A. Paneth, *Nature*, 1937, **139**, 181.

[7] E. Glückauf, *Proc. Roy. Soc.* 1946, **185**, 98.

[8] W. H. Keesom and K. W. Taconis, *Proc. K. Akad. Amst.* 1938, **41**, 95.

[9] K. Clusius, *Z. physikal. Chem.* 1936, B **31**, 459.

Helium is produced in the decay of radioactive elements (1 kg. of uranium in its conversion into 865 g. of lead forms 135 g. or 756 litres of helium), and also by the bombardment of lithium, beryllium, and other (mainly light) elements with projectiles or rays of high energy, such as cosmic rays, X-rays, and high-speed protons and deuterons. These bombardments must take place in nature, and give a continuous supply of helium.

On the other hand, owing to its lightness it will tend to escape from the earth's atmosphere. A molecule can do this[10] if it has a velocity of 11·2 km./sec. (on the moon, of 2·4 km./sec.). Thus the nearer the mean velocity is to this escape velocity, the more rapidly the gas will escape. The mean velocities at 0° C. are:

	Neutron	H_2	He	Ne	A	Kr	O_2	CO_2
Km./sec.	2·60	1·84	1·30	0·58	0·41	0·28	0·46	0·39

It can be shown that if the mean velocity of any gas is one-third of the escape velocity (i.e. on the earth 3·7 km./sec.), half of the gas will escape in a few weeks. It is therefore evident that the helium will escape fairly rapidly, though not so rapidly as the hydrogen or the neutrons, while the other inert gases will be retained. As Paneth has pointed out, helium, in spite of its name, is the only (non-radioactive) element on the earth that did not originate in the sun. All that we now have must have been born on the earth since its separation.

The technical source of helium is certain natural gases, especially oil gas in America and Canada, which often contains from 0·1 to 2 per cent. From this source the U.S. Government had obtained by 1940[11] nearly 150 million cubic feet, mostly at Amarillo, Texas: the price then was less than 1·5 cents per cubic foot. This has been used for airships, since it is not inflammable. Its lifting power as compared with hydrogen is

$$0{\cdot}93\left(=\frac{28{\cdot}8-4}{28{\cdot}8-2}\right).$$

A large airship will contain 2-3 million cubic feet.

Isotopes

Four isotopes of helium are known: ^{4}He, which forms practically all the natural element, and ^{3}He, ^{5}He, and ^{6}He, which can be made artificially, and of the first of which there may be a trace in the natural gas.

^{3}He was found by Bleakney[12] to be formed when deuterium is bombarded by deuterons; two reactions occur[13]:

$$^2D + {}^2D \rightarrow {}^3He + {}^1n \quad \text{and} \quad \rightarrow {}^3H + {}^1H$$

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[10] H. N. Russell, *Nature*, 1935, **135**, 223.

[11] *J. Ind. Eng. Chem.* (News Ed.), 1940, 830.

[12] W. Bleakney, G. P. Harnwell, W. W. Losier, P. T. Smith, and H. D. Smyth, *Phys. Rev.* 1934, **46**, 81.

[13] M. L. E. Oliphant, P. Harteck, and Lord Rutherford, *Proc. Roy. Soc.* 1934, **144**, 692.

the two resulting nuclei (composed respectively of two protons and one neutron, or of one proton and two neutrons) both weigh 3·0172[13,15]; both are unstable, though they are relatively long lived.

This ^{3}He has recently been found to be present in minute quantities in natural helium; Alvarez and Cornog,[16,17] using a 60-inch cyclotron as a mass spectrograph, have got evidence that it occurs to an extent of 10^{-7} in atmospheric helium and 10^{-8} in helium from gas wells.

The isotope ^{5}He is far more unstable. It is formed in several nuclear reactions; it is produced[18] when 'heavy' paraffin is bombarded with α-particles:

$$^{2}\mathrm{D} + {}^{4}\alpha \rightarrow {}^{5}\mathrm{He} + {}^{1}\mathrm{H}.$$

It can also be made[19,20] along with ordinary helium by bombarding lithium with swift deuterons:

$$^{7}\mathrm{Li} + {}^{2}\mathrm{D} \rightarrow {}^{4}\mathrm{He} + {}^{5}\mathrm{He}.$$

Its mass is 5·0106[21]; it rapidly decays thus:

$$^{5}\mathrm{He} \rightarrow {}^{4}\mathrm{He} + {}^{1}n.$$

^{5}He has a half-life of 0·85 sec.[22]

The following are the masses of the three isotopes:

^{3}He	^{4}He	^{5}He
3·0172 3 × 1·0057	4·00386^{a} 4 × 1·00097	5·0106^{b} 5 × 1·0021

$a = {}^{24}$, $b = {}^{21}$

From these figures it is evident that if four hydrogen atoms (4 × 1·00813 = 4·03252) could be made to form a ^{4}He nucleus, they would lose 0·02866 of a unit of mass, and hence emit 0·02866 × 940 = 26·94 m.e.v. of energy; this is 622 million k.cals. for 4 g. of hydrogen, or 156 millions per gramme. Bethe has shown[25] that this could be brought about in a star by the following series of reactions:

$$^{12}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{13}_{7}\mathrm{N};\quad {}^{13}_{7}\mathrm{N} \rightarrow {}^{13}_{6}\mathrm{C} + e^{+};\quad {}^{13}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{14}_{7}\mathrm{N};$$
$$^{14}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{15}_{8}\mathrm{O};\quad {}^{15}_{8}\mathrm{O} \rightarrow {}^{15}_{7}\mathrm{N} + e^{+};\quad {}^{15}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{4}_{2}\mathrm{He}.$$

[14] N. R. Sen and U. R. Burman, *Astrophys. J.* 1944, **100**, 347.
[15] T. W. Bonner, *Phys. Rev.* 1938, **53**, 711.
[16] L. W. Alvarez and R. Cornog, ib. 1939, **56**, 379.
[17] Ib. 613.
[18] F. Joliot and I. Zlotowski, *C.R.* 1938, **206**, 17, 1256.
[19] J. H. Williams, W. G. Shepherd, and R. O. Haxby, *Phys. Rev.* 1937, **51**, 888.
[20] H. Staub and W. E. Stephens, ib. 1939, **55**, 845.
[21] F. Joliot and I. Zlotowski, *J. Phys. Radium*, 1938, [vii] **9**, 403.
[22] H. S. Sommers and R. Sherr, *Phys. Rev.* 1946, ii. **69**, 21.
[23] J. H. Jeans, *Nature*, 1943, **151**, 7.
[24] K. T. Bainbridge, *Phys. Rev.* 1938, **53**, 922.
[25] H. A. Bethe, ib. 1939, **55**, 434.
[26] H. N. Russell, *J. Franklin Inst.* 1939, **228**, 143.

the carbon acting as a catalyst; and that these could occur in the interior of stars quickly enough to give the stellar temperatures required by astrophysicists (e.g. sun 18–21, Sirius 22 million °C.).[26]

The rate of these nuclear reactions under bombardment is very sensitive to temperature, and has a sharp maximum at a critical temperature which is higher the heavier the nucleus attacked. It can be shown[23] that as a star condenses under its own gravitation after separation from its galaxy, its temperature rises. When it reaches 3-7 million degrees, the Li, Be, and B nuclei are attacked by the protons, which is no doubt why these elements are abnormally rare. After they have mostly disappeared, a further rise of temperature occurs, and at about 20 million degrees, which actually is the approximate central temperature of the largest class of stars ('main-sequence' stars), the carbon nuclei are attacked, and the chain of reactions given above takes place, in which the carbon (unlike the Li, Be, and B) is not used up, but merely catalyses the conversion of the hydrogen into helium+energy. The amount of hydrogen being large, this process will last for some time; the sun is now emitting 250 million tons of energy a minute, and if it had only $\frac{1}{8}$ per cent. of hydrogen (it certainly has more) the energy of its conversion would last at this rate of loss for 2,000 million years.

When the hydrogen has at last disappeared, the star will begin to contract and warm up again, unless or until other nuclear reactions become possible in sufficient amount to balance the emission of energy. This is the condition of the very small and hot stars, whose central temperatures are found to be much above 20 million degrees. (See further Sen and Burman.[14])

The chief scientific use of helium, the most volatile of liquids, is for the production of low temperatures by its evaporation under reduced pressures. The process was developed by Kamerlingh Onnes and Keesom at Leyden, until finally Keesom succeeded, by the use of a large battery of pumps, in reaching 0·71° K. by keeping the pressure down to 0·00036 mm. of mercury. This is about as far as the process can be usefully carried. But much lower temperatures can be obtained by a method suggested by Debye and by Giauque, and carried out by Giauque, de Haas, and Simon. In a paramagnetic substance the atoms, or some of them, act as little magnets, which are normally oriented at random. When it is magnetized, these are all oriented parallel to one another, and this increase of order (or fall of entropy) must, if the substance is thermally isolated, be accompanied by a diminution of order in the atomic motions, that is, by a rise of temperature. Conversely when it is demagnetized by removing the magnetic field, heat is absorbed. The substance used must remain paramagnetic down to the lowest temperatures reached: Giauque used gadolinium sulphate, but Simon and de Haas have found that one can use much cheaper materials such as ammonium iron alum and potassium chromium alum. The salt is enclosed in a metallic vessel surrounded by a vacuum, the magnetic field is turned on, and liquid helium added. The helium gas is then pumped off until the vessel has fallen to 1° or 2° K., and the magnetic field removed. In this way Simon, using a field of 14,000 Gauss, has reached 0·03° K., while de Haas, with a much stronger magnet, claims to have reached 0·005° Abs. To realize the result we must remember that it is the ratio of the temperatures that matters, and not their difference. The change from 0·005° K. to 4·22° K., the boiling-point of helium, is an increase in the ratio 844 to 1; another step upwards of the same size would bring us to 4·22 × 844, or 3,562° K., nearly the boiling-point of carbon.

The success of this process is helped by the facts that the specific heat of the metallic container is almost negligible at these low temperatures (even at 12° K. 1 c.c. of helium under 100 atmospheres has as large a capacity for heat as 1 kg. of copper), and that owing to the low pressure of the gas (3×10^{-15} mm. at 0·2° K.) the vacuum jacket is an almost perfect insulator.

These temperatures are measured down to about 1° K. by a helium gas thermometer under low pressure, and below this by means of the magnetic susceptibility (to weak fields) of the paramagnetic material, which is approximately proportional to the reciprocal of the absolute temperature.

*Liquid and Solid Helium**

In the liquid and solid states helium has properties unlike those of any other substance.

Liquid helium occurs in two forms, He I and He II, with a sharp transition point (the λ-point) at 2·186° K. under 3·83 cm. mercury[27]; this falls as the pressure rises, and the triple point for solid—He I—He II is 1·774° K. under 28·91 atmospheres.[28] He I (above this temperature) is a normal liquid; He II, below it, is unlike any other known substance. He II expands on cooling; it has 10 times the specific heat of He I, but this rapidly falls; its conductivity for heat is enormous, being found (by the usual methods of measurement) to be about 3 million times that of He I, and about 200 times that of copper at the ordinary temperature. Again, while the viscosity of He I is normal, and that of He II as measured by a rotating disk,[29] though it drops rapidly with falling temperature, retains a finite value, the viscosity of helium II measured in a capillary of fine bore or by flow through a narrow slit appears to be zero[30] or at least less than 10^{-11} poises.

Still more remarkably, neither the heat conduction nor the viscosity obey what are otherwise universal rules: the heat transport is not

* I am greatly indebted to Dr. K. Mendelssohn for his help in dealing with this subject.

[27] G. Schmidt and W. H. Keesom, *Physica*, 1937, **4**, 971.

[28] J. J. van Laar, *Proc. K. Akad. Amst.* 1936, **39**, 612, 822.

[29] W. H. Keesom and G. E. Macwood, *Physica*, 1938, **5**, 737.

[30] P. L. Kapitza, *Nature*, 1938, **141**, 74: J. F. Allen and A. D. Misener, *Proc. Roy. Soc.* 1939, **172**, 467.

proportional to (i.e. the conductivity is dependent on) the temperature gradient, and the flow through a fine capillary is independent of the head, though it changes rapidly with temperature. It has further been shown[31] that when the liquid flows from a higher to a lower level through a capillary it is cooled.

These very remarkable facts have been explained up to a point by an observation of Allen and Jones,[32] who found that when one of two containers filled with liquid helium II and connected by a capillary is warmed (always below the λ-point), helium will flow through the capillary towards the higher temperature. By using a tube filled with emery (i.e. with many fine capillaries) heated in the upper part by radiation from a lamp outside, a jet of liquid helium 3 or 4 cm. high can be got. The effect diminishes as the tube gets wider, and vanishes at a diameter of about 1 mm. This anomalous flow seems to give rise to convection currents which are free of friction in one direction. For instance, if a small flask with a heating wire near the bottom is immersed horizontally in He II and the wire heated, a stream of helium flows out through the neck and will move a vane, though no helium appears to move in.[33] For some reason helium in this state can form a layer on any solid surface about 5×10^{-6} cm. thick (500 A.U., or, say, 140 atoms) which can move on the surface without any measurable friction. The occurrence of this flow is easily demonstrated.[34,35] If the bottom of an empty vessel is dipped into He II it fills up to the same level; if it is then raised the level falls to that of the liquid outside; if the vessel when full is lifted out of the helium, the liquid drips from the bottom until it is empty. The rate of flow in c.c./sec. for every cm. of contact with the walls is $2{\cdot}5 \times 10^{-5}$ at 2° K., and about $7{\cdot}5 \times 10^{-5}$ at 1° K.: it is independent of the difference of height (the rate of movement of the film at 1° K., if it is 5×10^{-6} cm. thick, must be about 20 cm./sec.).

The Debye X-ray pictures show that helium is not a crystalline liquid at any temperature from 1·72° to 4·22° K.,[36] and there is no change at the λ-point in refractive power,[37] molecular volume, or surface tension.[38] At very low temperatures many of these peculiarities disappear. For a general account of these phenomena see Darrow.[39] The physical structure underlying and explaining these peculiarities is not clear. Daunt and Mendelssohn[40] point out the analogy between the properties of He II

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[31] J. G. Daunt and K. Mendelssohn, *Nature*, 1939, **143**, 719; P. L. Kapitza, *Phys. Rev.* 1941, **60**, 354.

[32] J. F. Allen and H. Jones, *Nature*, 1938, **141**, 243.

[33] P. L. Kapitza, *J. Phys. U.S.S.R.* 1940, **4**, 181; 1941, **5**, 59.

[34] J. G. Daunt and K. Mendelssohn, *Nature*, 1938, **141**, 911; **142**, 475.

[35] Id., *Proc. Roy. Soc.* 1939, **170**, 423, 439.

[36] W. H. Keesom and K. W. Taconis, *Physica*, 1937, **4**, 28, 256 (the latter a small correction).

[37] E. F. Burton, *Nature*, 1937, **140**, 1015.

[38] J. F. Allen and A. D. Misener, *Proc. Camb. Philos. Soc.* 1938, **34**, 299.

[39] K. K. Darrow, *Rev. Mod. Phys.* 1940, **12**, 257.

[40] J. G. Daunt and K. Mendelssohn, *Nature*, 1942, **150**, 604.

(frictional transport up to a critical rate of flow) and the phenomenon of super-conductivity; they say that He II must contain atoms of low or zero thermal energy, separated by their velocities from the rest. A theory of liquid helium II based on the condensation of a Bose–Einstein gas has been proposed by F. London[42] and developed by Tisza.[41] The theory of Landau[43] follows similar lines but is not based on a special model. According to this there are two forms of liquid helium, one (N) a normal liquid, and the other (S) with zero entropy and no viscosity. Down to 2·19° K. the liquid is all N; below this S appears in increasing quantity until at 0° K. it is all S. Thus when the flask (p. 6) is warmed there is an outward flow of N and an inward flow of S, but the latter does not affect the vane since it has no viscosity; when this S reaches the heater it is changed into N. The heat conductivity is due to the fact that heat must be expended to transform the zero-entropy from S into N; the cooling on passage through a capillary is due to a kind of filter effect, the S passing through more easily than the N, and being then converted into N with absorption of heat.

The theories of Tisza and of Landau both predict that in He II temperature differences should be propagated in the form of wave motion with a characteristic temperature-dependent velocity. This so-called 'second sound' has indeed been observed.[44]

Solid Helium

Helium is the only liquid which cannot be frozen by lowering the temperature; at the ordinary pressure it must remain liquid down to the absolute zero. On the other hand, it is readily frozen by increasing the pressure; its freezing-point under various pressures has been found[45,46] to be:

Temp. °K. . .	1°	2°	3°	10°	20°	42°
Press., atm. . .	25	35	75·5	590	1,740	5,450

This is due to the 'zero-point energy'. We now know that substances still retain, even at the absolute zero, half a quantum of energy in every degree of oscillational freedom. This can be deduced from Heisenberg's Uncertainty Principle; it is really no more surprising than that a hydrogen atom at the absolute zero should still have its electron in the first quantum state and not in the nucleus. The result is that the atoms in liquid helium continue at the lowest temperatures to oscillate, and the energy of this oscillation is greater than the heat of fusion; their motions are too lively for them to form the crystal. It is only when these motions are restrained by external pressure that the liquid can solidify. The effect is still per-

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[41] L. Tisza, *Nature*, 1938, **141**, 913.

[42] F. London, *Phys. Rev.* 1938, **54**, 947.

[43] L. Landau, ib. 1941, **60**, 356.

[44] V. Peshkov, *J. Phys. U.S.S.R.* 1946, **10**, 389.

[45] W. H. Keesom, *Nature*, 1926, **118**, 81; *C.R.* 1926, **183**, 26, 189.

[46] F. Simon, M. Ruhemann, and W. A. M. Edwards, *Z. physikal. Chem.* 1929, **B 6**, 62.

ceptible even in the crystal, as the interatomic distances show (He 3·57; Ne 3·20; A 3·82 A.U.).

NEON, ARGON, KRYPTON, XENON, EMANATION

Of the later members of this group there is little to say, apart from a few special points, except on the obscure question of the formation of chemical compounds. Their more important physical properties have already been given in the table on p. 1.

Neon is used, generally mixed with helium, in the familiar neon lamps. The efficiency (light/energy) of these is about four times as great as that of the best metallic filaments, and nearly 25 per cent. of the theoretical maximum, at which all the energy appears as light.

Argon[47] is used for gas-filled incandescent lamps, mainly to prevent the evaporation and sputtering of the filament, and is usually mixed with about 15 per cent. of nitrogen to stop the formation of an arc.

Emanation. The importance of the three isotopic emanations—now known by the rather unpleasant names of radon, actinon, and thoron—in the discovery and development of the disintegration theory of radioactivity, and in the explanation of the periodic classification, is obvious. Their atomic weights and half-lives are:

	Actinon	*Thoron*	*Radon*
Atomic weight . .	219	220	222
Half-life . . .	3·9 sec.	54·5 sec.	3·8 days
Rel. half-life . .	1	14	84,200

Compounds of the Inert Gases

The compounds or supposed compounds of the inert gases are of three kinds: (1) molecules and molecular ions of the inert gases themselves; (2) supposed compounds of uncertain composition with other elements, mainly metals; (3) solid phases of definite stoichiometric formulae formed with certain other molecules such as water.

I. Ions of the He_2^+ type are undoubted diatomic molecules; He_2^+ is formed by the attachment of a metastable to a normal atom; the heat of dissociation is 108·4 k.cals./mole.[48] As long as they remain charged gaseous ions they are reasonably stable,[49,50] though they cannot act as the cations of salts; the atoms are 1·09 A apart (which should be compared with the He··He distance in solid helium of 3·57 A).

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[47] For entropy, etc., of argon (triple pt. 83·78° K. at 517 mm.) see K. Clusius and A. Frank, *Z. Elch.* 1943, **49**, 308.

[48] F. L. Arnot and M. B. M'Ewen, *Proc. Roy. Soc.* 1939, **171**, 106.

[49] L. Pauling, *Chemical Bond*, 1939, p. 246.

[50] E. Majorana, *Nuovo Cim.* 1931, **8**, 22; L. Pauling, *J. Chem. Phys.* 1933, **1**, 56; S. Weinbaum, ib. 1935, **3**, 547; L. Pauling and E. B. Wilson, *Introd. to Quantum Mechanics*, 358.

II. Various metals have been stated to form compounds with inert gases (practically only with helium), usually on sparking; when solid, the products have been found to give off their helium on heating or dissolving. Manley[51] describes a volatile compound with mercury, detected by the spectrum. Boomer[52] obtained with tungsten a solid of the composition WHe_2, decomposed by heat. Damianovich[53-5] found that on sparking helium with platinum a brown deposit was formed containing up to 34 c.c. of helium to 1 g. metal ($Pt_{3.3}He$); he obtained similar substances with bismuth and uranium.[56-7] None of these substances have been shown to be definite compounds, and it is at least possible that the solids merely contain adsorbed helium on the dispersed metal; indeed, Damianovich says[58] that his platinum product gave X-ray diagrams resembling those given by colloidal platinum.

III. Substances of the third class are formed by the inert gases other than helium, and the more easily the heavier the gas, with water, D_2O, phenol, and boron trifluoride. There is no doubt about the existence, nor usually about the composition and formulae of these substances; but there is no evidence of their occurring in anything but the solid state, and so they are presumably van der Waals crystal aggregates, like the solid hydrates of methane and methyl bromide.

The hydrates were discovered by de Forcrand,[59] who gives these compositions, melting-points, and dissociation tensions at 0° C.:

	A, $x H_2O$	Kr, $5H_2O$	Xe, $x H_2O$
Melting-point . .	8° C.	13° C.	24° C.
Diss. tens. at 0° C. .	98 atm.	15·5 atm.	1·3 atm.

Tammann and Krige[60] confirm these data for the solid Kr, $5H_2O$. Deuterates of similar types, with the compositions Kr, $6D_2O$ and Xe, $6D_2O$ were made by Godchot *et al.*[61]

Nikitin[62-4] showed that the solid SO_2, $6H_2O$ will absorb the inert gases other than helium if it is shaken with them, a definite ratio being established between the concentration of the inert gas in the solid and the

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[51] J. J. Manley, *Phil. Mag.* 1927, vii. 4, 699.

[52] E. H. Boomer, *Proc. Roy. Soc.* 1925, **109**, 198.

[53] H. Damianovich, *C.R.* 1929, **188**, 790.

[54] H. Damianovich and J. J. Trillat, ib. 991.

[55] H. Damianovich, *Anal. Quim. Argentina*, 1929, **17**, 95.

[56] Id., *Anal. Inst. invest. cient. techn.* 1934, **3/4**, 20.

[57] For a summary of the evidence for the formation by He, A, and Xe of compounds with metals see H. Damianovich, *Proc. 8th Amer. Sci. Congress*, 1942, **7**, 137.

[58] H. Damianovich, *Anal. Inst. invest. cient. techn.* 1931, **2**, 15, 24.

[59] R. de Forcrand, *C.R.* 1923, **176**, 355; 1925, **181**, 15.

[60] G. Tammann and G. J. R. Krige, *Z. anorg. Chem.* 1925, **146**, 179.

[61] M. Godchot, G. Cauquil, and R. Calas, *C.R.* 1936, **202**, 759.

[62] B. A. Nikitin, *Nature*, 1937, **140**, 643.

[63] Id., *J. Gen. Chem. Russ.* 1939, **9**, 1167, 1176.

[64] Id., *Z. anorg. Chem.* 1936, **227**, 81.

gaseous phase. He also[65] prepared with phenol the solid Xe, $2C_6H_5OH$, which had a dissociation pressure of xenon of 1 atmosphere at 0° C. (the v.p. of liquid xenon at 0° C. is about 46 atmospheres).

Booth and Willson[66] measured the freezing-point curve for the system A-BF_3, and got maxima for the compositions 1 argon to 1, 2, 3, 6, 8, and 16 BF_3; pressure up to 40 atmospheres had no effect. It is very singular that all the 6 maxima and the melting-point of BF_3 lie between −127° and −129° C.; the melting-points of the components are argon −189·4°, BF_3 −127° C. At higher temperatures (mostly from −40° to 0° C.) they find no evidence of the existence of compounds.[67]

We must conclude that apart from the molecular ions occurring in the gas, there is in no case satisfactory evidence of the existence of chemical compounds of any of the inert gases.

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[65] B. A. Nikitin, *C.R. Acad. Sci. U.S.S.R.* 1940, **29**, 571.

[66] H. S. Booth and K. S. Willson, *J.A.C.S.* 1935, **57**, 2273.

[67] Ib. 2280.

GROUP I

HYDROGEN, DEUTERIUM, AND TRITIUM

HYDROGEN, the lightest of the elements, was one of the chief problems of the original Periodic Table, since it has close affinities both with the alkali metals of Group I and with the halogens of Group VII. We now realize that it stands at the head of both groups, resembling the alkali metals in having a single easily detached electron, and the halogens in having one electron less than the next following inert gas. It thus occupies a unique position in the Table.

The amount of hydrogen in the earth's crust, including the water and the air, is estimated at 0·87 per cent. by weight and 15·4 per cent. by atoms. Free hydrogen occurs to a minute extent in the atmosphere (according to Paneth[1] less than 1 part in a million by volume); it is continually being produced on the earth's surface from various sources, including oil gas outflows, but at the same time the molecules move quick enough to escape from the earth's gravitational field (see above, p. 2). Natural gas may contain up to 10 or even 30 per cent. of hydrogen, the remainder being mainly methane and ethane. Commercially hydrogen can be obtained from this source or from coal gas (of which it forms some 50 per cent.) by liquefying the other components, but it is more often got (for example in making synthetic ammonia) from water gas, which is a mixture of hydrogen and carbon monoxide, made by passing steam over heated coal or coke; if this is mixed with more steam and passed over a suitable catalyst (oxides of iron and cobalt are commonly used) at a temperature not above 400° C., the carbon monoxide reacts with the steam to give carbon dioxide and hydrogen. The carbon dioxide is removed by washing with water under pressure, and the residual carbon monoxide by treatment with ammoniacal cuprous solution, or by passing over heated soda lime, which reacts with it to give sodium formate.

Hydrogen occurs in a surprisingly large number of forms.

1. There are three known isotopes of hydrogen, of mass-numbers 1, 2, and 3. The first two of these occur in nature in the proportions roughly of 6,000 to 1; the third is now known not to occur in natural hydrogen in detectable amounts, but it can be made by atomic bombardments, for example, of deuterium by deuterons. These isotopes are distinguished as Protium, Deuterium, and Tritium; but the properties of pure protium and its compounds are practically identical with those of the natural isotopic mixture. The peculiar properties of deuterium, and so far as they are known of tritium, are described in the next sections (deuterium, p. 36; tritium, p. 57).

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[1] F. A. Paneth, *Nature*, 1937, **139**, 181.

II. Elementary hydrogen exists in several states.

1. Diatomic hydrogen H_2, the normal state of the gas. This can assume two forms with different properties, known as ortho- and para-hydrogen, and is normally a mixture of the two; the same is true of deuterium D_2. The molecule can also have a positive charge H_2^+, as in positive ray tubes.

2. Monatomic or 'active' hydrogen H (see p. 15). This electrically neutral form can be produced in the gas by electrical excitement, and shows an intense chemical activity. The positively charged hydrogen atom H^+ is the hydrogen nucleus, proton, or hydrogen ion (formerly thought to be the unit of positive electricity), which is important both from its chemical activity, and as a projectile for, and a product of, nuclear disintegration.

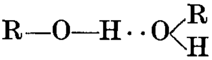
3. Triatomic hydrogen H_3 certainly occurs as the positive ion H_3^+ in positive ray tubes; its existence as a neutral H_3 molecule, though it has often been asserted, is very doubtful.

III. In its compounds hydrogen is found:

1. As a positive ion H^+ (except in the gas always solvated, as $H^+ \leftarrow X$).

2. As a negative ion H^- (with two unshared electrons), only in the hydrides of the alkalis and the alkaline earths, such as Li[H] and $Ca[H]_2$.

3. In the covalent form H—X (with two shared electrons), as in the hydrocarbons, and organic compounds generally.

4. In the form of the 'hydrogen bond' or (perhaps better) the 'hydrogen bridge' —H··, as in the ion $[F—H\cdot\cdot F]^-$ or in associated hydroxylic compounds  $R—O—H\cdot\cdot O\begin{matrix}\diagup R\\ \diagdown H\end{matrix}$; the mechanism of this link is different from that of ordinary coordination (and so it should not be written with an arrow $X—H \leftarrow X$), but its existence is indisputable (see p. 23).

Elementary Hydrogen

Ordinary hydrogen boils at −252·78° C. (20·38° K.) and melts at its triple point under 54 mm. pressure at −259·24° C. (13·92° K.).[2]

In the liquid and solid states it is the lightest substance known; the density of the liquid at 20° K. is 0·0700 and that of the solid at 13° K. 0·0763.

Its solubility at 25° (in c.c. per litre of solvent) is[3]: water 19·9; ethyl alcohol 89·4; acetone 76·4; benzene 75·6.

Ortho- and Para-Hydrogen

It has been shown that, quite apart from isotopes, hydrogen gas under all ordinary conditions is a mixture of two kinds of molecules. Of the two nuclei and two electrons of which the molecule is made up, each is spinning round its own centre, in a plane in which the axis of the molecule lies.

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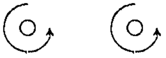
[2] F. G. Brickwedde, R. B. Scott, H. C. Urey, and M. H. Wahl, *Phys. Rev.* 1934, 45, 565, 762; *J. Chem. Phys.* 1934, 2, 454.

[3] G. Just, *Z. physikal. Chem.* 1901, 37, 342.

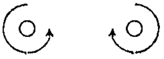
The electrons must spin in opposite directions (antiparallel), or the molecule would not hold together; but the spins of the nuclei may either be in the same (parallel) or in opposite directions, and certain properties of the molecule, especially its specific heat, will be different in the two arrangements. In 1927 Dennison pointed out[4] that the observed specific heats could be made to agree with the theory only if it was assumed that the time of transition was very long in comparison with the time in which the specific heats were measured, so that the gas was in effect a mixture of the two forms in fixed proportions. Subsequent work has entirely confirmed this view. The two differ especially in the fact that of the rotational energy (which is practically all the heat energy other than translational that the molecules have up to high temperatures) the ortho (parallel) molecules have the odd quantum states 1, 3, 5, etc., and the para (antiparallel) the even, 0, 2, 4, etc., which results in the ortho having, especially at low temperatures, a smaller specific heat than the para. We thus have:

Ortho



Spins parallel
Rotational quanta odd

Para



Spins antiparallel
Rotational quanta even

The proportions can be determined from the heat conductivity (which depends on the specific heat) by observing the rate of cooling of a heated wire in the gas.

At equilibrium at the ordinary temperature and above it the gas contains 25 per cent. of para and 75 per cent. of ortho, but on cooling the percentage of para rises, because more of the gas can thus go into the (even) zero-quantum state, and at the boiling-point of hydrogen (20·4° K.) only a fraction of 1 per cent. of ortho remains. The proportions at equilibrium and the specific heats are:

Temp.	*20° K.*	*50° K.*	*100° K.*	*200° K.*	*298° K.*	*Inf.*
Per cent. para	99·8	76·9	38·5	26·0	25·1	25·00
Sp. ht. Pure para	..	0·040	1·504	2·767	2·186	..
Pure ortho	..	0·000	0·073	1·151	1·838	..
Normal* H_2	..	0·010	0·431	1·555	1·925	..

* i.e. the equilibrium mixture at the ordinary temperature, which has 25 per cent. para.

In order to make para-hydrogen (it is of course impossible to get the ortho with less than 25 per cent. of para) the gas must be cooled (if possible with liquid hydrogen, though liquid air under reduced pressure will give a gas with 45 per cent. of para), and then brought to equilibrium by means of a catalyst. This is most easily done by absorbing the gas on charcoal, and then after some minutes or hours, according to the activity of the the charcoal, pumping it off.

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[4] D. M. Dennison, *Proc. Roy. Soc.* 1927, **115**, 483.

The physical properties differ slightly, and the values for some of them (those for pure ortho being got by extrapolation) are[2,5,6]:

	M.-pt.	*B.-pt.*	*Mol. vol. 20° K.*
Pure para . . .	13·88° K.	20·29°	28·54
Pure ortho . . .	13·93°	20·41°	28·35
Normal (25 per cent. p.) .	13·92°	20·38°	28·40

Pure para-hydrogen remains unaltered in the gaseous state for weeks; the half-life is calculated to be about 3 years. The interconversion can be effected (1) by heat, at about 1,000° C.; (2) slowly in the liquid or solid state: the half-life in the liquid is about 5 days; (3) by treatment with atomic hydrogen (this is probably the mechanism of most of the conversions):

$$H + H_2(o) \longrightarrow H_2(p) + H;$$

(4) by paramagnetic molecules (including contact with paramagnetic metals, oxides, and salts[7]; and (5) by the catalytic action of certain surfaces.

The last three of these methods have led to interesting results, and are likely to lead to more. The conversion by atomic hydrogen (3) gives a method of measuring the concentration of free hydrogen atoms in a chemical reaction, and has been used for this purpose. In the paramagnetic method (4) it has been shown that the transformation is catalysed by oxygen, nitric oxide, and nitrogen peroxide, which are all paramagnetic, but not by such diamagnetic gases as nitrogen, nitrous oxide, carbon monoxide, or ammonia, nor by diborane B_2H_6, which therefore is presumably diamagnetic also.

As to (5), a series of surfaces, especially platinum, and in a less degree nickel and copper (and to a small extent even sodium chloride), have been found to promote the change; this is no doubt due to the molecules breaking up, so that the hydrogen atoms may attach themselves separately to the surface.

This ortho-para difference should occur in all molecules containing two identical atoms if these atoms have a nuclear spin (in such molecules as He_2, $^{12}C_2$, $^{16}O_2$, and $^{32}S_2$ the nuclei have no spin). It may probably be found also with molecules of more than 2 atoms, such as H_2O, but here we should expect the equilibrium always to be maintained. The only other molecule for which it has been established is deuterium D_2, where the relations are much the same as with ordinary hydrogen, but the ratio of ortho to para at the ordinary temperature is 2:1 instead of 3:1.

For further information see Farkas[8]; for ortho- and para- D_2 see below, p. 39.

[5] K. Clusius and K. Hiller, *Z. physikal. Chem.* 1929, B 4, 158.

[6] R. B. Scott and F. G. Brickwedde, *J. Chem. Phys.* 1937, **5**, 736.

[7] H. S. Taylor and H. Diamond, *J.A.C.S.* 1935, **57**, 1251.

[8] A. Farkas, *Ortho-hydrogen, Para-hydrogen, and Heavy Hydrogen*, Cambridge, 1935.

The Molecule-ion H_2^+

This ion occurs in positive ray tubes,[9] and also gives a characteristic band spectrum. It is of great theoretical interest, as the simplest possible case of two nuclei held together by a single electron: it contains the most certain 'one-electron bond'. The physics of this link was first worked out by Hund, and has since been discussed in more detail especially by Pauling[10] and Dickinson[11]; Pauling has given a general account in his *Chemical Bond*, pp. 13-17, from which the following is derived. The formation of such a link from a neutral hydrogen atom and a hydrogen ion cannot be explained by classical mechanics, but only by wave mechanics through the theory of resonance; the molecule is a combination of the two states $H+H^+$ and H^++H; the bond may be said to owe its stability to the resonance of the electron back and forth between the two nuclei, with a resonance frequency equal to the resonance energy (50 k.cals./mole) divided by the Planck constant h; this frequency is 7×10^{14} per second, which is about one-fifth as great as the frequency of orbital motion about the nucleus, of the electron in the normal hydrogen atom.

A more detailed investigation of the problem by Dickinson[11] and others[12] has shown that the total energy of the bond is 61 k.cals./mole, and the internuclear distance 1·06 A, values which agree closely with experiment; the values for the normal 2-electron link in H—H are 103·4 k.cals. and 0·75 A.

Monatomic Hydrogen

At high temperatures hydrogen molecules are to some extent dissociated into atoms, but on account of the large heat of dissociation (103·4 k.cals.) the amount of atoms formed is very small, being at 1 atmosphere about 1 per cent. at 2,000° K. and about 9 per cent. at 3,000° K.[13]

The molecules can, however, be dissociated by other means at lower temperatures, and they recombine relatively slowly (owing to the difficulty of getting rid of the heat of reaction*) especially at low pressures, so that the gas can be more or less completely converted into single atoms, which remain in that state long enough for their properties to be examined. This is known as 'active' hydrogen, and it is probably the only active form which exists. It can be prepared in various ways.

1. Langmuir[14] has shown that wires of tungsten, platinum, or palladium, heated to temperatures of from 1,000° to 2,000° C. in hydrogen gas at pressures of 0·01 mm. or less, give rise to atomic hydrogen (by absorbing

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* See below, p. 17.

[9] First observed by J. J. Thomson, *Phil. Mag.* 1911, [6] **21**, 234, 239.

[10] L. Pauling, *Chem. Rev.* 1928, **5**, 173; cf. B. N. Finkelstein and G. E. Horowitz, *Z. Phys.* 1928, **48**, 118.

[11] B. N. Dickinson, *J. Chem. Phys.* 1933, **1**, 317.

[12] E. A. Hylleraas, *Z. Phys.* 1931, **71**, 739; G. Jaffé, ib. 1934, **87**, 535.

[13] I. Langmuir, *Gen. Electric Review*, 1926, **29**, 153.

[14] *J.A.C.S.* 1912, **34**, 1310; 1914, **36**, 1708; 1915, **37**, 417; 1916, **38**, 1145.

H_2 and emitting H) which is absorbed by the walls, especially at liquid air temperatures.

2. It was found by R. W. Wood[15] that if an electric discharge is passed through hydrogen at a fraction of a millimetre pressure in very long tubes, the central part of the tube gives a pure Balmer spectrum, showing that it contains a large proportion of hydrogen atoms. Harteck and Roeder[16] improved this method by using an inert carrier gas such as neon (e.g. 25 mm. neon and 1 mm. hydrogen); this enables the hydrogen to be passed into liquids of higher vapour pressures.

3. Cario and Franck[17] showed that hydrogen with the same reducing properties could be got in larger yields and at higher pressures (up to 15 mm.) by mixing it with mercury vapour and exposing it to the resonance radiation (wave-length 2,537 A) of a mercury arc. The energy of this radiation per g. atom ($h\nu \times N$) is 112·0 k.cals., so that the excited mercury atoms can disrupt the hydrogen, which needs 103 k.cals. This method has been used also by Taylor and his collaborators,[18] with hydrogen pressures up to half an atmosphere.

4. Hydrogen is also atomized when it is bombarded by slow (10–20 e.v.) electrons[19]; its formation in the electric arc is probably due partly to this effect and partly to the thermal action.

Hydrogen atoms recombine to molecules rapidly and with a large evolution of heat in contact with certain solids, especially metals. Bonhoeffer has shown[20] that the efficiency of different metals in causing the recombination of hydrogen atoms is almost exactly in the reverse order to their overvoltage values, as the following list shows; the metals are in the order of their catalytic efficiency, and the overvoltage stands below each:

Pt	>	Pd	>	W	>	Fe	>	Cr	>	Ag	>	Cu	>	Pb	>	Hg(zero)
0·000		0·000		0·157		0·175		0·182		0·097		0·19		0·40		0·57

This seems to show that the overvoltage is due to the slowness of recombination of the hydrogen atoms after they have neutralized their ionic charges at the cathode, and suggests that the activity of 'nascent hydrogen' is caused by the presence of neutral hydrogen atoms in the liquid.

The heat of recombination of the atoms (51·7 k.cals. per gramme) has been ingeniously utilized by Langmuir in his 'atomic blowpipe' in which a stream of highly atomized hydrogen is directed on the metal to be heated; this has the further advantage that the hot metal is in a reducing

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[15] *Proc. Roy. Soc.* 1920, **97**, 455; 1922, **102**, 1.

[16] P. Harteck and E. Roeder, *Z. physikal. Chem.* 1937, **178**, 389.

[17] G. Cario and J. Franck, *Z. Phys.* 1922, **12**, 161.

[18] H. S. Taylor. *J.A.C.S.* 1926, **48**, 2840; J. R. Bates and H. S. Taylor, ib. 1927, **49**, 2438; H. S. Taylor and A. L. Marshall, *J. physikal. Chem.* 1925, **29**, 1140; A. L. Marshall, ib. 1926, **30**, 1634.

[19] A. L. Hughes and A. M. Skellett, *Phys. Rev.* 1927, **30**, 11; K. E. Dorsch and H. Kallmann, *Z. Phys.* 1929, **53**, 80.

[20] K. F. Bonhoeffer, *Z. physikal. Chem.* 1924, **113**, 199.

atmosphere[21]; according to v. Wartenberg[22] the temperature of the flame near the electrode, as judged by the reversal of the spectral lines in comparison with those of the sun, is 4,600-4,800°. From the heats of reaction ($H+H = H_2+103{\cdot}4$ k.cals.; $2H_2+O_2 = 2H_2O+116$ k.cals.) it follows that for equal volumes atomic hydrogen is 34 per cent. more efficient than 'Knallgas', and for equal weights it is 24 times as effective.

In the gas the rate of recombination is much slower. A collision of two hydrogen atoms cannot of itself lead to the formation of a molecule, because the resulting pair cannot get rid of the energy of reaction, and so must separate again; it is only fruitful when there is a three-body collision

$$2H + M \rightarrow H_2M \rightarrow H_2 + M,$$

so that the energy can be removed as kinetic energy of the H_2+M (where M of course may be the wall); this difficulty arises in all reactions of association or addition. Various determinations of the rate of recombination of hydrogen atoms[23] have confirmed this view, and have shown that the rate is that required by the triple-collision theory; the half-life of the atoms is about 1 sec. at 0·2 mm. pressure.

The chemical reactions of atomic hydrogen are numerous, and have been the subject of many investigations.[24-41]

Atomic hydrogen is a strong reducing agent.[25] It converts oxygen into hydrogen peroxide[26,27]; it reduces ethylene to ethane[27]; it reduces oleic acid $C_8H_{17}{\cdot}CH{=}CH{\cdot}(CH_2)_7COOH$ to stearic, but leaves the carboxyl

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[21] I. Langmuir, *Science*, 1925, **62**, 463; *Gen. Electric Review*, 1926, **29**, 153, 160.

[22] H. v. Wartenberg and H. J. Reusch, *Nach. Ges. Wiss. Gött.* 1934, [ii] **1**, 141.

[23] (*a*) Z. Bay and W. Steiner, *Z. physikal Chem.* 1929, B **2**, 146; (*b*) H. Senftleben and O. Riechemeier, *Naturwiss.* 1930, **18**, 645; (*c*) K. G. Emeleus, R. W. Lunt, and C. A. Meek, *Proc. Roy. Soc.* 1936, **156**, 394; (*d*) Lunt and Meek, ib. **157**, 146; (*e*) Lunt, Meek, and E. C. W. Smith, ib. 1937, **158**, 729; (*f*) H. G. Poole, ib. 1937, **163**, 404; (*g*) id., ib. 415; (*h*) id., ib. 424.

[24] K. F. Bonhoeffer, *Z. physikal. Chem.* 1924, **113**, 199.

[25] Id., ib. 1925, **116**, 391.

[26] E. Boehm and K. F. Bonhoeffer, ib. 1926, **119**, 385.

[27] H. S. Taylor, *J.A.C.S.* 1926, **48**, 2840.

[28] F. Haber and H. D. v. Schweinitz, *Sitzb. Preuss. Akad.* 1928, 499.

[29] H. C. Urey and G. I. Lavin, *J.A.C.S.* 1929, **51**, 3286.

[30] E. Pietsch, F. Senferling, W. Roman, and H. Lehl, *Z. Elektrochem.* 1933, **39**, 577.

[31] K. H. Geib and P. Harteck, *Ber.* 1932, **65**, 1550, 1551.

[32] P. Harteck, ib. 1933, **66**, 423.

[33] K. H. Geib and P. Harteck, ib. 1815.

[34] Id., *Z. physikal. Chem.* 1934, **170**, 1.

[35] H. Kroepelin, E. Vogel, and H. Pfeiffer, *Ber.* 1935, **68**, 684.

[36] K. H. Geib and P. Harteck, *Trans. Far. Soc.* 1934, **30**, 131.

[37] H. Kroepelin and E. Vogel, *Z. anorg. Chem.* 1936, **229**, 1.

[38] P. Harteck and E. Roeder, *Z. physikal. Chem.* 1937, **178**, 389.

[39] P. Harteck and K. Stewart, ib. **181**, 183.

[40] J. K. Dixon, *J.A.C.S.* 1932, **54**, 4262.

[41] J. P. W. Houtman, K. van den Berg, and P. M. Heertjes, *Rec. Trav.* 1943, **62**, 672.

group untouched.[24,29,35] It reduces oxyazo to azo-compounds and ultimately to anilines; converts many dyes apparently into their leuco-bases; initiates an explosion in a mixture of hydrogen and oxygen,[28] and reacts with many metals and their vapours to form what seem to be hydrides.[30]

Kroepelin and Vogel[37] have shown that compounds of heavy metals are usually reduced with ease, alkaline salts are reduced to the metal when the anion is one that is destroyed by hydrogen atoms (e.g. NO_3', CN', ClO_3'). Aqueous solutions of silver nitrate, mercuric chloride, and cupric acetate are reduced to the metal, chromate and permanganate ions in acid solution to chromic and manganous salts, iodine to iodide, and hydrogen peroxide to water.

Harteck[38-9] finds that with solutions of sodium sulphate and sulphite the hydrogen atoms are all used up within the first 1,000 molecule layer; with reactions not too slow to measure the heat of activation is from 0 to 5 k.cals.; the heat of solution of hydrogen atoms in water is $1{\cdot}5 \pm 1$ k.cals. per g. atom.

Geib and Harteck[31-4] passed hydrogen at 0·5 mm. pressure, and about 60 per cent. atomized, along with another gas into a vessel cooled with liquid air. The low temperature hinders any reaction that has at all a considerable heat of activation (and substitutions usually have this), and leads chiefly to additions, since these have a small heat of activation but at ordinary temperatures are repressed by the necessity of triple collisions.

In this way they have been able to convert mercury into a hydride, apparently HgH, and identical with the hydride detected by its spectrum when a discharge occurs through hydrogen containing mercury; it is a solid which decomposes into its elements below $-100°$. With oxygen they get a white solid of the composition H_2O_2, different from ordinary hydrogen peroxide as it decomposes sharply at $-125°$ into oxygen and water. With nitric oxide they get a solid of the composition $(HON)_n$ which is explosive, and on warming slowly begins to decompose at $-95°$, and by the ordinary temperature has all disappeared, giving some 20 per cent. of nitrous oxide and water, and leaving a mixture of hyponitrous acid and nitramide. At this temperature atomic hydrogen reduces benzene to dihydrobenzene and ethylene to ethane, but it has little action on acetylene.

For further reactions, especially in the polymerization of unsaturated hydrocarbons, see Houtman, van den Berg, and Heertjes.[41]

The Proton H^+

H^+, the hydrogen nucleus, hydrogen ion, or proton, a particle with a mass of 1·0078 (O = 16), a radius of about 2×10^{-13} cm., and a charge of $+4{\cdot}802 \times 10^{-10}$ electrostatic units, was assumed to be the 'atom' of positive electricity until the discovery of the positron in 1933. Its behaviour is very different according as it is in a gas or in a solution.

1. In a gas it forms the hydrogen positive ray of J. J. Thomson and Aston, produced by the action of cathode rays on hydrogen gas. It can also be made by breaking off a hydrogen nucleus from a compound, as

when solid paraffin is bombarded by deuterons or neutrons. It is likewise formed when certain nuclei are artificially disrupted, as was shown in the first artificial nuclear disruption, that of nitrogen by swift α-particles, by Rutherford in 1919[42]; the first proof that this involves the capture of the α-particle by the bombarded nucleus was given by Blackett, by means of a Wilson-chamber photograph, in 1925.[43] It is also often formed in the spontaneous decomposition of artificially produced (though never, so far as is known, of natural) radioactive elements. It can itself be used as a projectile for nuclear bombardment, especially when it is accelerated by falling through a large potential drop; this is effected very powerfully in the cyclotron of E. O. Lawrence, in which protons with energies of many million electron volts can now be produced.[44]

When the proton has not these velocities, but only the ordinary gas-kinetic speeds, its life is very short, as it soon picks up an electron and becomes a neutral atom.

2. In solution as the hydrogen ion, H^+ plays a large part in many chemical and physiological phenomena. It has become evident that in a liquid it never exists as the free nucleus. From its minute size (its radius is only about 1/50,000 of that of the lithium ion, and its field strength, measured by the charge divided by the square of the radius, is 2,500 million times as great) its deforming power, in the sense of the Fajans theory, is so great that it always passes into the covalent state, and in water, for example, is always present as H_3O^+. It has been calculated[45] that the equilibrium constant for the reaction

$$H_2O + H^+ \rightleftharpoons H_3O^+$$

is 10^{-130}, which means that in 10^{70} universes filled with a normal acid solution there would be one unsolvated hydrogen ion. In solvents to which the hydrogen ion cannot attach itself, such as the saturated paraffins, all acids, even the strongest, if they dissolve at all do so as covalent molecules.

The strong tendency of the hydrogen ion to revert to the covalent state is shown by the limited ionization of acids as compared with, say, their alkaline salts. The ordinary organic acids (Ostwald's 'half-strong' acids) behave in water as mixtures of the covalent with a few per cent. of the ionized form, the latter being a strong electrolyte. Even strong acids like hydrochloric, though almost wholly ionized in water at ordinary concentrations, show in highly concentrated solutions (10 to 15 times normal), by the perceptible v.p. of the acid, that there is a good deal of the covalent form

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[42] *Phil. Mag.* 1919, [6] **37**, 537; *Proc. Roy. Soc.* 1920, **97**, 374.

[43] P. M. S. Blackett, ib. 1925, **107**, 349.

[44] See E. O. Lawrence *et al.*, *Phys. Rev.* 1939, **56**, 124; M. L. Oliphant, *Nature*, 1941, **148**, 717. Oliphant describes Lawrence's latest model; this has a magnet made of 3,700 tons of steel and 300 tons of copper (enough for 2 destroyers), standing on 1,200 tons of concrete; the poles are 184 in. (15 ft. 4 in.) across and 40 in. apart. It is to give 100 million e.v. deuterons. [Electrons from hot W wires ionize the gas, H_2, D_2, or He; dees about 100,000 volts difference, 10 million cycles per second.]

[45] I. M. Kolthoff, *Rec. Trav.* 1930, **49**, 401.

present; in the gas, and in the pure liquid and solid, hydrogen chloride is wholly covalent. On the other hand, the alkaline salts of these acids give no indication of the presence of covalent molecules; they are always completely ionized in solution, those of weak acids as well as those of strong, and it has been shown that the alkaline halides are ionized not only in the crystal but also in the vapour, where they are present as ion-pairs [M]X.

The Negative Hydrogen ion H^-

This has been found by J. J. Thomson[46] to occur in hydrogen discharge tubes and it has also been found when the discharge is passed through water vapour.[47] Its occurrence in compounds is limited to the hydrides of the most electropositive metals, those of the alkalis and the alkaline earths. That the hydrogen in these compounds, such as Li[H] and $Ca[H]_2$, is in the form of negative ions was predicted by G. N. Lewis in 1916, and has been confirmed by experiment; see p. 21.

Triatomic Hydrogen H_3 *and the ion* H_3^+

Both of these are described in the literature, but recent work, both theoretical and practical, has shown that while the ion H_3^+ exists, there is no good evidence for the uncharged molecule H_3. Bach[48] and Paneth[49,50] examined practically all the methods that are stated to give this molecule, and found no evidence for its existence. So, too, Smallwood and Urey[51] tried to make H_3 by the corona discharge, by the combustion of oxygen in hydrogen, by a vacuum discharge, and by passing hydrogen over heated metallic wires, but in vain. According to Conrad[52] the positive triatomic ions H_3^+ in canal ray tubes may be neutral for some part of their path.

On the other hand, the positive ion H_3^+ certainly exists, and has considerable stability. Eyring, Hirschfelder, and others in a series of papers[53-7] have calculated the energies of H_3 and H_3^+ by various methods and for various models; the lowest value is given by the triangular ion H_3^+; this has an energy content 184 k.cals. per mole less than that of the system $H+H+H^+$, so that the reactions

$$H_2 + H^+ \rightarrow H_3^+$$

and even

$$H_2 + H_2^+ \rightarrow H_3^+ + H$$

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[46] *Phil. Mag.* 1911, [6] **21**, 234, 239; 1912, **24**, 253.
[47] W. H. Bennett and P. F. Darby, *Phys. Rev.* 1936, **49**, 97.
[48] A. Bach, *Ber.* 1925, **58**, 1388.
[49] F. A. Paneth, *Z. Elektrochem.* 1924, **30**, 504.
[50] F. A. Paneth, E. Klever, and K. Peters, ib. 1927, **33**, 104.
[51] H. M. Smallwood and H. C. Urey, *J.A.C.S.* 1928, **50**, 520.
[52] R. Conrad, *Z. Phys.* 1932, **75**, 504.
[53] J. Hirschfelder, H. Eyring, and N. Rosen, *J. Chem. Phys.* 1936, **4**, 121.
[54] Id., ib. 130.
[55] J. Hirschfelder, H. Diamond, and H. Eyring, ib. 1937, **5**, 695.
[56] J. Hirschfelder, ib. 1938, **6**, 795.
[57] J. Hirschfelder and C. M. Weygandt, ib. 806.

are exothermic, the latter certainly by 11 and probably by 38 k.cals.; the molecule is triangular, with angles between 90° and 60°, and for the H—H distance they give the surprising value of 1·79 A[56] (the distance in H_2 is 0·75 and in H_2^+ 1·06 A). The quantum mechanics of the ion have also been discussed by Massey[58] and by Coulson[59]; the latter finds by the molecular orbital method that the molecule is triangular with an H—H distance of 0·85 A, which seems much more probable.

On the experimental side it has been shown that the H_3^+ ion can be produced in the positive ray tube. Its mass was found by Aston with the first mass-spectrograph to be 3·026 (3 × 1·0087), and this value is near enough to show that the particle measured contained 3 hydrogen atoms; no other molecule could have had so large an excess over a whole number except HD; but the concentration obtainable was too large for this. The corresponding mixed ions H_2D^+ and HD_2^+ have recently been observed.

Owing to its relatively high stability, the H_3^+ ion is formed spontaneously in the gas from the ordinary diatomic ion H_2^+. It has been shown by Luhr[60] that if the ions produced by a glow discharge in hydrogen at relatively high pressures are allowed to 'age' by drifting at a low speed through some centimetres of the gas, the ordinary diatomic ions H_2^+ (the number of protons present is small) change over almost completely to triatomic H_3^+ ions, which may be made to constitute 95 per cent. of all the ions present.

Binary Hydrides

The very numerous compounds of hydrogen with other elements are discussed later under the other elements, but some general remarks may be made here about one group of them, the binary hydrides H_xA_y. These fall into four classes:

I. Salt-like hydrides, such as $Ca[H]_2$.
II. Volatile hydrides, such as CH_4 and H_2O.
III. Metal-like hydrides, such as those of cerium and palladium: often of uncertain composition and structure.
IV. Spectroscopic hydrides of the composition HA, formed by the electric discharge in hydrogen in presence of the other element. They cannot be isolated in quantity, but are detected through the spectrum.

I. *Salt-like Hydrides*

These comprise the hydrides $M'[H]$ and $M''[H]_2$, formed by the metals of the alkalis and the alkaline earths (but not by beryllium or magnesium), and probably by them alone. They are colourless crystalline solids with high melting-points (LiH, 680° C.), and the alkaline hydrides all have

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[58] H. S. W. Massey, *Proc. Camb. Philos. Soc.* 1931, **27**, 451.
[59] C. A. Coulson, ib. 1935, **31**, 244.
[60] O. Luhr, *J. Chem. Phys.* 1935, **3**, 146.

NaCl (6:1) lattices, which are typical of salts. On electrolysis of the fused hydrides (LiH and CaH_2) hydrogen is evolved at the anode, in the quantities required by Faraday's law; they react readily with water to give the hydroxide and hydrogen. These compounds are clearly the salts of the unusual anion H^- (with the helium structure), as was suggested by G. N. Lewis before their electrolytic properties were known.

It is remarkable that while in the first group all the elements form hydrides, and lithium the most easily, in the second group they are formed by calcium, strontium, and barium, but not by the first two elements, beryllium and magnesium.

II. *Volatile Hydrides*

These include such compounds as the hydrocarbons, ammonia, and water. It was pointed out by Paneth[61] that hydrides of this type are formed by all the elements not more than 4 places before an inert gas, and by no others except boron. These are in the table:

B	C	N	O	F
	Si	P	S	Cl
	Ge	As	Se	Br
	Sn	Sb	Te	I
	Pb	Bi	Po	

The boron hydrides are anomalous in structure, the simplest being B_2H_6, which seems to involve a valency of 4 for boron; all of them have more hydrogen than corresponds to trivalent boron. The hydrides of the heavier elements in the table are nearly all unstable and difficult to prepare; PbH_4, for example, decomposes spontaneously in a few hours in the cold; the covalent link to hydrogen weakens in almost every group as the atomic number increases. The preparation and properties of these hydrides will be discussed later under the other elements concerned. They are obviously all covalent compounds, and so far as is known all except the boron hydrides are derived from the simple types CH_4, NH_3, OH_2, FH, the central atom always having a valency octet.

III. *Metal-like Hydrides*

These are compounds formed by transitional elements with hydrogen. They are all solid, infusible, non-volatile, and difficult to obtain with a definite stoichiometric composition. The hydrogen content is greatest in the thorium and cerium compounds (about MH_3) and least in such compounds as palladium hydride Pd_2H (see, for example, Hägg,[62] hydrides of Ti, Zr, V, Ta, etc.; Sieverts and Gotta,[63] hydrides of rare earth metals). They are more or less metallic in character, and form solid solutions with their own metals. They are mostly interstitial compounds, the small hydrogen atoms filling some of the holes between the atoms of the metallic

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[61] F. A. Paneth, *Ber.* 1920, **53**, 1710.

[62] G. Hägg, *Z. physikal. Chem.* 1931, **B 11**, 433: **B 12**, 33.

[63] A. Sieverts and A. Gotta, *Z. anorg. Chem.* 1928, **172**, 1.

lattice; this, however, leaves undetermined the nature of the linkage of the hydrogen to the metal, which must be fairly strong, since it causes a perceptible separation of the metallic atoms (for example, by 5-7 per cent.—from 0·05 to 0·12 A—in the hydrides $CeH_{2\cdot7}$, $TiH_{1\cdot6}$, and $ZrH_{1\cdot92}$). See further on interstitial compounds under binary carbides (IV. 519) and nitrides (V. 663).

The well-known copper hydride (recently shown to be a very ill-defined compound) obviously belongs to this third class.

IV. *Spectroscopic Hydrides*

When an electric discharge is passed through hydrogen gas in presence of another element, the spectrum usually gives bands which are due to diatomic hydrides of the type MH; these are practically never isolable, and their existence is only known from the analysis of the band spectra, which gives their heats of formation and the interatomic distances. There is no doubt about the existence of these hydrides, which are of great theoretical interest in relation to the physics of molecular structure, but they can scarcely be called chemical substances, and need not be further considered here.[64]

The type of binary hydride formed by a metal depends on the electronegativity of the metal. If this is not greater than 1·0, a salt-like hydride is formed: if it is between 1 and 1·6, the hydride is non-existent, unstable, or indefinite. If it is greater than 1·6, the hydride is volatile.[65]

The Hydrogen Bond

There can be no doubt that hydrogen is able under certain conditions to hold two other atoms together, as in the polymerization of hydroxylic compounds and in the formation of the acid fluoride ion $[F\cdots H\cdots F]^-$; the hydrogen is then said to form a hydrogen bond, link, or bridge. This was first recognized in 1912 by Moore and Winmill,[66] who explained the weakness of trimethylammonium hydroxide as a base, in comparison with tetramethylammonium hydroxide, by giving it the structure $Me_3N—H—O—H$; soon after, Pfeiffer[67] adopted the same view when he extended Werner's coordination formulae of the metallic derivatives of ortho-hydroxyanthraquinones to the hydrogen compounds themselves. The first electronic formulation of these bonds was given by Latimer and Rodebush in 1920,[68] who wrote the tertiary hydroxide $(CH_3)_3N{:}H{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{:}H$, assuming (as Lewis had done for the oxygen atoms in the SO_4 anion) that the second bond was formed by sharing two electrons derived from the oxygen, so that the hydrogen had increased its valency group from 2 to 4. Subsequent

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[64] For a further account of these hydrides see R. W. Berriman and C. H. D. Clark, *Proc. Leeds Philos. Soc.* 1938, **3**, 465.

[65] D. T. Hurd, *J.A.C.S.* 1947, **69**, 1647.

[66] T. S. Moore and T. F. Winmill, *J.C.S.* 1912, **101**, 1635.

[67] P. Pfeiffer, *Ann.* 1913, **398**, 137.

[68] W. M. Latimer and W. H. Rodebush, *J.A.C.S.* 1920, **42**, 1419.

work[69] showed that the bond is very widespread, and its existence was put beyond doubt by the X-ray measurements of crystals containing it; thus W. H. Zachariasen showed[70] that in sodium hydrogen carbonate two of the three oxygens of each CO_3 group are only 2·55 A from the nearest oxygen of another CO_3, while the third is 3·15 A away; it is obvious that the short links contain the hydrogen atoms of the $NaHCO_3$ molecules.

At the same time it has become clear that the original formulation of the hydrogen in this link with four shared electrons cannot be true. A hydrogen atom can only have two electrons in the first quantum group, and if the other two were in the second quantum group they would be too weakly held to form a bond, so that some other mechanism is needed.[71]

Much attention has been devoted to the structure of this bond[74-80]; a full discussion is given by Pauling in his *Chemical Bond*, ed. 2, 1942. pp. 284–334. See further references.[72-3]

The force which maintains this bond (which is commonly of the value of 5 to 10 k.cals.*) has been variously said to be resonance, electrostatic attraction (giving a sort of ionized link), and dipole attraction. Now that we realize that resonance between the ionized and the covalent link is almost universal (nearly all covalent links having more or less of an ionic character), these hypotheses are seen to be mutually compatible, and they are probably all to some extent true. In the simplest and most typical case, that of the acid fluoride anion, we may assume that we have a resonance between the three forms

$$\mathrm{F{-}H\ F^-}, \qquad \mathrm{F^-\ H^+\ F^-}, \qquad \mathrm{F^-\ H{-}F}.$$

A new difficulty, however, arises through the length of the link. This has been measured by X-rays and by electron diffraction for many molecules.

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* The heat of association per g.-mol. of methyl alcohol in carbon tetrachloride is found[81] spectroscopically to be 4·72 k.cals./25°. That of hydrogen fluoride in the vapour is about 6·8.[82] Harms calculates[83] the dipole attraction of two OH groups on one another to be at least 5 k.cals.

[69] For example, T. M. Lowry and H. Burgess, *J.C.S.* 1923, **123**, 2111; N. V. Sidgwick and R. K. Callow, ib. 1924, **125**, 527; N. V. Sidgwick, ib. 1925, **127**, 907 (keto-enols).

[70] *J. Chem. Phys.* 1933, **1**, 634.

[71] L. Pauling, *Proc. Nat. Acad.* 1928, **14**, 359.

[72] G. Briegleb, *Z. Elektrochem.* 1944, **50**, 35.

[73] R. Brill, ib. 47.

[74] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* 1933, **1**, 515.

[75] Id., *Trans. Far. Soc.* 1933, **29**, 1049.

[76] L. Pauling, *Z. Krist.* 1933, **85**, 380.

[77] J. D. Bernal and H. D. Megaw, *Proc. Roy. Soc.* 1935, **151**, 384.

[78] R. H. Gillette and A. Sherman, *J.A.C.S.* 1936, **58**, 1135.

[79] M. L. Huggins, *J. Org. Chem.* 1936, **1**, 407.

[80] E. N. Lassettre, *Chem. Reviews*, 1937, **20**, 259.

[81] R. Mecke and H. Hückel, *Naturwiss.* 1943, **31**, 248.

[82] R. W. Long, J. H. Hildebrand, and W. E. Morrell, *J.A.C.S.* 1943, **65**, 182.

[83] H. Harms, *Z. physikal. Chem.* 1939, **B 43**, 257.

Now the primary condition for resonance is that the atoms should be in nearly the same places for both forms, so that we should expect the distance from A to B in the H-link A···H···B to be nearly the sum of the distances in A—H and H—B. Some of the values calculated on this hypothesis together with those found experimentally are given in the following table, quoted from Pauling, *Chemical Bond*, 1942, p. 334. They show that the distance between the atoms attached to the hydrogen is greater, and sometimes as much as an A.U. greater, than the calculated value. This might mean either that the hydrogen atom is half-way between the other two, or that it is the expected distance from one, and much farther from the other (e.g. in the mean O—H—O link either $O\overset{1\cdot32}{\text{——}}H\overset{1\cdot32}{\text{——}}O$ or $O\overset{0\cdot96}{\text{——}}H\overset{1\cdot68}{\text{——}}O$), and in the latter event it might oscillate between the two positions. It has been suggested[77] that there are two kinds of hydrogen bonds, of which only the shorter is symmetrical, but there does not seem to be any good reason for making a sharp distinction, though in general it is clear that (as we should expect) the links are shorter the stronger they are. There is, however, definite evidence that the hydrogen bond can be unsymmetrical; in the first place the force constant for the A—H link as indicated by the absorption spectrum (see below) is not so much changed by the formation of the hydrogen bond as this lengthening would require,[84] and Pauling has shown[85] that the entropy of ice at low temperatures is incompatible with such a symmetry of the O—H—O bonds. On the other hand, the resonance energy gained by the oscillation of the hydrogen atom between the two positions would be very small, though the behaviour of the very similar deuterium bond shows that such oscillation may probably occur. Direct evidence of such oscillation of the hydrogen in the F—H···F anion has been obtained through infra-red measurements by Ketelaar[86]; see also Sutherland.[87]

TABLE

	Distance A···B		
Link A—H—B	*Obs.*	*Calc.*	*Diff.*
F—H—F	2·26	1·88	+0·38
O—H—O max.	2·76	1·92	+0·84
,, min.	2·54	,,	+0·62
,, mean	2·64	,,	+0·76
N—H—O	2·90	1·96	+0·94
N—H—N	3·17	2·00	+1·17
N—H—F	2·70	1·94	+0·76

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[84] P. C. Cross, J. Burnham, and P. A. Leighton, *J.A.C.S.* 1937, **59**, 1134.

[85] L. Pauling, ib. 1935, **57**, 2680.

[86] J. A. A. Ketelaar, *Rec. Trav.* 1941, **60**, 523.

[87] G. B. B. M. Sutherland, *Trans. Far. Soc.* 1940, **36**, 889.

The experimental evidence for the existence of the link is mainly of three kinds: (1) evidence of various sorts for the association of molecules; (2) determinations of structure by X-ray and sometimes by electron diffraction; (3) a very important section, the changes in the infra-red absorption.

The evidence for association is familiar; it includes the determination of molecular weight, volatility, solubility, heats of mixing,[88] etc.

The crystallographic evidence is extensive; a summary of the observed differences is given above (for details see Pauling, *Chemical Bond*, pp. 296–315). The F—H—F link in the polymerized vapour of hydrogen fluoride was found by electron diffraction to be $2{\cdot}55 \pm 0{\cdot}05$ A,[89] the value for the ion being shorter, namely, 2·26 and 2·30 in KHF_2[90-1] and 2·37 in NH_4F_2.[92]

An important part of the evidence for the hydrogen link depends on the observation of the infra-red absorption. This was first discovered by R. Freymann,[93] and developed by Wulf, Hendricks, *et al.* from 1933 onwards[94]; they examined OH and NH compounds in carbon tetrachloride solution; similar measurements were made by Errera on the pure liquids, and by Badger and Bauer on the vapours (see later).

The characteristic absorption band of an unassociated hydroxyl group is at about 2·76 μ (3,600 cm.$^{-1}$),* with a first harmonic at about 1·4 μ; the corresponding value of the fundamental for N—H is 2·94 μ (3,400 cm.$^{-1}$). It was shown by Hendricks *et al.*[95-8] that a series of compounds containing hydroxyl and imino groups whose structures allowed of chelation, such as salicylic aldehyde, *o*-nitrophenol, and methyl salicylate, failed to give these bands, though they were given by the corresponding meta- and para-compounds; it is a condition of chelation that the structure of the molecule should allow of the formation of O···H···O or O···H···N bonds in which the O···O or O···N distance is about 2·6 A. In the same way Errera and Mollet,[99] examining the pure liquids, found that the hydroxyl band which is present in phenol, and in meta- and para-hydroxybenzaldehyde, is

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* N cm.$^{-1}$ corresponds to $\frac{10^8}{N}\text{A} = \frac{10^4}{N}\mu$.

[88] L. A. K. Staveley, J. H. E. Jeffes, and J. A. E. Moy (*Trans. Far. Soc.* 1943, **39**, 5) find the effect of phenols, acids, amines, and ethers in increasing the solubility of water in benzene: the order is OH > NH_2 > $\Phi\cdot NO_2$, $\Phi\cdot NMe_2$: the ratio (mols extra water)/(mols org. donor) is usually 0·05 to 0·10.

[89] S. H. Bauer, J. Y. Beach, and J. H. Simons, *J.A.C.S.* 1939, **61**, 19.

[90] L. Helmholtz and M. T. Rogers, ib. 1939, **61**, 2590.

[91] J. L. Hoard and W. J. Martin, ib. 1941, **63**, 11.

[92] L. Pauling, *Z. Krist.* 1933, **85**, 380.

[93] R. Freymann, *C.R.* 1932, **195**, 39; *Ann. de Phys.* 1933, [x] **20**, 243.

[94] U. Liddel and O. R. Wulf, *J.A.C.S.* 1933, **55**, 3574.

[95] G. E. Hilbert, O. R. Wulf, S. B. Hendricks, and U. Liddel, *Nature*, 1935, **135**, 147.

[96] Id., *J.A.C.S.* 1936, **58**, 1991.

[97] Id., ib. 548.

[98] O. R. Wulf, U. Liddel, and S. B. Hendricks, ib. 2287.

[99] J. Errera and P. Mollet, *C.R.* 1935, **200**, 814.

absent from salicylic aldehyde. Later Errera and Mollet[100] and Errera and Sack[101] found similar effects with the change of association in alcohol. The pure liquid showed a strong band at 3,350 cm.$^{-1}$ (2·99 μ), which practically vanished at a dilution of 0·02 moles alcohol in 1 litre CCl_4, and must be due to the association of the hydroxyl groups. At the same time a new band appeared at 3,640 cm.$^{-1}$ (2·75 μ), which increased on dilution, the molecular extinction coefficient being 4 at 0·05 moles/L and 15 at 0·005 moles/L; this must be the band due to an isolated hydroxyl group, a conclusion supported by the fact that a rise of temperature from 0° to 70° C. greatly weakens the 3·0 and strengthens the 2·75 band. See further references.[102–7]

Badger and Bauer[108] show that in the vapour of acetic acid the usual hydroxyl band at 1·03 μ disappears as the concentration of the vapour increases, and its disappearance gives an exact measure of the association, agreeing with the vapour density measurements of MacDougall.[109] See further references.[110–16]

It is clear that when a hydrogen bond is formed, the normal hydroxyl or imine band is shifted towards the longer wave-lengths. Venkateswaran[117] produces evidence to show that this shift is greater the more acidic the hydrogen. Rodebush *et al.*[118] examine this conclusion, using the extreme examples of hydrogen chloride and chloroform. With hydrogen chloride the band shifts from 3·51 μ in carbon tetrachloride to 4·14 μ in ether; with chloroform the shift is difficult to recognize, but on the addition of quinoline the band moves from 3·28 to 3·37 μ, with a great increase in intensity.

The second overtone of the fundamental hydroxyl band should be, and is, at a wave-length of $2·86/3 = 0·97\ \mu$; the band at this place has been shown to give evidence of the association of phenols and alcohols.[119–21]

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[100] Id., *Nature*, 1936, **138**, 882.
[101] J. Errera and H. Sack, *Trans. Far. Soc.* 1938, **34**, 728.
[102] W. Gordy, *J.A.C.S.* 1938, **60**, 605.
[103] W. Gordy and A. H. Nielson, *J. Chem. Phys.* 1938, **6**, 12.
[104] H. W. Thompson, *J.A.C.S.* 1939, **61**, 1396.
[105] L. R. Zumwalt and R. M. Badger, *J. Chem. Phys.* 1939, **7**, 87.
[106] W. H. Rodebush and C. Kretschmer, ib. 1941, **9**, 284.
[107] R. Mecke, *Z. Elektrochem*, 1944, **50**, 57.
[108] R. M. Badger and S. H. Bauer, *J. Chem. Phys.* 1937, **5**, 369, 605.
[109] F. H. MacDougall, *J.A.C.S.* 1936, **58**, 2585.
[110] H. Hoyer, *Z. physikal. Chem.* 1940, B **45**, 389.
[111] M. M. Davies and G. B. B. M. Sutherland, *Nature*, 1938, **141**, 372.
[112] P. Barchewitz, *C.R.* 1939, **208**, 807.
[113] J. J. Fox and A. E. Martin, *Nature*, 1939, **143**, 199.
[114] Id., *Trans. Far. Soc.* 1940, **36**, 897.
[115] O. R. Wulf and L. S. Deming, *J. Chem. Phys.* 1938, **6**, 702.
[116] R. C. Herman and R. Hofstadter, ib. 1939, **7**, 460.
[117] C. S. Venkateswaran, *Proc. Indian Acad.* 1938, **7**, A 13.
[118] A. M. Buswell, W. H. Rodebush and M. F. Roy, *J.A.C.S.* 1938, **60**, 2528.
[119] O. R. Wulf and E. J. Jones, *J. Chem. Phys.* 1940, **8**, 745.
[120] O. R. Wulf, E. J. Jones, and L. S. Deming, ib. 753.
[121] L. R. Zumwalt and R. M. Badger, *J.A.C.S.* 1940, **62**, 305.

The corresponding deuterium bonds A—D—B present exactly the same problem as the hydrogen bonds, the only difference being that the O—D absorption band is in a more convenient place than the O—H. The work especially of Gordy[122-6] has shown that the O—D group in the non-associated form has a band at about 3·73 μ which shifts on association to 4·0 μ. Many donor solvents which may be expected to have an effect on the O—H group have themselves a band near 3·0 μ which cannot be distinguished from that of a free O—H group; but by substituting the O—D for the O—H compound this confusion is avoided, since the fundamental for associated O—D is at 4 μ, where most of the solvents do not absorb. Thus[123] liquid $CH_3 \cdot OD$ has a band at 4·01 μ, while in the vapour or in dilute benzene solution the band is at 3·73 μ. For further evidence from Raman spectra see reference[127]. See further reference[129].

The next question is the relation between the strength of an A—H—B link and the nature of A and B. Experiment shows that in general the tendency of an A—H group to form such a bond increases rapidly in the order C—H < N—H < O—H < F—H, the value for C—H being nearly zero: and that it also falls very greatly when we go from the first period to the second, i.e. from O—H to S—H and from F—H to Cl—H. This is natural, for we should expect atoms to be more ready to form such bonds the greater their 'electronegativity' in Pauling's sense, and, what follows from this, the larger the ionic part of the A—H link and the greater its heat of formation. The values, with the dipole moments are given below:

	H	C	N	O	F	S	Cl
Electronegativity	2·1	2·5	3·0	3·5	4·0	2·5	3·0
Ht. of X—H (k.cals.)	103·4	98·8	92·7	110·2	132·4	87·5	102·7
Dip. mom. X—H	0	(0·4)	1·31	1·51	?1·5	0·68	1·03 D

At the same time it is clear that the tendency of an atom to form such a bond is greatly modified by the other atoms attached to it, and in particular that the hydrogen of a hydroxyl group forms a hydrogen bond more readily the more acidic it is.

By far the greater number of hydrogen bonds known are those which unite two oxygen atoms. These may be formed from one molecule to another over an indefinite number of hydroxylic molecules: or between two molecules[128]: or within a single molecule. Examples of the three

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[122] W. Gordy, *Phys. Rev.* 1938, **53**, 851.

[123] Id., *J. Chem. Phys.* 1939, **7**, 93.

[124] W. Gordy and S. C. Stanford, ib. 1940, **8**, 170.

[125] Id., ib. 1941, **9**, 204.

[126] Id., ib. 215.

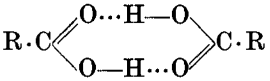
[127] G. V. L. N. Murty and T. R. Seshadri, *Proc. Indian Acad. Sci.* 1941, **14**, A 593; 1942, **15**, A 154, 230, 238; **16**, A 50.

[128] For the effect of steric hindrance on the association of the phenols see N. D. Coggeshall, *J.A.C.S.* 1947, **69**, 1620.

[129] R. E. Richards and H. W. Thompson, *J.C.S.* 1947, 1260.

kinds are alcohols, carboxylic acids, and many ortho-substitution products of phenol. An examination of any of the properties indicating association shows that with an alcohol the molecular weight in solution, say in benzene, rises continuously from the formula weight at great dilution to several times this value; with a carboxylic acid such as acetic the rise is more rapid at high dilutions, but it does not go beyond twice the formula weight; while with an ortho-aldehydo- or ortho-nitro-phenol it does not exceed the formula weight. It is clear that with an alcohol the formation of a hydrogen bond between two molecules still leaves the linkage of more molecules possible, and the complexes may be at least partially represented as in a state of resonance between the two systems

With a carboxylic acid the formation of a dimer makes further association impossible, as is shown by the formula



The stability of this complex is so great that it is formed to a considerable extent in the vapour; the structures are supported by the X-ray measurement of the crystals,[130] and electron diffraction of the vapour.[131]

With the third class of compounds, such as salicylaldehyde or the enolic form of acetylacetone, the associative power is used up within the single molecule by the formation of a ring (chelation), the stability of which is increased (as is that of the dimeric acids) by resonance between the two forms, for example, with acetyl acetone

The hydrogen bond with one or two fluorine atoms, though it is extremely strong (the association factor for hydrogen fluoride in the vapour at 1 atmosphere and 20° C. is 3·45), is confined in its occurrence, owing to the univalency of fluorine, to a few compounds such as hydrogen fluoride, ammonium fluoride, hydrazinium fluoride, and the 'acid fluoride' anion $[F—H\cdot F]^-$. It is particularly to be noticed that fluorine attached to carbon seems to have no tendency to form a hydrogen bond even with hydroxyl.

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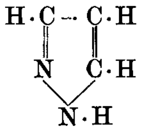
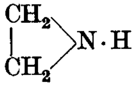
[130] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.* 1934, **20**, 336. In Pauling's *Chemical Bond*, p. 306, is a picture of dimeric formic acid, with the distances. See also IV. 1008.

[131] I. L. Karle and L. O. Brockway, *J.A.C.S.* 1944, **66**, 1974.

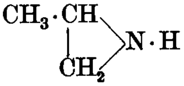
The N—H···N is much weaker. It is obvious both from molecular weight determinations and from infra-red measurements[132-3] that alkyl and aryl amines are very little associated, though there is some association with ammonia, and a shift in the infra-red bands has been detected in some amines.[134,137] Molecular weight determinations in naphthalene show[138] that glyoxalines and benziminazoles with unsubstituted NH groups are considerably associated. Volatility data confirm this conclusion. Hayes and Hunter[135] find that those alkyl derivatives of pyrazole in which the hydrogen attached to nitrogen is replaced are the most volatile, and the



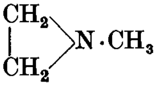
same is true[136] of the glyoxalines and benziminazoles. Thompson and Harris[139] find the same in the ethyleneimines; they quote the boiling-points:



55·5°



67°



27·5°

They get further evidence from the variation with concentration of the intensity of the band at 3·1 μ in a solution of ethylene-diamine in carbon tetrachloride. In the same way it can be shown that the cyanamides $H_2N\cdot CN$ and $HRN\cdot CN$ are highly associated in benzene, while $R_2N\cdot CN$ is monomeric.[140]

There is evidence that the N···H···O bond is stronger than N···H···N. Infra-red measurements indicate the formation of links of this kind in diketopiperazine[141] and glycine.[142] Hunter and Marriott[143] have shown that the molecular weights in solution of the nitrophenyl hydrazones of benzaldehyde $O_2N—C_6H_4—NH—N{=}CH\cdot C_6H_5$ give strong evidence of chelation when the nitro group is in the ortho position, and of association when it is in the meta or para; but this is no longer so if the hydrogen of the N—H is replaced by methyl.

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[132] A. M. Buswell, J. R. Downing, and W. H. Rodebush, *J.A.C.S.* 1939, **61**, 3252.
[133] W. Gordy and S. C. Stanford, ib. 1940, **62**, 497.
[134] G. Jung and E. Wygasch, *Z. physikal. Chem.* 1941, B **49**, 205.
[135] H. T. Hayes and L. Hunter, *J.C.S.* 1941, 1.
[136] T. G. Heafield, G. Hopkins, and L. Hunter, *Nature*, 1942, **149**, 218.
[137] W. Gordy, *J. Chem. Phys.* 1939, **7**, 167.
[138] L. Hunter and J. A. Marriott, *J.C.S.* 1941, 777.
[139] H. W. Thompson and G. P. Harris, *J.C.S.* 1944, 301.
[140] L. Hunter and H. A. Rees, *J.C.S.* 1945, 617.
[141] R. B. Corey, *J.A.C.S.* 1938, **60**, 1598.
[142] G. Albrecht and R. B. Corey, ib. 1939, **61**, 1087.
[143] L. Hunter and J. A. Marriott, *J.C.S.* 1940, 166.

Further evidence of these N···H···O bonds is afforded by the work of Marvel *et al.*,[144] who showed that the volatile alcohols have a high solubility in amines.

When we pass from N—H to C—H there is a further drop in the tendency to form hydrogen bonds. It is commonly assumed that the C—H link has no such tendency, and this is true except when the other groups attached to the carbon are of such a kind as to give the H some sort of acidic character. This is particularly marked when these other groups are halogen atoms, and the most familiar example is that of chloroform. It has long been known that mixtures of chloroform with ether or acetone behave abnormally and as though some kind of combination took place between the components. Glasstone[145] pointed out that this must be due to a hydrogen bond, especially as it does not occur with carbon tetrachloride or methyl chloroform; it is found to be less marked with bromoform, and still less with iodoform. Evidence of a C—H···N bond has been got by Rodebush,[146] who found that the chloroform band at 3·28 μ was slightly shifted (to 3·37 μ), and considerably intensified, on addition of quinoline. Later[147] Gordy, in solutions of chloroform and bromoform in donor solvents (i.e. in solvents with atoms—usually oxygen or nitrogen—able to coordinate as donors) such as ketones, esters, and amines, found a new band at 4 μ not given by either component, so intense that it probably indicates hydrogen-bonding[148]; it is stronger with chloroform than with bromoform; it is stronger with ketones (like acetone) than with esters, and is nearly as strong with pyridine or piperidine as with a ketone.

Zellhoefer and Marvel have given further evidence of the formation of hydrogen bonds by hydrogen attached to carbon through their measurements of the solubility of such volatile substances as $HCCl_2F$ in various solvents[149-51]; when the halide contains an unreplaced hydrogen atom it is always more soluble in solvents containing oxygen or nitrogen (where it can form C—H···O or C—H···N) than in hydrocarbons and their halides; no such difference is found when the solute has no hydrogen, as with CCl_4, CCl_3F, and CCl_2F_2[152]; measurements of the heats of mixing[153-5] support this: the heat is positive when such hydrogen bonds can be formed, and practically zero when they cannot.

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[144] M. J. Copley, E. Ginsberg, G. F. Zellhoefer, and C. S. Marvel, *J.A.C.S.* 1941, **63**, 254.

[145] S. Glasstone, *Trans. Far. Soc.* 1937, **33**, 200.

[146] A. M. Buswell, W. H. Rodebush, and M. F. Roy, *J.A.C.S.* 1938, **60**, 2528.

[147] W. Gordy, *J. Chem. Phys.* 1939, **7**, 163.

[148] See, however, G. B. B. M. Sutherland, *Trans. Far. Soc.*, 1940, **36**, 892.

[149] G. F. Zellhoefer, M. J. Copley, and C. S. Marvel, *J.A.C.S.* 1938, **60**, 1337.

[150] Id., ib. 2666.

[151] Id., ib. 2714.

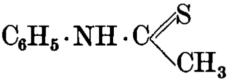
[152] Id., ib. 1939, **61**, 3550.

[153] G. F. Zellhoefer and M. J. Copley, *J.A.C.S.* 1938, **60**, 1343.

[154] D. B. Macleod and F. J. Wilson, *Trans. Far. Soc.* 1935, **31**, 596.

[155] C. S. Marvel, M. J. Copley, and E. Ginsberg, *J.A.C.S.* 1940, **62**, 3109.

All observers agree that the bonding is less marked with bromoform than with chloroform, and still less with iodoform; but the position of fluorine is less certain. On the whole it seems that it is less effective than chlorine; the ratio (real solubility)/(ideal solubility) falls in the order $CHCl_3 > CHCl_2F > CHClF_2$; thus with $CH_3\cdot O(CH_2)_4\cdot OCH_3$ as solvent the values are 2·20, 1·85, and 1·45 respectively, and the authors remark[151] on the close similarity of $CHCl_2F$ and CH_2Cl_2. The crucial experiments with fluoroform do not seem to have been made.

The position of sulphur is rather like that of carbon. From the fact that hydrogen sulphide, in sharp contrast to water, shows no signs of association, it has commonly been inferred that the S—H hydrogen cannot form a hydrogen bond, and this fact is good evidence of the instability of the form S—H···S; but it is now clear that the S—H hydrogen, though it cannot link up to another sulphur, can do so to some other atoms. Thus Gordy and Stanford[133] conclude from the intensity of the infra-red band at 3·7 to 4·3 μ that while thiophenol does not associate with itself, it does so with ether, aniline, pyridine, and dibenzylamine—i.e. it will not form S—H···S but it will form S—H···O and S—H···N. Hunter[156] finds from cryoscopic measurements in naphthalene that thioamides which have unreplaced hydrogen on the nitrogen are markedly associated, but if all the hydrogen is replaced they are monomeric; he also finds that the considerable association of thioacetanilide  $C_6H_5\cdot NH\cdot C\begin{array}{l}{=}S\\ {-}CH_3\end{array}$ is completely prevented by the presence of ortho-substituents on the phenyl which can chelate with the N—H hydrogen (such as $—NO_2$ or —CO·OMe), showing that the tendency of S—H to hydrogen bond formation is much less than that of O—H. Marvel[157] finds heats of mixture up to 1·1 k.cals./mole R·SH when thiophenol is mixed with ether, acetone, or dimethylacetamide, but not when the thiophenol is replaced by hexyl mercaptan.

For a recent account of the hydrogen bond see M. Davies, *Ann. Rep. Chem. Soc.* 1946, **43**, 5.

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[156] G. Hopkins and L. Hunter, *J.C.S.* 1942, 638.

[157] M. J. Copley, C. S. Marvel, and E. Ginsberg, *J.A.C.S.* 1939, **61**, 3161.

DEUTERIUM

[Numerous summaries of the literature of deuterium have appeared; there have been special sections devoted to it in the *Annual Reports of the Chemical Society* for 1933, **30**, 28–34; 1934, **31**, 13-21; 1935, **32**, 40–50; 1937, **34**, 32-41. Much of the earlier work is described by Farkas in his book.[158] Polanyi (1935)[159] gives a general account of the properties and theoretical importance of the isotope; a section of the French *Tables Annuelles*[160] is devoted to a complete list of the recorded constants of deuterium and its compounds up to June 1936. A discussion on the chemistry of deuterium was held by the Bunsen Gesellschaft in Leipzig in 1937[161]; several of the papers are of considerable importance and are quoted later. For a discussion of the thermodynamic properties of isotopes in general see Urey.[174]]

DEUTERIUM is the isotope of hydrogen with the mass number 2; it is the most distinctive isotope of any element, and so it is convenient to give it a special name.

The possibility of the existence of such an atom (and also of the neutron) was forecast by Rutherford in 1920[162]; arguing that nuclei in general are built up of electrons and hydrogen nuclei (he does not yet call them protons), he says: 'It seems very likely that one electron can bind two hydrogen nuclei, and possibly also one hydrogen nucleus. In the one case this entails the possible existence of an atom of mass nearly 2 carrying one charge, which is to be regarded as an isotope of hydrogen. In the other case it involves the idea of the possible existence of an atom of mass 1 which has zero nuclear charge.'

As a result of certain measurements of Aston's which curiously were found afterwards to be erroneous, physicists[163] were led to suspect that ordinary hydrogen contained an isotope ^2H, and soon afterwards Urey, Brickwedde, and Murphy[164] examined the final fraction from the evaporation of a large quantity of liquid hydrogen, and found that the usual Balmer lines were accompanied by faint companions with exactly the wave-lengths required for ^2H; thus for H_α (6,562·793 A.U.) the observed

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[158] *Ortho-hydrogen, Para-hydrogen, and Heavy Hydrogen*, Cambridge, 1935.

[159] M. Polanyi, *Nature*, 1935, **135**, 19.

[160] *Tables Annuelles*, Section by G. Champetier, Paris, 1937.

[161] *Z. Elektrochem.* 1938, **44**, 3-98.

[162] Rutherford, *Proc. Roy. Soc.* 1920, **97**, 396.

[163] R. T. Birge and D. H. Menzel, *Phys. Rev.* 1931, **37**, 1670.

[164] H. C. Urey, F. G. Brickwedde, and G. M. Murphy, ib. 1932, **39**, 864.

[165] W. Bleakney and A. J. Gould, ib. 1933, **44**, 265.

[166] G. N. Lewis and R. T. MacDonald, *J. Chem. Phys.* 1933, **1**, 341.

[167] N. F. Hall and T. O. Jones, *J.A.C.S.* 1936, **58**, 1915.

[168] N. Morita and T. Titani, *Bull. Chem. Soc. Japan*, 1936, **11**, 403.

[169] L. Tronstad and J. Brun, *Trans. Far. Soc.* 1938, **34**, 766.

[170] T. Titani and M. Harada, *Bull. Chem. Soc. Japan*, 1935. **10**, 261.

[171] M. Dole, *J.A.C.S.* 1936, **58**, 580.

[172] J. A. Swartout and M. Dole, ib. 1939, **61**, 2025.

[173] A. Unsöld, *Naturwiss.* 1932, **20**, 936.

[174] H. C. Urey, *J.C.S.* 1947, **562** (Liversidge Lecture).

difference was 1·791 and the calculated 1·793 A; the existence of the new isotope was thus established.

From measurements with the mass spectrograph Bleakney and Gould in 1933[165] concluded that the ratio H/D in natural water was between 4,500 and 6,500. Practically all later work gives values between these limits, but inclining towards the second of them; thus Lewis and MacDonald got 6,500[166]; Johnston from the densities of the water before and after electrolysis found 5,750±250; Hall and Jones[167] 6,400±200; Morita and Titani[168] not less than 5,400; Tronstad and Brun[169] 5,960±300. K. Wirtz,[175] from densities of pure D_2O and H_2O 5,900. Many other natural sources of hydrogen have been examined to see if they are richer in deuterium—salt lakes, petroleum, water of crystallization of minerals, and a whole series of animal and vegetable substances; but in none does the proportion vary seriously from the normal (probably never as much as 50 per cent., and very likely much less[166,170-2]). The only source that is distinctly richer is electrolytic liquor, as explained below.

On the other hand, the hydrogen lines in the solar spectrum indicate that there is much less deuterium in the hydrogen of the sun's atmosphere, the H/D ratio being greater than 100,000.[173]

Concentration

The original method used for the concentration of the deuterium was[164,176-7] the fractional distillation of the element. Other methods that have been proposed include the diffusion (especially the thermal diffusion) of the element, the fractional distillation of water, and above all the electrolysis of alkaline solutions in water, which is the usual commercial method.

Keesom[178] by the fractional distillation of 40 litres (2,800 g.) of liquid hydrogen near its triple point got 2 litres of gas (0·18 g. or 1/16000 of the whole) which was shown to contain 3 per cent. of D. A more hopeful method is the fractional distillation of water, which causes at the same time a concentration of the ^{18}O; Urey.[179] has described an elaborate apparatus for this purpose (see further under the isotopes of oxygen).

Diffusion

The diffusion method was elaborated in 1932 by Hertz,[180] who used porous-walled diffusion units, so designed that a number of them could be arranged in series, with a number of mercury diffusion pumps. In this way

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[175] *Naturwiss.* 1942, **30**, 330.

[176] H. C. Urey, F. G. Brickwedde, and G. M. Murphy, *Phys. Rev.* 1932, **40**, 1.

[177] E. W. Washburn and H. C. Urey, *Proc. Nat. Acad.* 1932, **18**, 496.

[178] W. H. Keesom, H. van Dijk, and J. Haantjes, *Proc. K. Akad. Amst.* 1933, **36**, 248.

[179] G. B. Pegram, H. C. Urey, and J. Huffman, *Phys. Rev.* 1936, **49**, 883.

[180] G. Hertz, *Z. Phys.* 1932, **79**, 108. See also *Ann. Rep. Chem. Soc.* 1938, **35**, 138.

he has been able[181-2] to obtain deuterium spectroscopically free from protium. This method has also been used by others.[183]

More recently a very efficient diffusion method of another kind for the separation of isotopes has been introduced by Clusius and Dickels[184]; this depends on thermal diffusion. The mixed gases are enclosed in a long vertical tube which has an electrically heated wire running along it, and is cooled externally; the difference of temperature causes through diffusion an accumulation of the lighter constituent at the hot and the cooler at the cold surface; at the same time there is a continuous convective streaming of the hot and intrinsically lighter layer upward and of the cold gas downward; these two processes lead to a concentration of the lighter isotope at the top and the lower at the bottom. (For more details see Welch.[185]) This method, with tubes up to 9 metres long, has been applied to a large number of isotopic separations (see especially under oxygen and chlorine) with great success; it was used for the isotopes of hydrogen by Seaborg.[186]

But the method most commonly used for the separation of deuterium is one which is not practically effective for other isotopes, that of electrolysis. This was first used by Washburn[187-8] and further developed by Lewis[189-90] and by H. S. Taylor[191]; it has since been adopted in Norway for the production of D_2O on the technical scale.

The method depends on the fact that if water containing deuterium is electrolysed, the gas evolved has a smaller D/H ratio than the liquid from which it comes. The separation factor $a = (H/D_{gas})/(H/D_{liquid})$, on which the success of the process depends, has a value which varies to some extent with the conditions* but is not far from the equilibrium constant, which is 3·8, of the reaction

$$HD + H_2O \rightleftharpoons H_2 + HOD.$$

* See the list of results in *Tables Annuelles*, Deuterium, p. 8.

[181] G. Hertz, *Naturwiss.* 1933, **21**, 884.

[182] H. Harmsen, G. Hertz, and W. Schütze, *Z. Phys.* 1934, **90**, 703.

[183] R. Sherr and W. Bleakney, *Phys. Rev.* 1936, **49**, 882.

[184] K. Clusius and G. Dickels, *Naturwiss.* 1938, **26**, 546.

[185] For a full account of this method with references see A. J. E. Welch, *Ann. Rep. Chem. Soc.* 1940, **37**, 153-62.

[186] G. T. Seaborg, A. C. Wahl, and J. W. Kennedy, *J. Chem. Phys.* 1940. **8**, 639.

[187] E. W. Washburn and E. R. Smith, ib. 1933, **1**, 426.

[188] E. W. Washburn, E. R. Smith, and M. Frandsen, *Bur. Stand. J. Res.* 1933, **11**, 453.

[189] G. N. Lewis, *J.A.C.S.* 1933, **55**, 1297.

[190] G. N. Lewis and R. T. MacDonald, *J. Chem. Phys.* 1933, **1**, 341.

[191] H. S. Taylor, H. Eyring, and A. A. Frost, ib. 823.

[192] R. H. Fowler, *Proc. Roy. Soc.* 1934, **144**, 452.

[193] O. Halpern and P. Gross, *J. Chem. Phys.* 1935, **3**, 452.

[194] J. A. V. Butler, *Z. Elektrochem.* 1938, **44**, 55.

[195] B. Topley and H. Eyring, *Nature*, 1934, **133**, 292.

[196] Id., *J. Chem. Phys.* 1934, **2**, 217.

[197] E. D. Hughes, C. K. Ingold, and C. L. Wilson, *J.C.S.* 1934, 493.

It is probable[192-7] that this reaction plays a large but not an exclusive part in determining the separation factor; according to Walton and Wolfenden[198] this also depends on the material of the cathode, and while for mercury or tin it is about 3, it rises to 5-7 for cathodes of silver, platinum, or nickel. Johnston and Davis[202] find it to vary from 1·5 for water on potassium to 6·1 for sulphuric acid on iron.

In this preparation the liquor from old electrolytic cells can conveniently be used as the starting material; in such cells, where the water flows in as fast as it is electrolysed, it is clear that the enrichment will go on until the H/D ratio is the same in the gas coming off as in the water going in, that is, till the liquid contains α times as much D as the water used, if α is the separation factor.

Analysis

Mixtures of hydrogen and deuterium are usually analysed either by converting the element into water and determining the density of this (which gives the proportion of deuterium with an accuracy of from 0·2 to 2 per cent., according to the amount of water available), or by converting it into hydrogen, and measuring the thermal conductivity of this from the rate of cooling of a hot wire. This second method is due to A. and L. Farkas,[199,200] who claim that it is possible in this way to determine the composition of 2–3 c.mm. of the gas in a few minutes, with an accuracy of 0·1 per cent. The details of the various methods of analysis are discussed by Harteck.[201]

Properties of Deuterium and its Compounds

Something may be said here about the uses of isotopes in general. These are of two kinds, one depending on the differences between the isotopes, and the other on their essential similarity. The amount of difference between the isotopes of an element depends on the ratio of their masses (here 2 : 1) and also is to some extent more marked the lighter the element (see further, p. 39), so that on both these grounds it is particularly great with hydrogen. Such differences enable us to test a whole series of theories (especially in chemical kinetics), since we can use two kinds of atoms differing in mass and in nothing else except the properties resulting from mass. For such work deuterium is a very convenient material, but the isotopes of carbon, nitrogen, and oxygen are also being used for this purpose.

The essential similarity of the isotopes of an element (even a light element) enables us to earmark a particular set of atoms or molecules; we can use the isotopic atoms as 'tracers'; in this way we can find, for

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[198] H. F. Walton and J. H. Wolfenden, *Trans. Far. Soc.* 1938, **34**, 436.

[199] A. and L. Farkas, *Proc. Roy. Soc.* 1934, **144**, 467.

[200] A. Farkas, *Trans. Far. Soc.* 1936, **32**, 413.

[201] P. Harteck, *Z. Elektrochem.* 1938, **44**, 3.

[202] H. L. Johnston and C. O. Davis, *J.A.C.S.* 1942, **64**, 2613.

example, how long a given quantity of water remains in the human body, whether free hydrogen is liberated in a reaction, whether an atom is ionized or not, and so forth. It is in this way that we can use the radioactive isotopes, natural and artificial. They have the additional advantage that their radioactivity makes them peculiarly easy to detect and estimate. This has already been done by Hevesy and Paneth with the very limited number of elements which have naturally both active and inactive isotopes, like lead. With the modern discovery of artificial radioactive isotopes the possibilities of the method are enormously widened.

Deuterium can of course exist in the same numerous states as hydrogen. The most important points about it are (1) the changes in physical and chemical properties that occur when hydrogen is replaced by deuterium, and (2) the conditions under which such replacements are brought about. Section 1 may be divided into

A. Deuterium atoms, neutral and positive.

B. The elementary diatomic gases HD and D_2.

C. Compounds of deuterium.

According to Mattauch (1940)[203] the atomic weight is 2·01472 (H = 1·00813).

The Deuteron

The deuterium nucleus D^+, the deuteron, is obviously made up of a proton and a neutron. Chadwick and Goldhaber[204] have succeeded in disrupting it into these products by exposure to the γ-rays from thorium C″; Chadwick, Feather, and Bretscher[205] found the heat of linkage of the proton to the neutron to be 2·25 m.e.v. (25 million k.cals. per gramme: 250,000 times the heat of linkage of hydrogen to hydrogen).

The deuteron has proved of great value in nuclear bombardments; these are always specific for the projectile used, since they involve its capture. Examples of nuclear reactions with high-speed deuterons are[206-7]:

$$^{6}\mathrm{Li} + {}^{2}\mathrm{D} = 2\,{}^{4}\mathrm{He}$$

$$^{6}\mathrm{Li} + {}^{2}\mathrm{D} = {}^{7}\mathrm{Li} + {}^{1}\mathrm{H}$$

$$^{7}\mathrm{Li} + {}^{2}\mathrm{D} = 2\,{}^{4}\mathrm{He} + {}^{1}n$$

Oliphant[208] separated ^{6}Li and ^{7}Li with a coarse mass spectrograph, getting about 10^{-6} g. of each, which he bombarded; the results completely supported these equations.

Rutherford's most spectacular effects were obtained by bombarding

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[203] J. Mattauch, *Phys. Rev.* 1940, **57**, 1155.

[204] J. Chadwick and M. Goldhaber, *Nature*, 1934, **134**, 237.

[205] J. Chadwick, N. Feather, and E. Bretscher, *Proc. Roy. Soc.* 1937, **163**, 366.

[206] M. L. Oliphant, B. B. Kinsey, and Lord Rutherford, ib. 1933, **141**, 722.

[207] P. I. Dee and E. T. S. Walton, ib. 733.

[208] M. L. Oliphant, E. S. Shire, and B. M. Crowther, *Nature*, 1934, **133**, 377.

deuterium or its compounds with deuterons.[209] If an ammonium salt is bombarded either with protons or with deuterons, the only result is that some of the protons are driven out of the salt. But if an ammonium salt containing deuterium is bombarded by deuterons, even of energies as low as 100,000 volts, an enormous evolution of swift protons occurs, more than in any other known reaction, and it is obvious that energy is being liberated in some nuclear change. On examination[210-12] it was found that the process is very complex, giving (1) protons of 14 cm. range (3×10^6 e.v.; 30 times the energy of the bombarding particles), (2) neutrons, (3) singly and (4) doubly charged particles of shorter range; (3) and (4) were found to be ^{3}H and ^{3}He. It thus appears that two reactions occur:

$$2\,{}^2\mathrm{D} = {}^3\mathrm{H} + {}^1\mathrm{H}$$
$$2\,{}^2\mathrm{D} = {}^3\mathrm{He} + {}^1n$$

In this way Dee was able to show that the mass of the tritium nucleus is 3·0151.

A further use of deuterons is as the ions in a cyclotron; they are more effective than protons, because the practical limit of the apparatus is the velocity rather than the energy of the particles.[213-16]

General Comparison of the Properties of Hydrogen and Deuterium in their Compounds

The deuterium atom has the same electronic structure as hydrogen (protium), and almost exactly the same atomic and molecular volumes, so that the electric fields round the nuclei are almost identical. This implies a close resemblance in properties, and as a first approximation we should expect the static properties of the corresponding hydrogen and deuterium compounds to be the same. These remarks apply to isotopes in general, and in those of the heavier elements it has been shown that the differences are barely perceptible, except in properties directly dependent on mass.

But with the hydrogen isotopes the 2 : 1 difference in mass will cause a considerable difference in the rate of reaction. The deuterium atom will oscillate more slowly than the lighter protium atom does under the same forces and accordingly the half-quantum $h\nu/2$ of zero-point energy will be smaller. The total energy required to make the molecule react will be almost the same for the deuterium as for the hydrogen compound, and so the critical increment will be larger, and hence the rate of reaction smaller, for the deuterium compound. Polanyi[159] points out further that the

[209] M. L. Oliphant, P. Harteck, and Lord Rutherford, *Nature*, 1934, **133**, 413.
[210] P. I. Dee, ib. 564.
[211] P. I. Dee and C. W. Gilbert, *Proc. Roy. Soc.* 1935, **149**, 200.
[212] P. I. Dee, ib. 1935, **148**, 623.
[213] G. N. Lewis, M. S. Livingston, and E. O. Lawrence, *Phys. Rev.* 1933, **44**, 55.
[214] E. O. Lawrence, ib. 1935, **47**, 17.
[215] E. O. Lawrence, E. McMillan, and M. C. Henderson, ib. 273.
[216] E. McMillan and E. O. Lawrence, ib. 343.

extent of the chemical differences between the isotopes of hydrogen is not only due to the high mass-ratio 2 : 1, but also to the small mass of both isotopes, which makes the zero-point energy much larger (for H_2O it is 13·10 and for D_2O 9·53 k.cals./mole); if we had two isotopes of, say, lead with atomic weights of 207 and 414, the differences would be much smaller.

The difference in mass also involves a difference in the chemical constant, and hence small differences will be found in the equilibrium constants, but these will seldom exceed 50 per cent., while the velocities may vary in the ratio of 10 to 1. All these differences will diminish as the temperature rises, and the half-quantum becomes relatively less important.

Thus in general we may expect large differences in the velocity of reaction wherever a D or H link is concerned, and rather small differences in the equilibrium constants. The differences in the physical properties will usually be small except in those which are directly dependent on mass. Among these is to be included the spectroscopic behaviour, and it is for this reason that the use of compounds in which protium is replaced by deuterium is of particular value in the assignment of the lines to the proper links, and the correct elucidation of the spectral analysis with Raman and infra-red spectra.[217-18]

Elementary Deuterium

Three kinds of diatomic hydrogen molecules occur, H_2, HD, and D_2. Some of their more important physical properties are given in the following table.[219]

	H_2	HD	D_2
M.-pt., °K.	13·95°	16·60°	18·65°
B.-pt., °K.	20·38°	. .	23·6°
Ht. of fusion, g.cals.	28·0	37	47·0
Ht. of evaporation/195 mm.	219·7	263	302·3
Press. at triple pt., mm.	53·8	95	128·5
Zero-pt. energy solid, g.cals.	305	260	215

Separate ortho and para forms occur of D_2 as of H_2[220] (not of HD), but with the differences that the no-quantum rotational state at low temperatures is ortho for D_2 but para for H_2, and also that at the ordinary temperature where H_2 has 25 per cent. ortho, D_2 has 33 per cent. para.[221,222] The rate of thermal transformation between the two at 850-1,000° K. is 2·4 times as great for H_2 as for D_2,[222] this difference being mainly due to the differences in the collision numbers and in the number of atoms formed

[217] E. Bartholomé and H. Sachsse, *Z. physikal. Chem.* 1935, B **30**, 40.

[218] E. Bartholomé, *Z. Elektrochem.* 1938, **44**, 15.

[219] K. Clusius, ib. 22.

[220] A. and L. Farkas and P. Harteck, *Proc. Roy. Soc.* 1934, **144**, 481.

[221] H. L. Johnston and E. A. Long, *J. Chem. Phys.* 1934, **2**, 389.

[222] K. Clusius, *Z. physikal. Chem.* 1935, B **29**, 159.

at these temperatures. The rate of conversion by paramagnetic nitric oxide and oxygen was found[223] to be 3·8 times as great for H_2; according to Wigner[224] this should be the ratio of the nuclear moments of H and D; if that of H is taken to be 2·46 nuclear magnetons this gives 0·65 for the moment of D, which agrees well with other determinations of this value.[225]

Chemical Properties of Deuterium

The interconversion of the elementary molecules H_2, HD, and D_2 will be discussed under the exchange reactions of deuterium. A few of the reactions of D_2 may be mentioned here, especially with the double carbon link C=C, with oxygen, and with the halogens. [For a discussion of theory of its reactions see Bawn and Ogden[238] and Bonhoeffer.[239]]

Pease and Wheeler[226-7] have shown that the addition to the double carbon link, both the thermal reaction at about 500° and the reaction at 0° catalysed by nickel or copper, goes from 1·5 to 2·5 times as quickly with H_2 as with D_2. [The collision rate is $\sqrt{2} = 1{\cdot}4$ times as great with H_2 as with D_2.]

Hinshelwood, Williamson, and Wolfenden[228-9] have made use of deuterium with great effect to test their theories of the mechanism of combination of hydrogen and oxygen. Further work on the same subject has been done by Melville[230-1] and by Clusius.[232-3]

Halogens. Farkas[234] showed that in light at 30° chlorine combines with hydrogen 3 times as fast as with deuterium. With bromine Bonhoeffer[235,236] has examined the thermal reaction at higher temperatures; at 578° it is 3·3 times as fast with H_2, and the heats of activation of the reaction ($X_2+Br_2 = 2\,XBr$) are 19·3 k.cals. for D_2 and 17·2 k.cals. for H_2; this may be explained by the difference in zero-point energy. With iodine Geib and Lendle[237] find that at 710° to 780° C. the velocity constant is 2·2 times as great with H_2 as with D_2; allowing for the difference in the

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[223] L. Farkas and U. Garbatski, *J. Chem. Phys.* 1938, **6**, 260.

[224] E. Wigner, *Z. physikal. Chem.* 1933, B **23**, 28.

[225] I. I. Rabbi, J. M. B. Kellogg, and J. R. Zacharias, *Phys. Rev.* 1934, **46**, 157.

[226] R. N. Pease and A. Wheeler, *J.A.C.S.* 1935, **57**, 1144.

[227] A. Wheeler and R. N. Pease, ib. 1936, **58**, 1665.

[228] C. N. Hinshelwood, A. T. Williamson, and J. H. Wolfenden, *Nature*, 1934, **133**, 836.

[229] Id., *Proc. Roy. Soc.* 1934, **147**, 48.

[230] H. W. Melville, *Nature*, 1934, **133**, 947. [231] Id. *J.C.S.* 1934, 797.

[232] K. Clusius and H. Gutschmidt, *Naturwiss.* 1934, **22**, 693.

[233] K. Clusius, W. Kölsch, and L. Waldmann, *Z. physikal. Chem.* 1941, **189**, 131.

[234] A. and L. Farkas, *Naturwiss.* 1934, **22**, 218.

[235] F. Bach, K. F. Bonhoeffer, and E. A. Moelwyn-Hughes, *Z. physikal. Chem.* 1934, B **27**, 71.

[236] K. F. Bonhoeffer, F. Bach, and E. Fajans, ib. 1934, **168**, 313.

[237] K. H. Geib and A. Lendle, ib. 1936, B **32**, 463.

[238] C. E. H. Bawn and G. Ogden, *Trans. Far. Soc.* 1934, **30**, 432.

[239] K. F. Bonhoeffer, *Z. Elektrochem.* 1934, **40**, 469.

number of collisions this implies that the heat of activation is 0·75 k.cals. less for H_2 than for D_2.

The chemical properties of the D^+ ion are discussed later under D_2O as a solvent.

Deuterium Compounds

By this time a large number of compounds of deuterium have been prepared, and have had their more important properties examined. A variety of methods of preparation have been used, and a general survey of these (with copious references) has been given by Erlenmeyer.[240] So far as the methods depend on the direct replacement of hydrogen by deuterium they are dealt with later in the section on exchange; in all the preparations the possibility of such an exchange occurring (particularly with the hydrogen of ordinary water) must be borne in mind, especially among the inorganic compounds.

For making deuterium compounds any reactions involving H_2 or H_2O can be adopted; thus lithium deuteride can be made from the metal and deuterium gas: deuteroacids such as D_2SO_4 or DCl by the action of sulphur trioxide on D_2O, or (at a higher temperature) of D_2O on magnesium chloride; salt deuterates like Na_2SO_4, $10\,D_2O$ can be synthesized directly.

These methods can also be used for organic compounds; the succinic acid $C_2D_4(COOD)_2$ can be made by the reduction of acetylene dicarboxylic acid $COOH\cdot C{\equiv}C\cdot COOH$ with sodium amalgam in D_2O, and the malonic acid $CD_2(COOD)_2$ by the action of D_2O on carbon suboxide C_2O_3; CH_3D and CD_4 can be got by the action of D_2O on methyl magnesium bromide CH_3MgBr and aluminium carbide Al_4C_3 respectively, and $CD_3\cdot CDO$ by the addition of D_2O to C_2D_2 (made from D_2O and calcium carbide) in presence of a mercury catalyst.

But on the whole the commonest method of making organic deuterium compounds is by exchange, usually with D_2O; in this way, for example, we can get from benzene a series of deuteration products up to C_6D_6 by the action of water in presence of a suitable catalyst, or by that of DCl in presence of aluminium chloride.[241]

Properties of Deuterium Compounds

The properties chiefly examined are, among the physical, the thermodynamic (including melting- and boiling-points) and the spectroscopic, for reasons discussed below: among the chemical, mainly those concerned with ionization and hydrogen exchange; with D_2O, which has for some years been obtainable in quantity, a very thorough examination of the properties both physical and chemical has been made.

The study of the absorption spectra of many of these compounds is of

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[240] H. Erlenmeyer, ib. 1938, **44**, 8.

[241] A. Klit and A. Langseth, *Z. physikal. Chem.* 1936, **176**, 65.

importance, because the changes produced when hydrogen is replaced by deuterium are of great value in the assignment of the observed frequencies to particular links. This subject is discussed by Bartholomé[242]; an instructive example of the application of the method is afforded by the work of Ingold and his colleagues[243] on the spectra of benzene and its deuteration products, which he has summed up in his Bakerian Lecture[244]; in this work he was able to show that the coincidence between the infra-red and the Raman lines which had led some physicists to reject the plane symmetrical structure for the molecule are accidental.

The melting- and boiling-points of a series of compounds of deuterium, inorganic and organic, along with those of their hydrogen analogues, are given in the following tables, being taken mainly from the paper of Clusius[219]; it should be remembered that sometimes, especially in the earlier work, the measurements were made with small and perhaps impure specimens.

The vapour-pressure differences are affected by several factors. They always diminish as the temperature rises, and so the actual differences in boiling-point depend partly on the absolute values of the boiling-points. But it was pointed out by Claussen and Hildebrand,[245] and their conclusion is supported by later work, that with respect to the differences in their boiling-points compounds fall into three classes: (1) non-associated substances, like methane and hydrogen chloride, where the vapour pressures of the deuterium and hydrogen compounds differ but slightly; (2) substances associated in the liquid but not (or only slightly) in the vapour, such as water and ammonia, where the deuterium compound has the lower vapour pressure; and (3) substances associated in both liquid and vapour, such as hydrogen fluoride and acetic acid; in this class the deuterium compound has the higher vapour pressure, and usually the lower boiling-point.

Molecular volumes. Where the substance is not associated, the molecular volume is scarcely affected by replacing H by D; the lengths of the H—X and D—X links are practically the same, though the 'deuterium bond' A—D···B may be considerably longer than the hydrogen bond.[246-8] As to the negative ions, Zintl[249] has shown that LiH and LiD both have the NaCl lattice, and that the *a* values for this are 4·085 and 4·065, giving the mol. vols. LiH 10·33, LiD 10·18 c.c. Similar results have been found with the volumes of the deuterated and hydrated salts.[250-1]

[242] E. Bartholomé, *Z. Elektrochem.* 1938, **44**, 15.

[243] *J.C.S.* 1936, 912–87; *Nature*, 1937, **139**, 880.

[244] *Proc. Roy. Soc.* 1939, **169**, 149.

[245] W. H. Claussen and J. H. Hildebrand, *J.A.C.S.* 1934, **56**, 1820.

[246] A. R. Ubbelohde and I. Woodward, *Nature*, 1939, **144**, 632.

[247] A. R. Ubbelohde, *Proc. Roy. Soc.* 1939, **173**, 417.

[248] A. R. Ubbelohde and I. Woodward, ib. 1942, **179**, 399.

[249] E. Zintl and A. Harder, *Z. physikal. Chem.* 1935, B **28**, 478.

[250] E. Saur, *Z. Krist.* 1937, **97**, 523.

[251] J. Bell, *J.C.S.* 1940, 72.

Deuterium Compounds: Melting- and Boiling-points

A. INORGANIC: Temperatures in °K.

	Melting-points			*Boiling-points*		
	D	H	*Diff.*	D	H	*Diff.*
X·F	. .	. .	. .	291·8°	293·1°	−1·3°
X·Cl	158·2°	162·2°	−4·0°	191·6°	188·1°	+3·5°
X·Br	185·7°	186·2°	−0·5°	206·3°	206·3°	±0°
X·I	221·5°	222·3°	−0·8°	237·0°	237·5°	−0·5°
X_2O	277·0°	273·2°	+3·8°	374·6°	373·2°	+1·4°
X_2S	187·1°	187·6°	−0·5°	. .	. .	. .
X_2Se	206·2°	207·4°	−1·2°	. .	. .	. .
X_3N	199·6°	195·3°	+1·3°	242·1°	239·8°	+2·3°

B. ORGANIC: Temperatures in °C.

	D	H	*Diff.*	D	H	*Diff.*
Hydrocarbons						
CX_4	−184·0°	−182·6°	−1·4°	. .	. .	. .
C_6X_6	+6·6°	+5·5°	+1·1°	+79·2°	+80·1°	−0·9°
$C_{10}X_8$	77·5°	80·2°	−2·7°	. .	. .	. .
$n\text{-}C_5H_{11}X$	−21·5°	−20·5°	−1·0°	+38·0°	+37·8°	+0·2°
Aldehydes						
$CX_3{\cdot}CXO$	−121·7°	−123·5°	+1·8°	20·5°	20·2°	+0·3°
Par. $(CX_3{\cdot}CXO)_3$	13·7°	10·5°	+3·2°	124°	124°	+0°
Acids						
$CH_3{\cdot}COOX$	15·4°	16·6°	−1·2°	. .	. .	. .
$CX_3{\cdot}COOH$	17·2°	16·6°	+0·6°	. .	. .	. .
$CX_3{\cdot}COOX$	15·8°	16·6°	−0·8°	. .	. .	. .
$C_2X_5{\cdot}COOH$	120·9°	121·7°	−0·8°	. .	. .	. .
$C_2H_4(COOX)_2$	179·5°	183·0°	−3·5°	. .	. .	. .
$C_2X_4(COOH)_2$	181·6°	183·0°	−1·4°	. .	. .	. .
$C_2X_4(COOX)_2$	178·5°	183·0°	−4·5°	. .	. .	. .
Ester						
$C_2X_4(COOCH_3)_2$	17·0°	18·2°	−1·2°	195·3°	196°	−0·7°
Anhydride						
$C_2X_4{\cdot}C_2O_3$	119·5°	119·5°	±0°	. .	. .	. .
N-compounds						
$CH_3{\cdot}NX_2$	−89·2°	−93·1°	+3·9°	−5·2°	−6·2°	+1·0°
$C_2H_5{\cdot}NX_2$	−78·5°	−80·6°	+2·1°	+17·4°	+16·6°	+0·8°
$(CH_3)_2NX$	−93·1°	. .	. .	+6·9°	+7·2°	−0·3°
X·CN	−12°	−14°	+2°	+25·9°	+25·3°	+0·6°

A remarkable effect of the replacement of hydrogen by deuterium on **the transition points** in the solid state of methane[252-3] and of ammonium

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[252] A. Kruis, L. Popp, and K. Clusius, *Z. Elektrochem.* 1937, 43, 664.

[253] E. Bartholomé, G. Drikos, and A. Eucken, *Z. physikal. Chem.* 1938, B 39, 371.

salts[254-8] has been detected and examined; it is no doubt connected with the rotation of the molecules in the crystals. The barrier to free rotation in C_2D_6 was found, however, by the specific heat measurements of Kistiakowsky[259,260] to be the same as in ethane, 2·75 k.cals. per mole.

Stereochemical Effect

The question whether the difference between hydrogen and deuterium is sufficient to produce optical activity in a molecule CabHD has been examined both theoretically and practically. On general grounds it seems clear that it must be so, since the atoms and the links are not identical; but the activity is likely to be very small. R. P. Bell[261] shows on theoretical grounds that the replacement of H by D must affect the refractive index and hence can cause optical activity; and the asymmetric *d–l* and *d–d* compounds used for the separation will form solid solutions, as do H_2O and D_2O, and also H_2Se and D_2Se.[262] Hence the resolution will be difficult, and its establishment will involve very accurate measurements. For these reasons much of the experimental evidence is of little value, because the quantities used were too small to admit of adequate purification and fractionation. Failures to detect any resolution are numerous[263-8]; in some cases it has been found[269-71] that an asymmetric molecule CabcOH has its rotatory power affected when the H is replaced by D, but it must be remembered that the replacement will affect the degree of association of the hydroxyl. It does not appear that so far we have any satisfactory evidence that the stereochemical difference between hydrogen and deuterium can be experimentally detected.

D_2O, '*Heavy Water*'

D_2O is by far the best known of the compounds of deuterium; since it is associated, its properties* differ more from those of water than the pro-

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* For the thermal properties see Lange[272]; for the electrolytic Schwarzenbach.[273] For a theoretical discussion of the differences between D_2O and H_2O see Bernal and Tamm.[274]

[254] I. Nitta and K. Suenaga, *Inst. Phys.-Chem. Res. Tokyo*, 1937, **32**, 83.
[255] A. Smits and G. J. Muller, *Nature*, 1937, **139**, 804.
[256] J. Weigle and H. Saini, *Arch. Sci. phys. nat.* 1937, [v] **19**, Suppl. 28.
[257] K. Clusius, A. Kruis, and W. Schanzen, *Z. anorg. Chem.* 1938, **236**, 24.
[258] I. Nitta and K. Suenaga, *Bull. Chem. Soc. Japan*, 1938, **13**, 36.
[259] G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.* 1939, **7**, 281.
[260] G. B. Kistiakowsky, J. R. Lacher, and F. Stitt, ib. 289.
[261] R. P. Bell, *Trans. Far. Soc.* 1942, **38**, 422.
[262] A. Kruis and K. Clusius, *Z. physikal. Chem.* 1937, B **38**, 156.
[263] M. T. Leffler and R. Adams, *J.A.C.S.* 1936, **58**, 1551.
[264] R. L. Burwell, F. Hummel, and E. S. Wallis, *J. Org. Chem.* 1936, **1**, 332.
[265] H. Erlenmeyer and H. Schenkel, *Helv. Chim. Acta*, 1936, **19**, 1169.
[266] M. T. Leffler and R. Adams, *J.A.C.S.* 1936, **58**, 1555.
[267] F. C. McGrew and R. Adams, ib. 1937, **59**, 1497.
[268] G. R. Clemo and G. A. Swan, *J.C.S.* 1942, 370.
[269] H. Erlenmeyer and H. Schenkel, *Helv. Chim. Acta*, 1936, **19**, 1199.

perties of, say, C_6D_6 from those of benzene, as the replacement affects the degree of association. The whole behaviour of D_2O indicates that it is more associated than H_2O, and that the degree of association at any temperature is the same as that of water at a lower temperature. The most obvious sign of this is that the temperature of maximum density (where on cooling the effect of the increase of association begins to overcome the normal contraction) is for D_2O 11·22° C.,[275-6] being 4·08° for H_2O; freezing-points in dioxane solution[277] give the association factor for a 2-molar solution as 1·78 for D_2O and 1·73 for H_2O; the Raman spectrum of liquid D_2O is like that of H_2O at a lower temperature.[278]

Of the other properties the freezing-point, as we have seen, is 3·8° and the boiling-point 1·4° higher than those of water. The heat of evaporation is 11·10 k.cals. [10·7]*; the critical temperature is 371·5° C.[279] [374·2°]; the density $^{20^\circ}_{20^\circ}$1·10726 [0·99998], giving a molecular volume at 20° of 18·092 [18·016], a difference of +0·4 per cent., due to the greater association of the D_2O. The specific heat of the liquid at 4–25° is 1·028 [1·018]: the heat of fusion in k.cals./mole 1·523 [1·435] and of evaporation 9·919 [9·719]. The dielectric constant at 0° is 80·7 [81·5] (Lewis[280]); the dipole moment in benzene at 25° is 1·78 [1·76][281] and in dioxane 1·87 [1·86].[282] The surface tension is very slightly smaller and the viscosity[283] at 25° 1·23 times as great as that of water.

On cooling, D_2O and H_2O form a continuous series of solid solutions, the freezing-point curve being almost but not quite a straight line[284]; the maximum difference between liquidus and solidus is 0·020° at 42 per cent. D_2O. The crystal structure of solid D_2O is the same as that of ice,[285] the values of *a* differing by less than 0·1 per cent. The solid-liquid relations have been measured by Bridgman[286] up to 12,000 kg./cm.^{2}, and found to be very similar to those of H_2O.

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* Figures given in square brackets in this way are the corresponding values for H_2O.

[270] L. Young and C. W. Porter, *J.A.C.S.* 1937, **59**, 328.
[271] C. Buchanan, *J.C.S.* 1937, 581.
[272] E. Lange, *Z. Elektrochem.* 1938, **44**, 31.
[273] G. Schwarzenbach, ib. 46.
[274] J. D. Bernal and G. Tamm, *Nature*, 1935, **135**, 229.
[275] K. Stokland, E. Ronaess, and L. Tronstad, *Trans. Far. Soc.* 1939, **35**, 312.
[276] T. L. Chang and J. Y. Chien, *J. Chinese Chem. Soc.* 1941, **8**, 74.
[277] R. P. Bell and J. H. Wolfenden, *J.C.S.* 1935, 822.
[278] I. R. Rao and P. Koteswaram, *Nature*, 1938, **141**, 331.
[279] E. H. Riesenfeld and T. L. Chang, *Z. physikal. Chem.* 1935, B **28**, 408.
[280] G. N. Lewis, A. R. Olson, and W. Maroney, *J.A.C.S.* 1933. **55**, 4731.
[281] F. H. Müller, *Phys. Z.* 1934, **35**, 1009.
[282] P. Abadie and G. Champetier, *C.R.* 1935, **200**, 1590.
[283] G. Jones and H. J. Fornwalt, *J. Chem. Phys.* 1936, **4**, 30.
[284] A. Eucken and K. Schäfer, *Nachr. Ges. Wiss. Gött.* 1935, [ii] **1**, 109.
[285] H. D. Megaw, *Nature*, 1934, **134**, 900.
[286] P. W. Bridgman, *J. Chem. Phys.* 1935, **3**, 597.

The mixed compound HDO undoubtedly exists, and it has been calculated to boil at 100·76° C., but in mixtures the equilibrium

$$H_2O + D_2O \rightleftharpoons 2\,HDO$$

must always be present; Wirtz has shown[287] by measurement of the absorption at 1·7 μ that the formation of HDO is complete within 20 seconds of mixing. It is presumably owing to this reaction that there is an evolution of heat (30 k.cals./mole) when D_2O and H_2O are mixed.[288]

D_2O *as solvent*

An important group of the properties of D_2O are those which it exhibits as a solvent, especially in relation to ionization both of the solvent itself and of the salts dissolved in it. Small differences are found in the mutual solubilities with organic solvents such as ether and phenol, the upper critical solution temperature being higher and the lower when it can be observed lower, in D_2O; small differences are also found in the heats of solution, that of mercuric cyanide, for example, being at 35° −3·7 k.cals. in D_2O and −3·5 in H_2O. The partition of iodine between carbon tetrachloride and water is 85 : 1, while with D_2O it is 103 : 1.[289] Greater differences occur in the solubilities of salts; the heats of solvation of the ions (obtained from the heats of solution of the salts) show individual differences up to 0·8 k.cals., the D_2O values being usually the smaller. The salts themselves are usually less soluble in D_2O: the ratio of the solubilities $M_s = \dfrac{\text{Mols salt}}{\text{Mols } X_2O}$ for D_2O/H_2O at 25° are (Lange,[290] p. 41):

$M_s\frac{D_2O}{H_2O}$ for	LiF	LiCl, 1 aq.	NaCl	KCl	$BaCl_2$
	1·15	1·02	0·928	0·912	0·89

$BeSO_4$, 4 aq.	$CuSO_4$, 5 aq.	$AgMnO_4$(20°)	Quinone
0·994	0·947	0·735	1·11

The related question of solid salt-deuterates is discussed below (p. 49).

In considering the ionization in D_2O it must be remembered that owing to the instantaneous interchange of D and H in hydroxyl groups we can only measure ROD compounds in D_2O and ROH compounds in H_2O (and the same with the halogen acids). The ionic mobilities in D_2O are smaller than in H_2O, as is to be expected from the 1·23 times greater viscosity of the former. When the D_2O values are multiplied by 1·23, the mobilities are nearly the same for all ions except H^+ and D^+ (and perhaps OH^- and OD^-). Thus the very accurate values obtained by McInnes[291] at 25° give the results shown in the following table:

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[287] K. Wirtz, *Z. Phys.* 1937, 104, 613.
[288] E. Doehlemann and E. Lange, *Z. physikal. Chem.* 1935, 173, 295.
[289] T. L. Chang, *J.A.C.S.* 1944, 66, 1940.
[290] E. Lange, *Z. Elektrochem.* 1938, 44, 31.
[291] L. G. Longsworth and D. A. MacInnes, *J.A.C.S.* 1937, 59, 1666.

Ion	Λ_∞	$\Lambda_\infty \eta$, D_2O	$\Lambda_\infty \eta$, H_2O	*Ratio* D/H
D(H)	250·05	307·6	351	0·896
Na	41·64	51·2	51·3	0·998
K	61·31	75·4	74·4	1·013
Cl	62·79	77·2	76·6	1·013

In the same way LaMer[292] find the ratio 1·019 for the acetate ion.

In considering the ionization, we may call the equilibrium constant, $\frac{[X_3O^+]\cdot[A^-]}{[X_2O]\cdot[XA]}$, K_h when X = H, and K_d when X = D; this will apply to acids in the wider definition of Brönsted as including all molecules that can lose a proton. It has been shown (see Schwarzenbach,[293] p. 47) that at the ordinary temperature K_h/K_d is never less than 1, and on the average is about 3; but it tends to rise as the acids get weaker: thus for oxalic acid it is 1·04, for phosphoric 1·61, for chloracetic 2·7, for acetic 2·87, and for water itself 5·43. (For a theoretical discussion of this see Halpern.[294])

Replacement of non-ionized H by D seems to have little effect on the ionization in water; Erlenmeyer[295] found no difference between the dissociation constants of $C_6H_5\cdot COOH$ and $C_6D_5\cdot COOH$ in water at 25°, both of which were $6\cdot6\times10^{-5}$.

Effects on the Rates and Equilibria of Chemical Reactions

The rate may be affected[296] by three causes: (1) the pure solvent effect; (2) the replacement of H by D in a reactant; (3) the formation or decomposition in the reaction of water: these three factors usually cannot be separated. Effect (1) is likely to be small: D_2O differs from H_2O in dielectric constant by less than 1 per cent. and in viscosity by about 20 per cent.; we may thus expect the effect (1) to be of the same order as the effect on the solubilities, that is, some 20 per cent. We have perhaps an example of this in the bromination of acetone as catalysed by the acetate anion,[297] which goes 20 per cent. quicker in H_2O than in D_2O. (2) All hydrogen atoms attached to oxygen or nitrogen are replaced in presence of D_2O practically at once; thus the rate of decomposition of nitramide in D_2O is really that of $D_2N\cdot NO_2$. On the other hand, hydrogen atoms attached to carbon, if the carbon is also joined to a carbonyl or a nitro group, are indeed replaced in D_2O, but only slowly, so that we can usually determine the rate of the reaction before and after replacement. It is found that the replacement sometimes makes a great difference. Thus the rate of bromination, either with H^+ in H_2O or with D^+ in D_2O, of

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[292] V. K. LaMer and J. P. Chittum, ib. 1936, **58**, 1642.

[293] G. Schwarzenbach, *Z. Elektrochem.* 1938, **44**, 47.

[294] O. Halpern, *J. Chem. Phys.* 1935, **3**, 456.

[295] H. Erlenmeyer and A. Epprecht, *Nature*, 1936, **138**, 367.

[296] O. Reitz, *Z. Elektrochem.* 1938, **44**, 72.

[297] Id., *Z. physikal. Chem.* 1936, **176**, 363.

$CH_3\cdot CO\cdot CH_3$ is 7·7 times as quick as that of $CD_3\cdot CO\cdot CD_3$,[298] while with either of these acetones the rate in H_2O is 2·1 times as great as in D_2O; this shows that the rate-determining step is that in which the H or D is removed from the carbon.

The following are a series of reactions catalysed by the H^+ or D^+ ion, with the values of $K_{D_2O^+}/K_{H_2O^+}$ at about the ordinary temperature (for references see Reitz[297]):

		Ratio of K's
1.	Saponification of methyl acetate	1·85
2.	,, ,, ethyl	1·5
3.	,, ,, ethyl orthoformate	2·05
4.	,, ,, acetal	2·66
5.	Enolization of acetone	2·1
6.	,, ,, 'heavy' acetone	2·1
7.	Decomposition of diazoacetic ester	2·70(0°)
8.	Inversion of cane sugar	2·05
9.	Mutarotation of *d*-glucose	0·7

It will be seen that all but the last are quicker in D_2O. Since reactions are as a rule slower with deuterium, as we should expect, this implies that the equilibrium constant $\frac{[X_3O^+]\cdot[A^-]}{[X_2O]\cdot[XA]}$ is smaller for $X = D$ than for $X = H$. This also agrees with the observation that when reactions 5, 6, 7, and 8 above are carried out in mixtures of H_2O and D_2O, the change on adding D_2O is at first slow, and then at high concentrations of D_2O is rapid: in the lighter water D will be present as HDO, and this will lose its H rather than its D, since the dissociation constant of H_2O is 5·4 times that of D_2O.

Reactions catalysed by OH^- (OD^-) show similar effects, and here too the mutarotation reaction is an exception to the general behaviour. The following table shows some results:

	$K_{\text{in } D_2O}/K_{\text{in } H_2O}$
Saponification of ethyl acetate	1·33
Hydrolysis of diacetone alcohol	1·22
,, ,, monochloracetate	1·2
Mutarotation of glucose:	
with H_2O (D_2O)	0·38
with acetate anion	0·42

An interesting reaction whose rate has been measured in H_2O and in D_2O is the conversion of aluminium carbide Al_4C_3 into methane. Urey and Price[299] using a specimen of finely powdered carbide found that with H_2O it began to react in the cold, and at 80° a given quantity gave 100 c.c. of CH_4 in 2 minutes. When D_2O was used there was no visible action until it was heated at least to 65°, and at 80° the same quantity needed at least 45 minutes to give 100 c.c. of CD_4: the ratio of the rates is thus 23:1.

[297] O. Reitz, *Z. physikal. Chem.* 1937, **179**, 119.

[299] H. C. Urey and D. Price, *J. Chem. Phys.* 1934, **2**, 300.

Barrer[300] claims to have found at 0° (where the reaction is of course very slow) a ratio of 3·9: if this is so, the reaction (which is heterogeneous) must be more complicated than appears; the ratio could not otherwise increase (6 times) when the temperature was raised from 0° to 80°.

The effect of the solvent on equilibrium is, as we should expect, very much less than on the rate. Kailan and Ebeneder[301-2] found with a series of alkyl acetates and benzoates that while the rate of the uncatalysed reaction is much slower with D_2O, the proportions at equilibrium are practically unaffected; the same results were got by Nachod,[303] who also found[304] that the percentage of enol at equilibrium in a solution of acetylacetone changes from 19·6 to 12·0 when D_2O replaces H_2O; with methyl acetylacetone the change is from 3·6 to 2·5; the solubilities in H_2O and D_2O show the corresponding differences.

D_2O *of Crystallization*

The relative affinity of anhydrous salts for H_2O and for D_2O of crystallization depends on the salt. It does not seem that the difference is great; if it were, we should expect the proportions of hydrogen and deuterium in water derived from hydrated minerals to be different from the usual value. Riesenfeld and Tobiank[305] examined several such minerals (tincal $Na_2B_4O_7$, 10 aq.; carnallite KCl, $MgCl_2$, 6 aq.; polyhalite K_2SO_4, $MgSO_4$, $2CaSO_4$ 2 aq.; and gypsum $CaSO_4$, 2 aq.) and found that the density of the water got from them did not differ from that of ordinary water by more than 3 p.p.m. (about 3/100,000 in the D/H ratio, or 5 per cent. in the abundance) much the same as the differences found in the density of ordinary water. Experiments on artificial deuterates have given similar results; Erlenmeyer and Gärtner[306] found that if sodium sulphate is recrystallized from 5 per cent. heavy water, the D/H ratio is the same in the liquid as in the solid; Ingold *et al.*[307] using 2 per cent. heavy water got the same results with Li_2SO_4, H_2O; $SrCl_2$, 6 aq.; $CuSO_4$, 5 aq.; Na_2CO_3, 10 aq.; and also with the oxalate $K_2C_2O_4$, H_2O, in which the water is usually thought to be attached to the anion; they conclude that the water in hydrates is not structurally linked, but the D_2O concentration was obviously too low to justify this conclusion.

Later experiments, made when heavy water was more readily obtainable, show small but definite differences in the physical properties of the hydrates and deuterates, including the heats of formation. Saur[250] finds that the replacement of H_2O by D_2O has no measurable effect (less than 0·1 per cent.) on the lattice constants of potassium aluminium and potas-

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[300] R. M. Barrer, *Trans. Far. Soc.* 1936, **32**, 486.

[301] A. Kailan and F. Ebeneder, *Z. physikal. Chem.* 1937, **180**, 157.

[302] Id., ib. 1938, **182**, 397.

[303] F. C. Nachod, *Z. Elektrochem.* 1938, **44**, 80.

[304] Id., *Z. physikal. Chem.* 1938, **182**, 193.

[305] E. H. Riesenfeld and M. Tobiank, *Ber.* 1935, **68**, 1962.

[306] H. Erlenmeyer and H. Gärtner, *Nature*, 1934, **134**, 327.

[307] J. N. E. Day, E. D. Hughes, C. K. Ingold, and C. L. Wilson, *J.C.S.* 1934, 1593.

sium chromium alum, $KCr(SeO_4)_2$, 12 aq., or $UO_2(NO_3)_2$, 6 aq. The small differences of solubility of salts in the two solvents have already been discussed; we can, of course, only measure the hydrates in H_2O and the deuterates in D_2O. Bell[309] finds for a number of hydrated salts that the replacement of H_2O by D_2O causes a decrease of not more than 2 per cent. in the molecular volume, except in oxalic acid, 2 aq. (+2·3 per cent.) and anhydrous KH_2PO_4 (+1·4 per cent.), in both of which the hydrogen (deuterium) bonds are important.

In the transition points of the hydrates there are again only small differences. The following table is mainly from Bell[309]; the Na_2SO_4 value is from Taylor[308] and those for $SrCl_2$ and $CuSO_4$ from Menzies.[310]

Transition Points

Salt	*Mols. Water*		$T^{\circ}_{H_2O}$	$T^{\circ}_{D_2O}$	*Diff.*
Na_2SO_4	10 $\rightleftharpoons$	0	32·38°	33·48°	+1·10°
$CoCl_2$	6	2	52·3°	51·1°	—1·2°
$SrCl_2$	6	2	61·3°	56·5°	—4·8°
,,	2	1	132°	127°	—5°
$NiCl_2$	6	4	36·3°	35·9°	—0·4°
NaBr	2	0	50·7°	47·7°	—3·0°
$MgSO_4$	7	6	48·4°	46·8°	—1·6°
$CuSO_4$	5	3	95·0°	95·9°	+0·9°

For several of these the vapour pressures have been measured at various temperatures, and the heats of hydration of the solid salts determined. Thus Bell[251] has in this way measured the heats for a large number of salts; the general conclusion is that the deuterates have higher vapour pressures and lower heats of formation; the differences in the heats are from 0·31 to 3·2 k.cals.

Other D-compounds include the amines, D_2O_2, D_2S, D_2Se, and the D-halides; their more important points of interest have already been mentioned.

Exchange of Hydrogen and Deuterium

Many investigations have been made on this subject, the importance of which is obvious as throwing light on the conditions of rupture of the link of hydrogen to other atoms, and on the extent to which free hydrogen atoms form part of a chemical reaction. The literature is very extensive, and up to 1938 has been summed up by Ingold and Wilson.[311]

Like other isotopic exchanges, these are essentially chemical reactions, with their own rates and heats of activation; the rates range from practically zero, as with hydrocarbons in the cold in the absence of catalysts, to practically infinite, as with ionizable hydroxylic hydrogen and deuterium.

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[308] H. S. Taylor, *J.A.C.S.* 1934, **56**, 2643.

[309] J. Bell, *J.C.S.* 1937, **459**.

[310] F. T. Miles and A. W. C. Menzies, *J.A.C.S.* 1937, **59**, 2392.

[311] C. K. Ingold and C. L. Wilson, *Z. Elektrochem.* 1938, **44**, 62–70.

The rate of reaction obviously depends on both of the reactants, the hydrogen compound and the deuterium compound. For practical purposes we are mainly concerned with two deuterating agents, D_2 and D_2O; the exchanges go much more readily with the latter.

Deuteration with D_2

Elementary deuterium acts only or almost only when it is broken up into atoms, either by heat, or by the electrical discharge (Wood's atomization of hydrogen), or by solid catalysts like platinum, or by irradiation in the presence of mercury vapour. The simplest example is the reaction of D_2 with H_2 to give HD, which occurs above 600°; at these temperatures D_2 will react with H compounds in general, such as CH_4, NH_3, or OH_2. The deuterium atoms have in some cases[312-13] been prepared in a Wood's tube by electric discharge, and then mixed with the hydrogen compound. The rate of deuteration depends of course on the nature of the latter; it has been shown that the heat of activation of the reaction

$$D + X\text{—}H = D\text{—}X + H$$

is about 17 k.cals. for CH_4,[313] 11 for NH_3,[314-15] and probably about 7 for H_2O.[315]

Numerous solid catalysts have been used, mainly metals (see Ingold and Wilson,[311] p. 69). Thus D_2 reacts with hydrogen in presence of nickel: with water in presence of platinum or nickel, and at higher temperatures of iron, silver, copper, or chromic oxide[316]; Hirota and Horiuti find the order[317] of catalytic activity in promoting the reaction

$$H_2O + HD = HDO + H_2$$

to be
$$Pt > Ni > Fe > Cu > Au > Ag > Hg,$$

the last having none; this is practically the order for promoting the recombination of 2 H to H_2, for overvoltage, and for hydrogenation.

In these substitutions with deuterium the rate depends primarily on the ease with which the X—H link of the hydrogen compound is broken, and so varies in the order O—H > N—H > C—H, but among the hydrocarbons there is a large range of velocities. The olefines react more readily (usually both by substitution and by addition) than the paraffins, and among the latter the ease increases in the order

$$CH_4 < \text{—}CH_3 < {>}CH_2 < {\succ}CH;$$

thus Taylor has shown[318] that with a nickel catalyst reaction occurs within a few hours with C_2H_4 down to −85°, with CH_4 at 180° C., with

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[312] E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.* 1936, **4**, 461.

[313] N. R. Trenner, K. Morikawa, and H. S. Taylor, ib. 1937, **5**, 203.

[314] K. H. Geib and E. W. R. Steacie, *Z. physikal. Chem.* 1935, B **29**, 215.

[315] A. Farkas and H. W. Melville, *Proc. Roy. Soc.* 1936, **157**, 625.

[316] K. Morikawa, W. S. Benedict, and H. S. Taylor, *J.A.C.S.* 1935, **57**, 592.

[317] K. Hirota and J. Horiuti, *Inst. Phys.-Chem. Res. Tokyo*, 1936, **30**, 151.

[318] K. Morikawa, N. R. Trenner, and H. S. Taylor, *J.A.C.S.* 1937, **59**, 1103.

ethane at 110°, with propane $H_3C \cdot CH_2 \cdot CH_3$ at 65°; even with normal paraffins the rate increases as the chain lengthens; thus the Farkases[319-21] find the relative rates over platinum to be

$$C_2H_6 : C_3H_8 : C_4H_{10} = 1 : 36 : ca.\ 160.$$

Tertiary hydrogen reacts with D_2O with exceptional ease. The effect of D_2 photosensitized by mercury has been examined by Taylor,[322-3] Melville,[324] and others.

A remarkable reaction is that discovered by Bonhoeffer and Wirtz[325] of H_2 with D_2O. At 100° C. in presence of 0·2 to 1-normal sodium hydroxide there is in some hours a considerable exchange with the formation of HD. The OD^- ion must form a complex with the dissolved hydrogen thus:

$$\boxed{D{-}O^- + H}{-}\boxed{H + D{-}O{-}D} = DOH + HD + OD^-.$$

Deuteration with D_2O

The second class of reactions are those with D_2O (and similar compounds such as ND_3, D_2SO_4, or C_2H_5OD). Here it is obvious that the deuterium is already in the ionic state, and that if the hydrogen compound is also ionized the interchange should be instantaneous, as it is in fact found to be. An early observation of Bonhoeffer[326] was that while ammonium chloride on solution in D_2O has all its hydrogen replaced by deuterium, sugar only has about half, these being obviously the hydroxylic hydrogens. In general it is found that D_2O reacts at once with hydrogen attached to halogens, oxygen, sulphur, or nitrogen, but with hydrogen on carbon only under special conditions—i.e. it reacts readily with the hydrogen only so far as this is ionized.

The rapid reaction of D_2O with H_2O is shown by the heat evolved when the two are mixed, and by the impossibility of isolating HDO from the mixture; with ammonia, hydrazine, and the amines all the evidence[327-9] is that the reaction is instantaneous, even when the ammonia is combined in cuprammonium and cobaltammine salts.[330-1]

The behaviour of hydrogen attached to carbon is of great importance in its bearing on theories of organic reaction. With unsaturated hydrocarbons the addition of D_2O will of course occur under the same conditions as that

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[319] A. and L. Farkas, *Nature*, 1939, **143**, 244.

[320] Id., *Trans. Far. Soc.* 1939, **35**, 917.

[321] A. Farkas, ib. 1940, **36**, 522.

[322] H. S. Taylor, K. Morikawa, and W. S. Benedict, *J.A.C.S.* 1935, **57**, 383.

[323] K. Morikawa, W. S. Benedict, and H. S. Taylor, *J. Chem. Phys.* 1937, **5**, 212.

[324] A. Farkas and H. W. Melville, *Proc. Roy. Soc.* 1936, **157**, 625.

[325] K. Wirtz and K. F. Bonhoeffer, *Z. physikal. Chem.* 1936, **177**, 1.

[326] K. F. Bonhoeffer and W. G. Brown, ib. 1933, B **23**, 172.

[327] G. N. Lewis, *J.A.C.S.* 1933, **55**, 3502.

[328] P. C. Cross and P. A. Leighton, ib. 1938, **60**, 981.

[329] H. J. Emeleus and H. V. A. Briscoe, *J.C.S.* 1937, 127.

[330] H. Erlenmeyer and H. Gärtner, *Helv. Chim. Acta*, 1934, **17**, 1008.

[331] H. Erlenmeyer and H. Lobeck, ib. 1935, **18**, 1218.

of water (not necessarily at quite the same rate), and reversible addition will lead to deuteration. This will apply also to those compounds which can assume an unsaturated structure by a tautomeric change, especially to those which contain the groups H·C—C=O (keto-enols) and $H \cdot C \cdot NO_2$. Many of the reactions of such compounds (bromination, enolization, racemization, etc.) are assumed to proceed by a similar ionization of the hydrogen, and if this is so, the rate of deuteration should be the same as that of the other reaction. In several cases this equality has been established experimentally. Thus Ingold[332] showed that the rate of deuteration of phenyl-β-*n*-butyl ketone is equal to its rate of racemization in D_2O: with such optically active ketones the rates of racemization and of halogenation are known to be equal. Walters and Bonhoeffer[333] showed that the rate of exchange of acetone with D_2O in presence of sodium hydroxide is equal to that of iodination under the same conditions, so far as the latter can be calculated. Ives and Wilks found[334] that the active form of the acid Φ(tol)CD·COOH in H_2O with excess of sodium hydroxide exchanges its deuterium at the same rate as it racemizes.

As we should expect, the exchange of hydrogen in the H·C·C=O group is much slower when the CO forms part of a carboxyl group. Thus Klar[335] finds no exchange between D_2O and sodium acetate below 100°, nor at the ordinary temperature even after some weeks.[336] The free acid[337] reacts even more slowly than its ion (this of course does not apply to the carboxyl hydrogen). In presence of normal sodium hydroxide acetic acid will react with D_2O at 100° in 100–400 hours; but the higher acids like propionic and isobutyric, as well as acids with the carboxyl directly attached to the benzene ring (and so with no α-hydrogen) like benzoic and toluic, will not.[338]

The acid hydrolysis of acetamide in D_2O is instructive (Reitz[339]). In N/10 acid the rate is 1·5 times as great in D_2O as in H_2O; with 2-3-normal acid the rates are the same; with 3-4-normal acid the rate in D_2O is only 0·85 of that in H_2O; a similar result is found in the enzymatic splitting of the glucosides. This is because the velocity of the reaction is the product of the concentration of the complex formed with the catalyst (in the Brönsted sense) and its rate of decomposition. At low concentrations of the catalyst the amount of the complex is much greater in D_2O while at high concentrations practically all the substance is in the form of complex, and this factor does not come in: the velocity is then lower in D_2O because the intrinsic rate of decomposition of the complex is less in that solvent.

The reactions by which D_2O can be made to replace the hydrogen in unsaturated and aromatic hydrocarbons, and even in paraffins and cyclo-

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[332] S. K. Hsü, C. K. Ingold, and C. L. Wilson, *J.C.S.* 1938, 78.

[333] W. D. Walters and K. F. Bonhoeffer, *Z. physikal. Chem.* 1938, **182**, 265.

[334] D. G. J. Ives and G. C. Wilks, *J.C.S.* 1938, 1455.

[335] R. Klar, *Z. physikal. Chem.* 1934, B **26**, 335.

[336] S. Liotta and V. K. LaMer, *J.A.C.S.* 1937, **59**, 946.

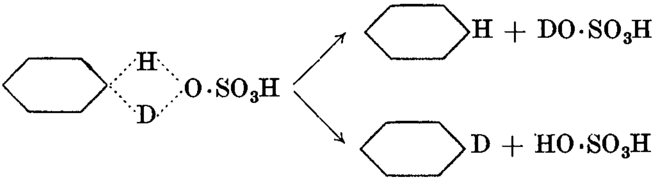
[337] L. D. C. Bok and K. H. Geib, *Naturwiss.* 1938, **26**, 122.

[338] D. J. G. Ives, *J.C.S.* 1938, 91.

[339] O. Reitz, *Z. physikal. Chem.* 1939, **183**, 371.

paraffins, are remarkable (see Ingold and Wilson,[311] p. 66); it was shown by Ingold[340] that this can be brought about by D_2SO_4, or by a concentrated solution of H_2SO_4 in D_2O. As we might expect, it goes much more easily with aromatic hydrocarbons than with paraffins. With benzene Ingold, Raisin, and Wilson[341] found that if it is shaken at the ordinary temperature for 12 hours with an equimolecular mixture of D_2O and D_2SO_4 (D_2O, D_2SO_4, or $(D_3O)\cdot[SO_4D]$: 85 per cent. by weight), a large amount of deuteration occurs, which by repetition of the process can be carried to C_6D_6. This cannot be due to reversible sulphonation, because it can be shown that at this concentration (i.e. as soon as the composition reaches that of $(D_3O)\cdot[SO_4D]$) sulphonation ceases; also an acid of this strength will not split off the sulphonic group from benzene sulphonic acid.[342]

Ingold *et al.* emphasize the impossibility of this sulphonation theory[342]; it might hold for unsaturated hydrocarbons like ethylene, but not for benzene. Ingold points out that this reaction has the characteristics of substitution by electrophilic reagents (it will be shown later that it obeys the ordinary orientation laws for such reactions) and he gives the same explanation for it as he had previously given[343] for nitration:



This view is supported by the results of their investigation of the efficiency of other catalysts in this reaction.[344] They conclude that the efficiency decreases in the order

$$H_2SO_4 > H_2SeO_4 > H_3O^+ > \Phi\cdot OH > H_2O > OH^-$$

The efficiency of the substituents in the benzene is in the order

$$O^- > NMe_2 > O\cdot Me > H > SO_3H.$$

This is the order of the proton-accepting and donating power.

These conclusions are further supported by the positions taken up by the introduced deuterium atoms, which are governed by the ordinary rules of benzene substitution, that are of course derived from the behaviour of electrophilic substituting agents. This is well illustrated by the behaviour of the phenols; the deuterium always takes up the positions to be expected on the ordinary rules for bromine or nitro groups; this is easily ascertained by brominating or nitrating the product, and seeing whether it is the hydrogen or the deuterium that has been replaced; it is often indicated

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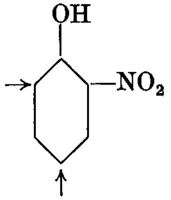
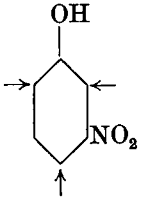
[340] C. K. Ingold, C. G. Raisin, and C. L. Wilson, *J.C.S.* 1936, 1643.
[341] Id., ib., 915.
[342] C. K. Ingold, *Nature*, 1934, 134, 847.
[343] C. K. and E. H. Ingold, *J.C.S.* 1926, 1310.
[344] C. K. Ingold, C. G. Raisin, and C. L. Wilson, ib. 1936, 1637.

without any such test by the number of deuterium atoms that can be introduced (the hydroxylic hydrogen is of course replaced at once); in this way Best and Wilson[345] showed that the deuteration of phenol and of aniline goes to the ortho and para positions.

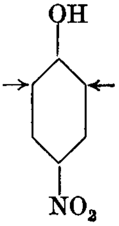
Koizumi and Titani[346] find that with ortho-, meta-, and para-nitrophenol in alcohol at 100° the OH hydrogen goes at once; then there are replaced two H atoms of the ortho and para and three of the meta:



o



m

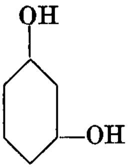


p

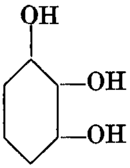
i.e. all the hydrogen atoms that are ortho or para to the hydroxyl are readily replaced.

It is remarkable that while meta- and para-nitrophenol react at equal rates, the ortho reacts much more slowly; this they ascribe, no doubt correctly, to the chelation of the ortho compound, which has an interesting bearing on the mechanism of the reaction. They find[347] the heat of activation of the nuclear replacement in meta- and para-nitrophenol to be 29 and 28 k.cals., while in the unsubstituted phenol it is 25.

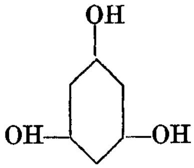
The simple poly-phenols behave similarly. Resorcinol[348] in D_2O exchanges its hydroxyl hydrogens at once; of the three hydrogen atoms ortho to OH two are replaced at a measurable rate, and the third (presumably the one between the OH groups) much more slowly; Geib[349] has shown that the reaction goes 5,000 times as quick in normal hydrochloric acid as in water; but even in acid solution the last hydrogen atom (which is not ortho to an OH) is not exchanged, even at 230°. In the same way in pyrogallol[350] the two hydrogen atoms ortho to OH are much more easily replaced than the third, while in phloroglucinol all the hydrogens are easily replaced.



Resorcinol



Pyrogallol



Phloroglucinol

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[345] A. P. Best and C. L. Wilson, ib. 1938, 28.

[346] M. Koizumi and T. Titani, *Bull. Chem. Soc. Japan*, 1938, **13**, 318

[347] Id., ib. 1939, **14**, 40.

[348] F. K. Münzberg, *Z. physikal. Chem.* 1936, B **33**, 39.

[349] K. H. Geib, ib. 1937, **180**, 211.

[350] F. K. Münzberg, ib. 1936, B **33**, 23.

Kharasch[351] finds that in the absence of acid, aniline only exchanges the hydrogen on the nitrogen, and dimethyl aniline does not exchange at all. Also the exchange from amines of nuclear hydrogen occurs with about equal ease with aniline, diphenylamine, and triphenylamine, so that the formation of the ion does not seem to be a necessary intermediate stage.

Deuterium can also be introduced into benzene by treating it with DCl in presence of aluminium chloride.[352-3] The DCl is conveniently made from D_2O+thionyl chloride; by the repetition of the treatment all the hydrogen in benzene can ultimately be replaced.

The reaction of D_2O with acetylene has been disputed, but it seems that it exchanges its H in presence of normal sodium hydroxide, though not in neutral or acid solution.[354-7] See further reference.[359]

In all these exchanges the distribution of the deuterium between the water and the other compound is never equal, though it does not depart far from equality. Ingold and Wilson (ref. [311], p. 64) give these values of

$$K = \frac{\text{D/H in compound}}{\text{D/H in water}}.$$

Link	*Compound*	*K*
C—H	Acetone	0·70–0·87
,,	Nitromethane	0·78
N—H	Aniline	1·11
,,	Pyrrol	0·88
O—H	Benzoic acid	1·04
,,	Benzyl alcohol	1·10
,,	*n*-Amyl alcohol	1·09
,,	Phenol	1·08
S—H	Ethyl mercaptan	0·43

Theoretical calculations on the partition have been made and compared with experiment by Halford.[358]

[351] W. G. Brown, M. S. Kharasch, and W. R. Sprowls, *J. Org. Chem.* 1939, **4**, 412.
[352] A. Klit and A. Langseth, *Nature*, 1935, **135**, 956.
[353] Id., *Z. physikal. Chem.* 1936, **176**, 65.
[354] L. H. Reyerson, *J.A.C.S.* 1935, **57**, 779.
[355] L. H. Reyerson and B. Gillespie, ib. 2250.
[356] Id., ib. 1936, **58**, 282.
[357] Id., ib. 1937, **59**, 900.
[358] J. O. Halford, *J. Chem. Phys.* 1940, **8**, 243.
[359] G. B. Kistiakowsky and R. L. Tichenor, *J.A.C.S.* 1942, **64**, 2302.

TRITIUM

THE third isotope of hydrogen, ^{3}H or tritium, was at one time supposed to occur in very small quantities in natural hydrogen, but later work makes this very improbable. Oliphant, Harteck, and Rutherford[360-1] got from the Norsk Hydro-Elektrisk Actieselskab of Oslo 11 c.c. of water which was the residue of the electrolysis of 43·4 kg. of 99·2 per cent. heavy water, which itself had been got by the electrolysis of 13,000 tons of ordinary water. This 11 c.c. was examined by Aston in his precision mass-spectrograph; he found that the 5-line for D_2H was strong, but there was no sign of the 5-line of DT, which should have been 0·5 mm. away; the D_2 line was clear after 1 second exposure, but the DT line did not appear at all after 50 minutes; hence the ratio DT/D_2 is less than 1/50,000 in this small residue from 13,000 tons of water. This conclusion was confirmed by allowing an accelerated beam of the ions to fall on a deuterium compound; if there had been any tritium, α-particles should have been formed according to the equation

$$^{2}\mathrm{D} + {}^{3}\mathrm{H} \rightarrow {}^{4}\mathrm{He} + {}^{1}n.$$

No signs of α-particles were got, and the results showed that by this test even in the electrolytic residue the T/D ratio is less than 1/5,000. Bleakney *et al.*[362] confirmed this conclusion. Geiger-counter measurements with pure deuterium show that if we assume that tritium has a half-life of 31 years,[368] the amount of it in ordinary hydrogen is less than 1 part in 10^{17}.[373]

On the other hand, this isotope can be made by the bombardment of deuterium by deuterons, as we have already seen (p. 38).[360,363] The tritium so formed, which has a mass of 3·0171 (for H = 1·0081), was at first supposed to be stable, but it has been shown that it does actually decay, though only slowly,[364-7] probably changing to (the also slowly decaying) ^{3}He; the half-life is 31±8 years.[368] That the substance is actually hydrogen was demonstrated by Alvarez and Cornog,[369] who showed that the bombardment of deuterium compounds by deuterons produces a radioactive gas of long life which will diffuse through palladium. Seaborg *et al.*[370]

[360] M. L. E. Oliphant, P. Harteck, and Lord Rutherford, *Proc. Roy. Soc.* 1934, **144**, 692.

[361] Lord Rutherford, *Nature*, 1937, **140**, 303.

[362] R. Sherr, L. G. Smith, and W. Bleakney, *Phys. Rev.* 1938, **54**, 388.

[363] E. Hudspeth and T. W. Bonner, ib. 308.

[364] T. W. Bonner, ib. 1938, **53**, 711.

[365] A. J. Ruhlig, ib. **54**, 308.

[366] G. J. Perlow, ib. 1940, **58**, 218.

[367] S. C. Brown, ib. 1941, **59**, 954.

[368] R. D. O'Neal and M. Goldhaber, ib. 1940, **58**, 574.

[369] L. W. Alvarez and R. Cornog, ib. 1939, **56**, 613.

[370] G. T. Seaborg, A. C. Wahl, and J. W. Kennedy, *J. Chem. Phys.* 1940, **8**, 639.

[371] J. F. Black and H. S. Taylor, ib. 1943, **11**, 395.

[372] W. F. Libby, ib. 101.

[373] M. L. Eidinoff, ib. 1947, **15**, 416.

have shown that the mixture of deuterium and tritium got by Alvarez and Cornog, which contains about $1/10^{11}$ of tritium, can be concentrated by the Clusius-Dickel hot-wire diffusion method. The electrolytic protium/tritium separation factor with platinum electrodes in alkaline solution at 20° is 14.[374]

Black and Taylor[371] measure the equilibrium in the reaction

$$HT + H_2O = H_2 + HTO$$

and show that this reaction from left to right evolves 1·46 k.cals. at 25°. The equilibrium constant in this reaction at 20° has been calculated to be 6·24, and found experimentally to be 6·47.[371]

For a theoretical discussion of the equilibria between X_2 and X_2O, where $X = H$, D, and T, see Libby.[372]

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[374] M. L. Eidinoff, *J.A.C.S.* 1947, **69**, 977, 2507.

GROUP I(2)

Li, Na, K, Rb, Cs, 87 : A

Cu, Ag, Au : B

THIS group consists of two subgroups: (1) elements whose atoms contain one more electron than an inert gas (typical and A elements: alkali metals) and (2) those with 7 less than the next following inert gas, i.e. one more than the pseudo-inert-gas structure ending in 18 instead of 8 (B elements: copper, silver, and gold, the coinage metals). These two subgroups agree in having one electron more easily removed than the rest: how much more easily may be seen for Group I. A by comparing the ionization potentials of neon, sodium, and the sodium ion, as obtained from the spectroscopic data; they are given below in electron-volts and in k.cals. per g. atom.

(e.v. = 23·07 k.cals. per g. atom: the average heat of formation of a covalent link from its atoms is about 70 k.cals. or 3 e.v.)

	Ne	Na	Na^+
	21·5	5·18	47·0 e.v.
K.cals./g.atom	496·0	119·5	1085

Hence all the elements of this group have a valency of 1. The resemblance between the two subgroups scarcely extends beyond this; it is a characteristic of the Periodic Table that the difference between the two divisions of a group is greatest in the earliest and latest groups. In Group I the lack of resemblance between the two subgroups is mainly due to two causes. The first is the great difference in the energy required to detach the valency electron, as is shown most clearly in the first gaseous ionization potentials, or in the electrode potentials in solution:

	Li	Na	K	Rb	Cs	Cu	Ag	Au
Gas ion. potl.	5·36	5·18	4·41	4·16	3·96	7·7	7·5	9·3
Soln. el. potl.	−2·09	−2·71	−2·92	−2·92	−2·93[a]	+0·35	+0·81	+1·38

a = [375]

This results in the B elements having, even in their monovalent state, a much greater tendency to form covalent links.

The second difference is that while the A elements are invariably monovalent, the B can assume higher valencies, because the 18-group of electrons can be broken down by chemical action, whereas the 8-group cannot. This is shown by the ratios of the gaseous ionization potentials

$$Na^+/Na = 47{\cdot}0/5{\cdot}18 = 9{\cdot}09,$$
$$Cu^+/Cu = 20{\cdot}2/7{\cdot}68 = 2{\cdot}63.$$

Hence the two subdivisions of Group I must be treated separately.

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[375] H. E. Bent, C. S. Forbes, and A. F. Forziati, ib. 1939, 61, 709.

GROUP IA

THE ALKALI METALS

This is the most closely related series of elements with which we shall have to deal. The radii of the neutral atoms and of the monatomic ions are as follows (the values for the B elements are given for comparison):

	Li	Na	K	Rb	Cs	Cu	Ag	Au
At. rad.	1·33	1·57	2·03	2·16	2·35	1·35	1·53	1·50 A.U.
Ionic rad. M^+	0·78	0·98	1·33	1·49	1·65	1·0	1·13	*ca.* 1·1 A.U.

Hence on the principles of Fajans the alkali metals have every reason to form electrovalencies rather than covalencies: the charge on the ion is only 1, the ion is relatively large, and it has an inert gas structure.

The chemistry of the alkali metals, as ordinarily understood, is almost entirely that of the ions Li^+, Na^+, K^+, Rb^+, and Cs^+; it is concerned with the behaviour and the reactions of the salts, which are practically all strong electrolytes—that is, they are ionized under all conditions. The reactions and structures of their anions will be dealt with later, under the electronegative elements from which they are derived, so that the discussion of the salts will not take long. The covalent compounds of the alkali metals, though they are formed both by the charged and by the uncharged atoms, are comparatively few. In general the attachment of an alkali metal atom to hydrogen, nitrogen, oxygen (and hence to the anions of oxy-acids), and to a halogen, is electrovalent. There are only two serious exceptions: the link to carbon in the alkaline derivatives of the hydrocarbons can certainly be covalent, and there must of course be covalent links in the limited number of complex compounds.

The alkali metals form so closely knit a series that it is best to consider them all together, so as to see how each property changes as we proceed from lithium to caesium.

In this, as in every other periodic Group, the most peculiar of the elements is the first; lithium differs far more from the other members than they do from one another. The gap between sodium and potassium, though less than that between lithium and sodium, is considerable, and is greater than that between any of the later elements. The general order of change of any property is along the series in one direction or the other, though not infrequently the order is not exactly that of the atomic numbers; this is largely because we are nearly always considering the behaviour of solids, and the stability of the crystal lattice may vary for geometrical reasons in a somewhat complicated way. Disregarding such small irregularities we find the following directions of change (for simplicity only the extreme values are quoted) in the physical properties:

Melting-points ⟵ Li 179° to Cs 28·5°
Boiling-points ⟵ Li 1336° to Cs 760°
Hardness ⟵ Li 0·6 to Cs 0·2
Ion. potl. in gas ⟵ Li 5·36 to Cs 3·96

Atomic radius ⟶ Li 1·33 to Cs 2·35
Ionic radius ⟶ Li 0·78 to Cs 1·65
Ionic mobility ⟶ Li 39·6 to Cs 79·9
Density ⟶ Li 0·534 to Cs 1·87

Elements

The amounts of these elements in the earth's crust, in grammes per ton, are[376]:

Li	Na	K	Rb	Cs	[87]
65	28,300	25,900	310	7	[0]

Though they differ greatly in abundance they are all very widely distributed. The general tendency of these elements to become rarer as the atomic number increases is obvious, as is also the exceptionally small proportion of lithium, which (like that of beryllium) is undoubtedly due to its disappearance through the natural process of nuclear bombardment.

The almost equal abundance of sodium and potassium in the earth's crust is remarkable, especially in view of the large excess of sodium in natural waters; there is about 4 times as much sodium as potassium in river waters, and at least 30 times as much in the sea.

There are two special questions of interest to be discussed with reference to the elements, the radioactivity of potassium and rubidium, and the possible existence of element No. 87.

Lithium Isotopes

The isotopic nuclei of lithium are of special interest because they take part in a variety of important nuclear reactions. Lithium consists of 7·5 per cent. of ^{6}Li (at. wt. 6·0177) and 92·5 per cent. of ^{7}Li (7·0182). The difference of 17 per cent. in mass makes their separation possible, and it has been effected in various ways.

Oliphant *et al.*[377] and Rumbaugh *et al.*[378-9] used modified forms of mass-spectrograph (for details see Walker,[380]) and the latter were able to get as much as 0·018 mg. of ^{6}Li and 0·200 mg. of ^{7}Li. A considerable degree of enrichment of the isotopes has been obtained in other ways too. On electrolysis the ^{6}Li is found to separate preferentially with a factor of 1·02–1·08.[381-5]

Lewis and MacDonald[386] found that if a thin stream of liquid lithium

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[376] V. M. Goldschmidt, *J.C.S.* 1937, 656.

[377] M. L. Oliphant, E. S. Shire, and B. M. Crowther, *Proc. Roy. Soc.* 1934, **146**, 922.

[378] W. R. Smythe, L. H. Rumbaugh, and S. S. West, *Phys. Rev.* 1934, **45**, 724.

[379] L. H. Rumbaugh and L. R. Hafstad, ib. 1936, **50**, 681.

[380] For details see O. J. Walker, *Ann. Rep. Chem. Soc.* 1938, **35**, 136, 143, 146.

[381] A. Eucken and K. Bratzler, *Z. physikal. Chem.* 1935, **174**, 269.

[382] T. I. Taylor and H. C. Urey, *J. Chem. Phys.* 1937, **5**, 597.

[383] Id., ib. 1938, **6**, 429.

[384] L. Holleck, *Z. Elektrochem.* 1938, **44**, 111.

[385] H. L. Johnston and C. A. Hutchinson, *J. Chem. Phys.* 1940, **8**, 869.

[386] G. N. Lewis and R. T. MacDonald, *J.A.C.S.* 1936, **58**, 2519.

amalgam falls through lithium chloride solution, the ^{6}Li goes preferentially with the amalgam. With half a ton of 0·6 molar amalgam in 18-metre tubes they raised the percentage of ^{6}Li from 7·5 per cent. nearly to 20.

Some of the nuclear reactions of the two isotopes may be quoted; for details and references see Braddick.[387]

$$\begin{aligned}
{}^{6}\mathrm{Li} + {}^{1}n &= {}^{3}\mathrm{H} + {}^{4}\mathrm{He}\\
+ {}^{1}\mathrm{H} &= {}^{3}\mathrm{He} + {}^{4}\mathrm{He}\\
+ {}^{2}\mathrm{D} &= 2\ {}^{4}\mathrm{He}\\
{}^{7}\mathrm{Li} + {}^{1}n &= {}^{8}\mathrm{Li}\ (0{\cdot}7\ \mathrm{sec.})\\
+ {}^{1}\mathrm{H} &= 2\ {}^{4}\mathrm{He}\\
+ {}^{2}\mathrm{D} &= {}^{8}\mathrm{Li} + {}^{1}\mathrm{H}\\
,, &= {}^{8}\mathrm{Be} + {}^{1}n\\
,, &= 2\ {}^{4}\mathrm{He} + {}^{1}n
\end{aligned}$$

Radioactivity of Potassium and Rubidium

With the exception of the two rare earth metals, samarium and luteceium, whose radioactivity has recently been discovered, these are the only elements lighter than thallium (81) that show natural radioactivity. In 1906[388] N. R. Campbell found that potassium and rubidium have a feeble β-ray activity, about a thousandth of that of uranium; about 4 times as many β-rays are emitted by rubidium as by potassium. No other alkali metals (except of course No. 87) show any sign of radioactivity. The activity of the potassium is undoubtedly due to the element itself and not to an impurity, since it is constant for specimens of potassium from the most diverse sources, animal, vegetable, and mineral.[389]

By 'ideal distillation' (i.e. by distillation under such conditions that the distance between liquid and condensate does not exceed the free path in the vapour, when the rates of distillation are proportional to the square roots of the atomic masses) Hevesy was able[390] to separate from potassium a small fraction of higher atomic weight, and show that this had a greater radioactivity.[393] As the only isotopes then known were ^{39}K and ^{41}K, he assumed that the active atoms were ^{41}K, though this did not seem consistent with the fact that calcium extracted from old potassium minerals was found to have the normal atomic weight of 40·08[391] and to be free from ^{41}Ca (Aston).[392]

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[387] H. J. J. Braddick, *Ann. Rep. Chem. Soc.* 1936, **33**, 25, 27.

[388] N. R. Campbell and A. Wood, *Proc. Camb. Phil. Soc.* 1906, **14**, 15; N. R. Campbell, ib. **14**, 211, 557. Indications had been obtained by J. J. Thomson, *Phil. Mag.* 1905, [6] **10**, 584.

[389] See M. C. Neuburger, *Ahrens Sammlung*, 1922, **26**, 229; W. D. Harkins and W. G. Guy, *Proc. Nat. Acad. Wash.* 1925, **11**, 628.

[390] G. v. Hevesy, *Nature*, 1927, **120**, 838; G. v. Hevesy and M. Lögstrup, *Z. anorg. Chem.* 1928, **171**, 1; G. v. Hevesy, W. Seith, and M. Pahl, *Bodenstein Festschrift*, 1931, 309.

[391] G. v. Hevesy, M. Pahl, and R. Hosemann, *Nature*, 1934, **134**, 377.

[392] F. W. Aston, ib. 1934, **133**, 869.

[393] The electrolytic separation factor for potassium 39/41 is 1·0054/20°; D. A. Hutchison, *J. Chem. Phys.* 1946, **14**, 401.

In 1935, however, a third isotope of potassium, ^{40}K, present only in very small quantity, was discovered by Nier[394] and by Brewer.[395-6] The proportions of the isotopes in potassium from any source are:

Atomic weight	39	40	41
Proportion	8300	1	585
Per cent.	93·5	0·011	6·5

Smythe and Hemmendinger[397] have succeeded by means of a high-intensity mass-spectrograph in separating the three isotopes in sufficient quantity to show that only the ^{40}K is active, and that its β-rays on analysis give the same two bands as the rays from ordinary potassium. The half-life of this isotope is $2{\cdot}4 \times 10^8$ years[397a] (about one-seventeenth of that of UI). This discovery removes the difficulty about the atomic weight of the calcium produced, since the loss of a β-particle would convert ^{40}K into the common isotope of calcium ^{40}Ca.

With rubidium also the isotopes have been separated in sufficient quantity for examination by Hemmendinger and Smyth,[398] and by Walcher,[399] who have shown that the only radioactive isotope is ^{87}Rb, which forms about 28 per cent. of the whole; its half-life must thus be $6{\cdot}3 \times 10^{10}$ years. This should of course go by a β-ray change into ^{87}Sr; and it has been shown by Otto Hahn, Strassmann, and Walling[400] that the strontium extracted from a Canadian mica rich in rubidium contains 99 per cent. of ^{87}Sr, of which ordinary strontium contains only about 7 per cent. This conclusion has been confirmed by Mattauch[401] by means of the mass-spectrograph.

It is interesting to consider the amounts of the products of disintegration of these two elements.[402] Potassium emits β- and γ-rays; rubidium only β. The potassium change can thus go in two ways:

$$^{40}_{19}\mathrm{K} \longrightarrow {}^{40}_{20}\mathrm{Ca} + e \qquad (1)$$

$$^{40}_{19}\mathrm{K} + e \longrightarrow {}^{40}_{18}\mathrm{A} + \gamma \qquad (2)$$

The greater intensity of the β-radiation shows that the disintegration must go by (1) much more than by (2).

With rubidium as there are no γ-rays we have only:

$$^{87}_{37}\mathrm{Rb} \longrightarrow {}^{87}_{38}\mathrm{Sr} + e.$$

The older rocks are about $1{\cdot}5 \times 10^9$ years old. In this time about 50 per

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[394] A. O. Nier, *Phys. Rev.* 1935, ii. **48**, 283.

[395] A. K. Brewer, ib. 640.

[396] A. K. Brewer, *J. Ind. Eng. Chem.* 1938, **30**, 895.

[397] W. R. Smythe and A. Hemmendinger, *Phys. Rev.* 1937, ii. **51**, 178.

[397a] F. Birch, ib. 1947, **72**, 1128.

[398] A. Hemmendinger and W. R. Smythe, ib. 1937, ii. **51**, 1052.

[399] W. Walcher, *Physikal. Z.* 1937, **38**, 961.

[400] O. Hahn, F. Strassmann, and E. Walling, *Naturwiss.* 1937, **25**, 189; O. Hahn, *Ber.* 1938, **71**, 1.

[401] J. Mattauch, *Naturwiss.* 1937, **25**, 189.

[402] A. K. Brewer, *J.A.C.S.* 1938, **60**, 691.

cent. of the ^{40}K must have changed over, and about 1·5 per cent. of the ^{87}Rb. The amounts of these substances which are now present in and above the earth's crust are, in parts per million:

^{40}K	^{40}Ca	^{40}A	^{87}Rb	^{87}Sr
2·9	35,200	3·5	86·3	29·4

Thus the amounts produced during the last $1·5 \times 10^9$ years are about 3 parts per million of ^{40}Ca or ^{40}A, and about 1·2 of ^{87}Sr. Thus anything up to the whole of the ^{40}A now present in the atmosphere (which is 99·4 per cent. of the total argon) might have been formed in this way.

Caesium neither has nor has had such a radioactive isotope; Hahn has pointed out[403] that if it had, barium from caesium minerals must contain ^{133}Ba (which does not occur in normal barium) formed by a β-ray change; Wahl found no ^{133}Ba in the residues from pollucite, and this has been confirmed by Hahn *et al.*, who showed that barium from pollucite has the isotope composition of ordinary barium.

Element No. 87, Francium

The last member of the alkali metal series, element 87 (eka-caesium), has not been observed until lately, and even now its existence is not quite certain. On general grounds we should expect that it would be of short life if it existed at all. Of all the elements heavier than bismuth (83) only radioactive isotopes are known. Aston has shown by an elaborate investigation that there is no inactive isotope of 86 (emanation) in the atmosphere, the stablest isotope being radon (half-life 3·85 days): and the longest-lived isotope of 88, radium, has a half-life of 1,600 years only; as an odd-numbered element No. 87 is likely to be shorter lived than either of its neighbours. All the three ordinary radioactive series jump over 87, as they do over 85, in an α-ray change. Hevesy has shown[404] that if any 87 is formed by a β-ray change from radium, it is less than 1 in 500,000 of the main product. The supposed discovery of a stable isotope of 87 in certain minerals, especially samarskite,[405-6] has been shown[407-8] to be probably erroneous.

Quite recently, however,[411] reasons have been given for thinking that No. 87 exists as a very shortlived by-product of the decay of actinium. This decay is mainly a β-ray process, in which the actinium (89) with a

[403] O. Hahn, F. Strassmann, J. Mattauch, and H. Ewald, *Naturwiss.* 1942, **30**, 541.

[404] G. v. Hevesy, *Kgl. Dansk. Vid. Selsk.* 1926, **7**, no. 11, 1.

[405] J. Papish and E. Wainer, *J.A.C.S.* 1931, **53**, 3818.

[406] L. L. Barnes and R. C. Gibbs, *Phys. Rev.* 1932, ii. **40**, 318.

[407] F. R. Hirsh, ib. 1937, ii. **51**, 584.

[408] Id., ib. 1943, ii. **63**, 93.

[409] J. A. Cranston, *Phil. Mag.* 1913, **25**, 712.

[410] G. Gueben, *Ann. Soc. Sci. de Bruxelles*, 1932, **52**, 66; 1933, **53**, 115.

[411] M. Perey, *C.R.* 1939, **208**, 97; *J. Phys. Radium*, 1939, **10**, 435; M. Perey and M. Lecoin, ib. 439; M. Perey, *J. Chim. Phys.* 1946, **43**, 155. See also O. R. Frisch, *Ann. Rep. Chem. Soc.* for 1939, **36**, 23, and F. Paneth, *Nature*, 1942, **149**, 565.

half-life of 20 years goes to radioactinium, an isotope of thorium (90). It has long been known that a feeble α-radiation accompanies the change, but this was ascribed to impurities. Perey has shown that the α-radiation continues when all the impurities are removed, and that while the β-radiation of the normal actinium B and C only begins to appear after some days, a minute β-radiation (some $\frac{1}{2}$ per cent. of the final value) develops up to a maximum in an hour or so, and hence must be due to a direct product of the decay of actinium by a branched-chain reaction, with a ratio of about 1:100 to the main reaction and a half-life of 21 ± 1 minutes. This active product can be separated chemically, and is found to follow the reactions of an alkali metal; it cannot be removed by precipitation with sulphides or carbonates, but it crystallizes out with $CsClO_4$ and with Cs_2PtCl_6. This is to be expected of an α-ray product of actinium, which would have the atomic number 87. It would thus seem that this last alkali metal does actually exist. It is also possible that it may be formed to a minute extent by the α-ray decomposition of mesothorium 2 (at. no. 89). Cranston[409] claimed to have found that 3 atoms in 100,000 decomposed in this way; Hevesy[404] could find no sign of this occurring even to the extent of 1 atom in 500,000; but later work by Gueben[410] has confirmed Cranston's results.

Metals

The more important physical properties of the alkali metals have already been mentioned. As regards their chemical properties there is a marked increase in reactivity as we go from lithium to caesium. Metallic lithium is relatively inert, and can be melted and poured in the air without losing its bright surface; dry oxygen does not combine with it below 100°, and it reacts only slowly with cold water: Troost proposed to free it from sodium and potassium by washing with water. Sodium and potassium tarnish rapidly in the air, as we all know, but they do not catch fire in dry air unless they are heated. Rubidium and caesium catch fire at once on exposure to air. Lithium and sodium react only superficially with liquid bromine, whereas potassium detonates when brought in contact with it.

In general the reactivity with oxygen and the halogens is least with lithium and greatest with caesium, whereas with hydrogen, carbon, and nitrogen it is greatest with lithium and least with caesium.

The vapours of the alkali metals, though mainly monatomic, contain a perceptible proportion (of the order of 1 per cent.) of diatomic molecules, which give a characteristic band spectrum. From an examination of this, especially over a range of temperature, we can calculate[413] the heat of linkage and the distance between the nuclei. The values are given below, the heats of linkage (the heats evolved in forming the link from its atoms) being expressed in k.cals. per g. mol., and the 'calculated' distance being that between two nearest neighbours in the solid metal, with its much larger 'co-ordination number'.

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[412] J. H. Bartlett and W. H. Furry, *Phys. Rev.* 1931, 38, 1615.

[413] N. Rosen and S. Ikehara, ib. 1933, 43, 5.

Diatomic Molecules of the Alkali Metals

Compound	*Heat of formation*	*Internuclear distance*		*Reference*
		Observed	*Calculated*	
Li_2	26·3	2·67	2·66	412
Na_2	17·5	3·08	3·14	413
K_2	11·8	3·91	4·06	413
Rb_2	11·3	—	4·32	415
Cs_2	10·4	4·55	4·70	414, 416

The nature of the links in these molecules is discussed by Pauling,[417-18] who concludes that they are covalent bonds formed by the valency electrons in a normal manner Li:Li, and that the weakness of the link is explained by the large spatial extension of the orbitals. It is singular that the link should always be some 14 per cent. shorter than the metallic link, which usually has the same length as the single covalent link.

Hydrides

All the alkali metals form hydrides of the general formula MH. As has already been mentioned under hydrogen (p. 21), these are alkaline salts of the negative hydrogen ion H^-. They are all colourless crystalline compounds; the lithium salt melts at 680°,[419,420] and the sodium salt at 700-800° with decomposition[420]; the rest dissociate below their melting-points.

They all have the sodium chloride lattice[421-3] which is characteristic of ionized crystals; further, it has been shown[419,424] that when fused lithium hydride is electrolysed, hydrogen appears at the anode, and[425] in the amounts required by Faraday's Law. The compounds are formed by the direct combination of the elements on heating, lithium hydride at 700-800°, the rest at 360-400°.

In their general properties the hydrides closely resemble one another, dissociating at high temperatures, dissolving in water to the hydroxide and hydrogen, and reacting with halogens or acids to form their salts. But lithium hydride is far more stable than the others, behaving more like an alkaline earth hydride. It is not attacked in the cold by dry oxygen (which does not react with it below a red heat) or by chlorine or hydrogen

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[414] F. W. Loomis and P. Kusch, *Phys. Rev.* 1934, **46**, 298.

[415] N. T. Ze and T. S. Tsiang, ib. 1937, **52**, 91.

[416] W. Finkelnberg and O. T. Hahn, *Phys. Z.* 1938, **39**, 98.

[417] L. Pauling, *The Chemical Bond*, 1942, p. 50.

[418] For a mathematical treatment of the Li_2 molecule by the Heitler-London methods see H. M. James, *J. Chem. Phys.* 1934, **2**, 794; 1935, **3**, 9.

[419] K. Moers, *Z. anorg. Chem.* 1920, **113**, 179.

[420] D. C. Bardwell, *J.A.C.S.* 1922, **44**, 2499.

[421] LiH: J. M. Bijvoet, *Rec. Trav.* 1923, **42**, 859.

[422] NaH: G. F. Hüttig and F. Brodkorb, *Z. anorg. Chem.* 1927, **161**, 353.

[423] KH, RbH, CsH: E. Zintl and A. Harder, *Z. physikal. Chem.* 1931, B **14**, 265.

[424] W. Nernst and K. Moers, *Z. Elektrochem.* 1920, **26**, 323.

[425] K. Peters, *Z. anorg. Chem.* 1923, **131**, 140.

chloride; but it is decomposed by water with the evolution of hydrogen. Metallic lithium can be freed[426] from traces of potassium by heating it in hydrogen to 700–800°; at this temperature the potassium does not combine with the hydrogen but distils off; the lithium remains behind as the hydride LiH, which can then be decomposed by heating to 1,000°.

The heats of formation of these salts, and the interatomic distances, are of interest. In the following table are given the heats of formation[427-8] (1) H_f from the solid metal and hydrogen gas, (2) H_a from the atoms, for (*a*) the gaseous MH molecule, so far as this is known, and (*b*) for the solid hydride. The distances[423] include the observed separation M—H in the solid, the normal value of the M^+ radius, and the resulting radius of H^+. To show what the deformation amounts to in other salts, the corresponding values for the fluorine and iodine ions in the alkaline halides are added.

Compound	(1) H_f	(2) H_a	M—H	Rad. M^+	Rad. H^-	M—F	Rad. F^-	M—I	Rad. I^-
LiH gas	—33	+57·9	2·04	0·78	1·26	2·04	1·26	3·03	2·25
solid	+21·6	112·5							
NaH gas	—25·3	52·5	2·44	0·98	1·46	2·31	1·33	3·23	2·25
solid	14	91·8							
KH gas	–27·2	44·5	2·85	1·33	1·52	2·66	1·33	3·53	2·20
solid	10	81·7							
RbH solid	12	82·8	3·02	1·49	1·53	2·82	1·33	3·66	2·17
CsH solid	12	82·7	3·19	1·65	1·54	3·00	1·35	[3·95]	[2·30]
						Corrected		3·83	2·18

The CsI value is for an 8:1 instead of a 6:1 lattice; this causes an expansion amounting (according to V. M. Goldschmidt) to 3 per cent.; a 6:1-CsI lattice would thus have a Cs–I distance of 3·83 A, giving 2·18 as the radius of the iodine ion.

The variation in the apparent radius of the H^- ion is remarkably large, amounting to 20 per cent., while that in the fluorine ion is only 8 per cent. The change in the iodine ion is only 4 per cent., and for some reason is in the opposite direction.

Alkaline Derivatives of Hydrocarbons

The compounds included under this heading are of several kinds, and the structures of most of them are not yet clear. They can all be regarded as derived from hydrocarbons of one kind or another by the replacement of one or more of their hydrogen atoms by atoms of an alkali metal; their peculiarities and especially their reactivity are largely due to the fact that the normal link of an alkali metal atom is electrovalent, while the normal link of a carbon atom is covalent.

The tendency of the C—H link in a hydrocarbon to ionize is always small; in a paraffin it is practically zero, but with the introduction of multiple links and the attachment of aryl groups to the carbon it is

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[426] A. Guntz and W. Broniewski, *J. Chim. Phys.* 1909, 7, 468.

[427] F. R. Bichowsky and F. D. Rossini, *Thermochemistry*, 1936.

[428] Pauling, *Chemical Bond*, 1942, p. 50.

increased; a triple link has an especially strong effect, and acetylene and all those of its derivatives in which the $C\equiv C—H$ group remains can be regarded as definite though extremely weak acids.

The alkaline derivatives of the hydrocarbons vary in properties according to the acidity of the hydrocarbons from which they are derived. They can be divided into three groups, although intermediate cases occur.

I. Derivatives of the paraffins, such as $LiCH_3$ or NaC_2H_5. They are colourless, are non-conducting in the fused state or in solution (except in zinc ethyl, with which they almost certainly react); all but the lithium compounds are insoluble and decompose on heating without melting. They are all extremely sensitive to air and moisture; in air they are in the highest degree spontaneously inflammable. It is to be noticed that the aryl derivatives in which the metal is directly linked to the aromatic nucleus, like KC_6H_5, belong to this class.

II. Derivatives of hydrocarbons in which the 'activity' of the $C—H$ link is increased by the attachment to its carbon atom of doubly linked or aromatic radicals, as in sodium benzyl, $NaCH_2 \cdot C_6H_5$. These are more or less highly coloured; they usually dissolve in ether and then form conducting solutions. These are also very sensitive to air and water, and usually, though not always, spontaneously inflammable in air.

III. Derivatives of hydrocarbons with definitely acidic hydrogen. The extreme examples are the derivatives of acetylene and the mono-substituted acetylenes such as $C_6H_5—C\equiv C—H$. These are definite salts of the $[C\equiv C]$ or $[R \cdot C\equiv C]$ anions, like calcium carbide $Ca[C\equiv C]$, whose structure has been determined by X-ray analysis. They are colourless and insoluble, being hydrolysed by ionizing solvents like water or alcohol. They are easily oxidized, but usually stable in air at the ordinary temperature. Intermediate between classes II and III are such compounds as the derivatives of cyclopentadiene and fluorene which usually have some colour and are more or less easily oxidized by air, but have not the spontaneous inflammability of the compounds of classes I and II.

1. *Simple Alkyls and Aryls* (*colourless*)

The alkaline alkyls are so similar to those aryls in which the metal is directly attached to the aryl nucleus that the two groups can be treated together.

All these compounds are so sensitive to air and moisture that special precautions are necessary in working with them. Schlenk, who first isolated them, carried out the reactions as far as possible in exhausted and sealed

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[429] W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.* 1914, **47**, 473.

[430] W. Schlenk and E. Marcus, ib. 1664.

[431] W. Schlenk and J. Holtz, ib. 1916, **49**, 603.

[432] W. Schlenk and R. Ochs, ib. 608.

[433] W. Schlenk and J. Holtz, ib. 1917, **50**, 262.

[434] Id., ib. 274.

[435] W. Schlenk and E. Bergmann, *Ann.* 1928, **463**, 1–322; **464**, 1–42.

[436] K. Ziegler and F. Thielmann, *Ber.* 1923, **56**, 1740.

vessels, but it has since been found[445] that it is usually sufficient to work in a stream of pure and dry nitrogen.

Wanklyn in 1858 observed that sodium will dissolve in zinc ethyl $ZnEt_2$ with separation of zinc to form a compound of the composition $NaZn(C_2H_5)_3$. But the alkaline alkyls proper were first isolated by Schlenk and Holtz.[433] They can be made:

(1) By the action of the alkali metal on mercury dialkyl (this is reversible).

(2) By the action of the alkali metal on an alkyl halide, especially in benzene solution.[442] In such reactions the liquid potassium-sodium alloy (usually with about 80 per cent. potassium) is often found to be very reactive[436]; when excess of this alloy has been used the product has been shown to be the potassium and not the sodium alkyl.[451]

(3) The compounds can also be made from one another; thus lithium ethyl and mercury dimethyl give the relatively insoluble lithium methyl: potassium acts on lithium phenyl to form potassium phenyl and lithium.

The ease of formation varies. Of the halides (method 2) the alkyl derivatives, as we should expect, are more reactive than the aryl; also a chloride is more effective (in the percentage yield) than a bromide, and a bromide than an iodide[445-6]; this rather surprising result is largely due to a further reaction taking place between the alkaline alkyl produced and the unchanged halide; for example:

$$\mathrm{Li \cdot R + RI = LiI + R{-}R},$$

which occurs most readily with the heavier halogen; this is more prominent with the alkyls than with the aryls. Another competing reaction[446] is with ether:

$$\mathrm{Li \cdot R + Et_2O = Et{-}R + Li \cdot OEt}:$$

but this can be avoided by using benzene as the solvent.

[437] K. Ziegler and K. Bähr, ib. 1928, **61**, 253.

[438] K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer, *Ann.* 1929, **473**, 1.

[439] K. Ziegler and H. Kleiner, ib. 57.

[440] K. Ziegler and H. Zeiser, *Ber.* 1930, **63**, 1847.

[441] K. Ziegler and H. Wollschitt, *Ann.* 1930, **479**, 123.

[442] K. Ziegler and H. Colonius, ib. 135.

[443] K. Ziegler and H. Zeiser, ib. 1930, **485**, 174.

[444] K. Ziegler and F. Dersch, *Ber.* 1931, **64**, 448.

[445] H. Gilman, E. A. Zoellner, and W. M. Selby, *J.A.C.S.* 1932, **54**, 1957.

[446] Id., ib. 1933, **55**, 1252.

[447] H. Gilman and R. H. Kirby, ib. 1265.

[448] H. Gilman and R. V. Young, ib. 1935, **57**, 1121.

[449] H. Gilman and M. Lichtenwalter, *Rec. Trav.* 1936, **55**, 561.

[450] H. Gilman and R. H. Kirby, *J.A.C.S.* 1936, **58**, 2074.

[451] H. Gilman and R. V. Young. *J. Org. Chem.* 1936, **1**, 315.

[452] H. Gilman, A. L. Jacoby, and H. Ludeman, *J.A.C.S.* 1938, **60**, 2336.

[453] H. Gilman and M. Lichtenwaltor, ib. 3085.

[454] H. A. Pacevitz and H. Gilman, ib. 1939, **61**, 1603.

[455] J. A. Wanklyn, *Ann.* 1858, **108**, 67.

[456] J. U. Nef, ib. 1899, **308**, 264.

Gilman[488] finds that the rate of the reaction

$$\alpha\text{-}C_{10}H_7\cdot Br + Li\cdot R \longrightarrow \alpha\text{-}C_{10}H_7\cdot Li$$

goes in various solvents in the decreasing order

$$Bu_2O > Et_2O > P\cdot NMe_2 > C_6H_6 > \text{Cyclohexane}:$$

and with different R's in the order

$$n\text{-}Pr > Et > n\text{-}Bu > C_6H_5 > CH_3,$$

the last hardly reacting at all.

The simple alkyls have now been made with all five alkali metals. The lithium compounds show some remarkable differences from the rest; like the others they are colourless, but with the exception of the methyl compound* they are soluble in benzene and ligroin, and from the propyl compound upwards they are liquid at the ordinary temperature.

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* A high melting-point and a low solubility often distinguish a methyl compound from its homologues.

[457] J. Thiele, *Ber.* 1901, **34**, 68.
[458] R. Weissgerber, ib. 1659.
[459] H. Moissan, *C.R.* 1903, **136**, 1219.
[460] F. S. Acree, *Amer. Chem. J.* 1903, **29**, 588.
[461] Id., *Ber.* 1904, **37**, 2753.
[462] P. Schorigin, ib. 1908, **41**, 2723.
[463] R. Weissgerber, ib. 2913.
[464] Id., ib. 1909, **42**, 569.
[465] Id., ib. 1911, **44**, 1436.
[466] E. Krause, ib. 1924, **57**, 216.
[467] F. Hein, E. Petzchner, K. Wagler, and F. A. Segitz, *Z. anorg. Chem.* 1924, **141**, 161.
[468] E. W. Guernsey and M. S. Sherman, *J.A.C.S.* 1925, **47**, 1932.
[469] F. D. Hager and C. S. Marvel, ib. 1926, **48**, 2689.
[470] E. Krause and H. Polack, *Ber.* 1926, **59**, 777.
[471] A. v. Grosse, ib. 2646.
[472] K. Fredenhagen and G. Cadenbach, *Z. anorg. Chem.* 1926, **158**, 249.
[473] W. H. Carothers and D. D. Coffman, *J.A.C.S.* 1929, **51**, 588.
[474] D. D. Coffman and C. S. Marvel, ib. 3496.
[475] E. Bergmann and J. Hervey, *Ber.* 1929, **62**, 893.
[476] M. E. P. Friedrich and C. S. Marvel, *J.A.C.S.* 1930, **52**, 376.
[477] W. H. Carothers and D. D. Coffman, ib. 1254.
[478] H. E. Bent, ib. 1498.
[479] H. P. A. Groll, ib. 2998.
[480] F. Hein and H. Schramm, *Z. physikal. Chem.* 1930, **151**, 234.
[481] K. Ziegler and O. Schäfer, *Ann.* 1930, **479**, 178.
[482] C. B. Wooster and F. B. Smith, *J.A.C.S.* 1931, **53**, 179.
[483] H. E. Bent, ib. 1786.
[484] J. B. Conant and G. W. Wheland, ib. 1932, **54**, 1212.
[485] A. Schleede and M. Wollmann, *Z. physikal. Chem.* 1932, B **18**, 1.
[486] N. D. Scott, J. F. Walker, and V. L. Hansley, *J.A.C.S.* 1936, **58**, 2442.
[487] N. B. Keevil and H. E. Bent, ib. 1938, **60**, 193.
[488] H. Gilman and F. W. Moore, ib. 1940, **62**, 1843.

Lithium methyl, $LiCH_3$,[433] is a white microcrystalline solid, almost insoluble in benzene or ligroin. It burns brilliantly on exposure to the air.

Lithium ethyl, LiC_2H_5, is best made by the action of the metal on mercury ethyl in benzene. It is readily soluble in benzene or ligroin especially when hot, and separates in colourless crystals which melt at 90° and distil at a higher temperature partly undecomposed.

Lithium propyl,[433] butyl, amyl, and heptyl[469] are liquids at the ordinary temperature.

Lithium ethyl[489] is a non-conductor of electricity in the fused state[467]; it is highly associated in benzene solution, the average value of the association factor being 6: this is further discussed below. The dipole moment of *n*-butyl lithium in benzene is 0·97 D, indicating that the Li—C link is essentially covalent.[490]

Lithium phenyl, LiC_6H_5. This can be made in all the usual ways, including the action of lithium on the Grignard reagent; it is most conveniently prepared[441,445] by adding phenyl bromide to lithium in ether. It is a fine, colourless powder, slightly soluble in benzene. On oxidation it is chemiluminescent, and gives a mixture of phenyl, diphenyl, and *p*-hydroxydiphenyl.[454,490]

The alkyl and aryl compounds of the other alkali metals are all colourless, solid, amorphous, non-volatile, and insoluble in all solvents other than zinc ethyl (see below, p. 73) except with decomposition.[491] Their inflammability gets less violent as the size of the alkyl group increases. Sodium methyl, ethyl, propyl, and octyl have been prepared[433]; even the octyl compound is quite insoluble in ligroin.

Sodium phenyl was the first compound of the group to be isolated, being prepared in 1903 by Acree[460-1] by the action of sodium on mercury phenyl. It is a white[433] infusible solid.

The potassium analogues of most of these compounds have been made,[447,450-1] and the rubidium and caesium ethyls[451]; they all resemble the sodium compounds very closely; they are colourless, infusible, insoluble, and non-volatile.

In their chemical reactions* the derivatives of all the five alkali metals are very similar; the reactivity (especially with halides and with nitriles) seems to be greatest with the caesium alkyls, and to fall off in the order[447]

$$Cs > Rb > K > Na > Li > MgBr.$$

On heating, all but the lithium alkyls decompose without melting;

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* A great deal of work on the formation and reactions of the alkaline alkyls and aryls has been published by Gilman *et al.*, especially in *J.A.C.S.* 1940, 1941: but it is mainly of organic interest.

[489] For its reactions see further: G. Wittig, G. Pieper, and G. Fuhrmann, *Ber.* 1940, **73**, 1193; G. Wittig and H. Witt, ib. 1941, **74**, 1474.

[490] M. T. Rogers and A. Young, *J.A.C.S.* 1946, **68**, 2748.

[491] For long-chain alkyl derivatives of Li, Na, and K, e.g. the normal dodecyl-Na, $Na.C_{12}H_{25}$, see R. N. Meals, *J. Org. Chem.* 1944, **9**, 211.

Carothers and Coffman[473,477] have shown that sodium methyl and potassium methyl break up at temperatures from 100° to 300° according to the equation

$$8\,\mathrm{MCH_3} = 6\,\mathrm{CH_4} + \mathrm{M_2C_2} + 6\,\mathrm{M},$$

while sodium ethyl decomposes into sodium hydride and ethylene, though some of the latter is reduced by the sodium hydride to ethane.

The alkaline hydrides are formed from the alkyls in other ways too; the alkyls absorb hydrogen gas, or remove hydrogen from hydrocarbons which easily lose it (such as dihydronaphthalene) with the formation of the hydrocarbon and the hydride[452]:

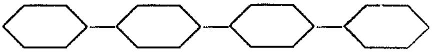
$$\mathrm{MR} + \mathrm{H_2} = \mathrm{MH} + \mathrm{HR}.$$

Again, the tendency of the metal to combine with oxygen is very strong; not only does the alkyl react with elementary oxygen with violence, but it will attack ether (even so stable an ether as diphenyl ether) thus[438]:

$$\mathrm{MR} + \mathrm{R_1OR_1} = \mathrm{MOR_1} + \mathrm{R\cdot R_1}.$$

Müller and Töpsel[492] show that lithium alkyls, like Grignard reagents, when dissolved in ether readily react with oxygen to give carbinols (probably through the peroxides: lithium phenyl reacts with a peroxide to give alcohol+$\mathrm{Li\cdot O\cdot \Phi}$). Lithium aryls with substituted aryl groups (such as tolyls) give with oxygen diaryls (as ditolyl) and much $\mathrm{Ar\cdot O\cdot Et}$, the Et being got from the solvent.

Lithium aryls do so too when the aryl groups are substituted (as with tolyls); but lithium phenyl gives 65 per cent. diphenyl, and $\mathrm{Li\cdot C_6H_4\cdot \Phi}$ gives 85 per cent. quaterphenyl,



of which this is the best method of production.

These alkyl compounds exchange their alkyls with great readiness (as when lithium ethyl and mercury methyl give lithium methyl and mercury ethyl); also one metal can expel another, as in the conversion of lithium phenyl and potassium into potassium phenyl and lithium; and the reaction of the alkali metal with a mercury alkyl is reversible so that mercury will turn the alkali metal out of its alkyl compound.

Conversely it is possible by treating an alkyl with a hydrocarbon to replace one radical by another; thus potassium or sodium ethyl (but not lithium ethyl) when boiled in benzene give some potassium or sodium phenyl.[462,450] This reaction has been called by Gilman 'metalation' of the hydrocarbon[448] on the analogy of chlorination, and has been very extensively used.

From their exceptional reactivity these compounds can be used for the alkylation of other elements where even the Grignard reagents fail. Thus thallium triethyl has been made from lithium ethyl and diethyl-thallium

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[492] E. Müller and T. Töpsel, *Ber.* 1939, **72**, 273.

chloride (Groll[479]), and platinum tetramethyl from trimethyl platinum chloride and sodium methyl (Gilman and Lichtenwalter[453]). The fact that Marvel and his collaborators have in vain endeavoured to prepare the penta-alkyl compounds of nitrogen,[469] phosphorus,[474] and arsenic[476] in this way is good evidence that these penta-alkyls cannot exist.

All these alkyls, even those that are insoluble in all other solvents, will dissolve in zinc ethyl (Wanklyn, 1858[455]) and the solution is a good conductor of electricity.[466] This is commonly taken as evidence that the alkaline alkyls are ionized compounds, but on evaporation a crystalline compound, $MZnEt_3$, is left, and this is probably a complex zinc salt, $M[ZnEt_3]$, which dissociates ionically in the zinc ethyl solution. See also Hein.[480] This is further discussed under zinc (see II. 277).

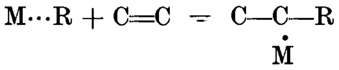
ii. *Coloured Alkaline Alkyls, Aryls, etc.*

In these compounds the carbon attached to the metallic atom is also joined to one or more aromatic nuclei, or to a system of conjugate double links. The simplest examples are the derivatives of toluene or triphenyl methane, such as $C_6H_5 \cdot CH_2K$ and $(C_6H_5)_3CNa$.

Compounds of this class can be made by any of the methods described in the last section, for example, by the action of the alkali metal on the halide, or on the mercury compound,[433] or on the Grignard reagent,[444] or on a mixed ether such as benzyl ethyl ether, which gives the reaction[436]:

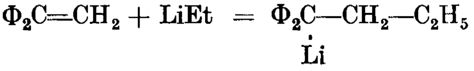
$$\Phi \cdot CH_2{-}O{-}Et + 2\,Na = \Phi \cdot CH_2Na + Na \cdot O{-}Et:$$

also by several reactions which cannot be used for preparing the simple alkyls and aryls, of which the most important are (1) the addition of an atom of the metal to the free trivalent-carbon radical, and (2) the addition of two atoms to the double C=C link in certain unsaturated or aromatic hydrocarbons. Another reaction (3) is the addition of the alkaline alkyl itself to a double link:



$$M \cdots R + C{=}C = C{-}\underset{\overset{\bullet}{M}}{C}{-}R$$

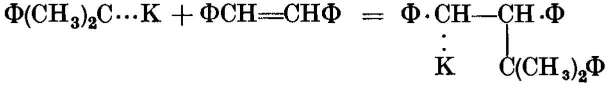
This reaction seems to occur only when at least one of the two doubly linked carbons (that to which the metal attaches itself) is linked to an aromatic ring; for example[438]:



$$\Phi_2C{=}CH_2 + LiEt = \Phi_2\underset{\overset{\bullet}{Li}}{C}{-}CH_2{-}C_2H_5$$

This reaction gives for the first time an explanation of the well-known effect of the alkali metals in causing the polymerization of unsaturated hydrocarbons. Butadiene and its derivatives, styrene, and other hydrocarbons with conjugated double links, can be converted by the catalytic influence of sodium powder into highly polymerized 'artificial rubbers'.

Ziegler and Bähr have shown[437] that 2-phenyl-isopropyl potassium will react with stilbene thus:



$$\Phi(CH_3)_2C\cdots K + \Phi CH{=}CH\Phi = \underset{\underset{\textstyle K}{\vdots}}{\Phi\cdot CH}-\underset{\underset{\textstyle C(CH_3)_2\Phi}{|}}{CH}\cdot\Phi$$

The product will obviously be able to react in the same way (as it still has the metal attached to carbon) with another molecule of stilbene, giving a substance which again has the active Φ—C···K (i.e. C=C—C···K) grouping, and so the polymerization can proceed without limit. Ziegler and Kleiner showed[439] that phenylisopropyl potassium reacts with butadiene to give unsaturated polymerization products containing up to 10 molecules of butadiene.

The intermediate formation of free radicals when, for example, triphenyl methyl chloride is treated with sodium, is shown[396] by the solution first going yellow from the production of triphenyl methyl, and then darkening with separation of the brick-red salt $\Phi_3C\cdots Na$.

Other radicals, such as biphenyl naphthyl phenyl methyl, react in the same way; the products are always deeply coloured (indigo, dark violet, reddish-yellow, etc.). Not only can hexaphenyl ethane be converted in this way into sodium triphenyl methyl, but dibenzyl $\Phi\cdot CH_2\cdot CH_2\cdot\Phi$ will react with sodium to give sodium benzyl, though dibenzyl itself shows no signs of dissociation.[436]

Reaction (2), the addition of alkali metal to a double C=C link, which produces dialkaline compounds, is considered later (p. 76).

Of the mono-alkaline compounds the best known are the benzyl and triphenyl methyl derivatives.

Lithium benzyl, $C_6H_5\cdot CH_2Li$, cannot be made directly from lithium and benzyl chloride, since it reacts with the unchanged benzyl chloride to give lithium chloride and dibenzyl; it can be made from lithium phenyl and mercury dibenzyl,[467] or from benzyl magnesium bromide and lithium phenyl.[444] It differs in some ways from the other benzyls; it is bright yellow[467] whereas the sodium compound is deep red, and it also differs from the latter in not attacking ether.[481]

Sodium benzyl[433] forms garnet-red crystals, which are insoluble in benzene or ligroin, but in ether give a dark yellow-red conducting[433] solution very like that of sodium triphenyl methyl, which soon loses its colour owing to the reaction

$$\Phi\cdot CH_2\cdots Na + Et{-}O{-}Et = \Phi\cdot CH_2\cdot Et + NaOEt.$$

A similar compound of phenyl isopropyl $\Phi(CH_3)_2C\cdot K$ is known[439,448]; it also is dark red.

The most fully investigated series is that of the triphenyl methyl compounds.*

---

* v. Grosse has pointed out[471] that there is a curiously close correspondence in colour solubility and solvation between this $MC\Phi_3$ series and the series of boron compounds $MB\Phi_3$ (both of which are known for all the alkali metals from lithium to caesium) obtained by Krause[469] and Polack.[470] See further under Boron, III. 378.

Lithium triphenyl methyl $LiC\Phi_3$[471] forms an etherate $LiC\Phi_3, 2\,Et_2O$ in bright orange-red crystals. At 90° *in vacuo* this loses its ether and is converted into a pale yellow powder of $LiC\Phi_3$; the ethereal solution is also yellow, and much paler than those of the other alkaline triphenyl methyls (a similar difference of colour was noticed in the benzyls).

Sodium triphenyl methyl $NaC\Phi_3$[430] is best made by the action of sodium on triphenyl methyl chloride; it forms no etherate. It consists of red crystals which dissolve in ether to give a red conducting solution. Careful measurements of the conductivity in ether of derivatives of sodium triphenyl methyl, such as phenyl diphenyl naphthyl methyl sodium, indicate[487] that the dissociation constants in this solvent are very small, of the order of 10^{-12}.

The potassium, rubidium, and caesium compounds were prepared by v. Grosse[471]; they are all blood-red powders, which are very slightly soluble in ether; they form no etherates.

Apart from the characteristic colour, and the solubility and conductivity in ether, these compounds behave very much like the simple alkaline alkyls. They are[430] spontaneously inflammable in air, and at once decomposed by water to the hydrocarbon and the alkaline hydroxide; methyl iodide converts triphenyl methyl sodium into triphenyl ethane $\Phi_3C{-}CH_3$ and sodium iodide. On slow oxidation they first yield the free radical (as Φ_3C) and sodium peroxide Na_2O_2, and then on further treatment the organic peroxide

$$\Phi_3C{-}O{-}O{-}C\Phi_3.$$

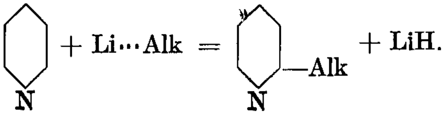
Their reactivity is so high that acetone and ethyl acetate react with them as pure enols,[432] for example,

$$CH_3\cdot CO\cdot CH_3 + Na\cdots C\Phi_3 = CH_2{=}C(ONa)CH_3 + \Phi_3CH.$$

They are much more reactive than the Grignard reagents, which will not do this.[432]

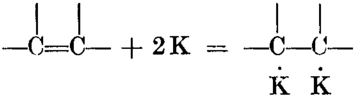
The alkaline triphenyl methyls absorb carbon dioxide to form the triphenyl acetate, and sulphur dioxide in a similar way to form the sulphinate $\Phi_3C\cdot SO_2Na$. It is curious that they will not react with carbon monoxide at all.

Ziegler has shown[441] that triphenyl methyl sodium dissolves in pyridine to give a solution of high conductivity, which, however, soon loses its colour. The reaction is obscure, but with a simple lithium alkyl the same loss of colour occurs, and it can there be shown that this is due to the replacement of the α-hydrogen of the pyridine not by the lithium but by its alkyl group[440,443]:

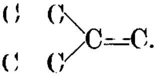


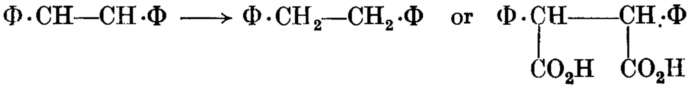
Di-metallic compounds

These are formed by the direct addition of sodium or potassium to a double carbon link[429,435]:



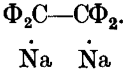
$$—\overset{|}{C}=\overset{|}{C}— + 2K = —\underset{\dot{K}}{\overset{|}{C}}—\underset{\dot{K}}{\overset{|}{C}}—$$

(This reaction does not occur, or hardly ever, with the Grignard reagent.[449]) With the alkali metals the addition occurs only when the C=C group has an aryl group attached to it, or at least two conjugated double links as in . For example, if stilbene[429] is dissolved in ether and left for days in contact with sodium in a sealed tube from which all air has been expelled, a dark brown-violet powder separates, which must be the di-sodium derivative, since it is converted by water into symmetrical diphenyl ethane, and by carbon dioxide into the salt of *s*-diphenyl succinic acid:



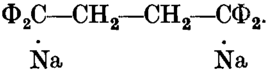
$$\Phi\cdot CH—CH\cdot\Phi \longrightarrow \Phi\cdot CH_2—CH_2\cdot\Phi \quad \text{or} \quad \Phi\cdot\underset{CO_2H}{CH}——\underset{CO_2H}{CH}\cdot\Phi$$

In the same way tetraphenyl ethylene $\Phi_2C=C\Phi_2$ gives the dark red



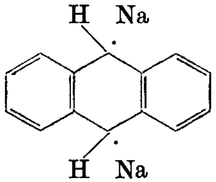
$$\Phi_2\underset{\dot{Na}}{C}—\underset{\dot{Na}}{C}\Phi_2.$$

If only one of the doubly linked carbons is conjugated with double links, this alone as a rule takes up the alkali metal, while the other saturates itself by polymerization: thus unsymmetrical diphenylethylene gives the symmetrical tetraphenyl butane derivative



$$\Phi_2\underset{\dot{Na}}{C}—CH_2—CH_2—\underset{\dot{Na}}{C}\Phi_2.$$

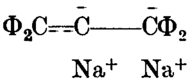
Anthracene itself is converted with great readiness into the di-sodium compound



a dark blue solid only slightly soluble in ether, but giving a violet solution in it. Recently it has been shown[486] that this addition of sodium to aromatic hydrocarbons goes much more readily in dimethyl ether at − 30°, or in glycol dimethyl ether at the ordinary temperature. In these solvents diphenyl and naphthalene and its homologues readily add on two atoms of sodium; the action of the solvent is obscure: if the naphthalene compound is formed in dimethyl ether, and ordinary diethyl ether added, the compound dissociates again into naphthalene and sodium.

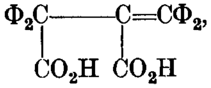
These dimetallic compounds have much the same properties as the monometallic derivatives; they are strongly coloured: the naphthalene compound is dark green and its ethereal solution is a good conductor. They are all spontaneously inflammable, and have two main reactions: (1) when treated with mercury, oxygen (slowly), or benzyl chloride they reform the original hydrocarbon; (2) with water, alcohol, or any organic compound that evolves hydrogen with sodium—even with acetylene—they are converted into the dihydro-derivatives. In solution in liquid ammonia naphthalene will even take up 4 atoms of sodium,[482] which must all be attached as H—C···Na groups to one ring, since the compound on treatment with water gives 1, 2, 3, 4-tetrahydronaphthalene (tetraline).

An interesting compound was obtained by Schlenk and Bergmann[478] from tetraphenyl allene $\Phi_2C{=}C{=}C\Phi_2$. This takes up 2 atoms of sodium to give a product which should probably be written (since its colour indicates ionization)



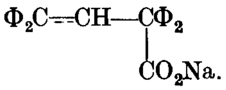
$$\Phi_2C{=}\underset{Na^+}{\overset{-}{C}}{-\!-\!-}\underset{Na^+}{\overset{-}{C}}\Phi_2$$

in which each carbon atom has a complete octet. This with alcohol is converted into diphenylmethyl-diphenyl ethylene $\Phi_2CH{-}CH{=}C\Phi_2$, and with carbon dioxide gives a dicarboxylate, presumably



$$\underset{CO_2H}{\Phi_2\overset{}{C}}{-\!-\!-}\underset{CO_2H}{C}{=}C\Phi_2,$$

which loses carbon dioxide to give the salt of tetraphenyl-vinyl-acetic acid

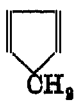


$$\Phi_2C{=}CH{-}\underset{CO_2Na.}{C}\Phi_2$$

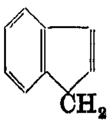
Other similar compounds have been obtained.[475]

III. *Cyclopentadiene Derivatives*

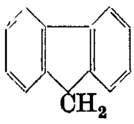
A remarkable series of hydrocarbons which give relatively stable alkaline compounds consist of cyclopentadiene and its mono- and dibenzo-derivatives indene and fluorene:



Cyclopentadiene



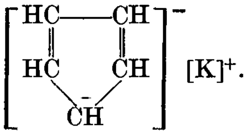
Indene



Fluorene

In all these substances the CH_2 group of the 5-ring is extremely reactive, and one of its hydrogen atoms can be replaced by an alkali metal.

Thiele[457] showed that if cyclopentadiene is dissolved in benzene and treated with potassium powder (but not with sodium) it evolves hydrogen even in the cold. Yellowish flocks separate which after drying form a yellowish powder which catches fire in air in a few minutes; it was not analysed, but its ready reactions with water (regenerating the hydrocarbon), with halides, and with carbon dioxide (this last causing polymerization and giving a dicarboxylic acid of dicyclopentadiene) are enough to show that it is the expected compound



The behaviour in this reaction of indene[464-5] and of fluorene[458,463] was examined by Weissgerber. The readiness with which fluorene reacts is remarkable; if it is heated with solid potassium hydroxide to 260-280° water is evolved and the compound $C_{13}H_9K$ formed (none of the hydrocarbons hitherto mentioned is able to react with alkaline hydroxide). Sodium reacts at a lower temperature (200°) and sodamide $NaNH_2$ at 120°. Indene reacts with sodamide in the same way as fluorene, at 110°.

The indene derivative is a dark mass which when pure seems to be transparent and ruby-red; none of these three compounds could be made to dissolve, and so it was not possible to purify any of them. In the air the indene derivative oxidizes fairly rapidly, the surface darkening; but it does not catch fire.

Sodium fluorenyl is a brownish-yellow mass which readily gives the usual reactions with water, carbon dioxide, and alkyl halides. Nothing is said of its oxidation.

It will be seen that these three compounds are much more stable, especially to oxidation, than those which preceded them, and that this stability is greater the more rings the molecule contains. In the fluorene derivative we have an alkaline compound which is formed from the hydroxide like a salt, and does not appear to be oxidized by air at all readily.

IV. *Acetylene Derivatives*

These constitute the last term in the series, as being formed from the most acidic of all hydrocarbons. Alkaline derivatives are formed by acetylene and by a variety of mono-substituted acetylenes $R—C{\equiv}C—H$ which still have a hydrogen attached to a triply linked carbon.

The acetylides MC_2H and M_2C_2 are the only definite carbides (in the usual sense of the term) of the alkali metals that are known. They can be made by the action of acetylene on the heated metal or on its solution in liquid ammonia; this latter reaction commonly produces in the first instance the hydrogen compound MC_2H, which can then be converted into the binary compound M_2C_2 and acetylene by heating to 200° or so. Both types, MC_2H and M_2C_2, have been prepared with all the five alkali metals, largely by Moissan.

These acetylides are colourless crystalline substances, which are violently decomposed by water to the alkaline hydroxide and acetylene, are stable to air when cold, though they are oxidized by it with great readiness if they are warmed,[459] and react with alkyl halides to give homologues of acetylene. Though their crystal structure has not yet been examined, there can be no doubt that they are salts, like calcium carbide and the acetylides of the alkaline earths generally, which have been shown by X-ray analysis to be the salts of the anion $[C{\equiv}C]^{--}$.

With lithium and sodium[468] the acetylides can be made by heating the elements together, but with the heavier alkali metals this does not occur; instead of acetylides, rather indefinite solid solutions of the metal in carbon are formed, in which the metallic atoms are interposed between the layers of the graphite lattice.[472,485]

Mono-alkyl acetylenes produce similar alkaline derivatives, such as $CH_3{-}C{\equiv}C[Na]$.

The alkaline salts of phenyl acetylene have been examined in some detail. The sodium salt $\Phi \cdot C{\equiv}C[Na]$ was first made by Glaser in 1870, and his work was repeated by Nef in 1899.[456] If phenyl acetylene is dissolved in ether and treated with sodium wire, hydrogen is rapidly evolved and the salt is deposited as a white very hygroscopic powder. If exposed to the air when moist with ether it catches fire.

The other alkaline salts of phenyl acetylene have been made by Gilman and Young.[451] The potassium, rubidium, and caesium salts can be made like the sodium salt by the action of the metal on the hydrocarbon. The lithium salt cannot be made in this way (metallic lithium is of course the least reactive of the alkali metals), but it can be prepared by the action of lithium butyl on phenyl acetylene. The colours of these salts are[451]:

Li	Na	K	Rb	Cs
Colourless	Colourless	Light tan	Dark tan	Dark tan

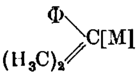
The reactivity is greater the heavier the alkali metal: the times for reaction under the same conditions with benzonitrile are

	MgBr	Li	Na	K	Rb	Cs
Hours	86	60	6·8	5·0	4·7	3·8

An interesting study of the acidities of these hydrocarbons by means of the behaviour of their alkaline salts has been made by Conant and Wheland.[484] The acidities are of course far too small to be determined by the usual methods; but the hydrocarbons and their alkaline salts are soluble in ether, and if we may assume that the degree of ionization of the salts is the same independent of the strengths of the acids from which they are derived,* then the acid which displaces another from its salt in solution must be the stronger. The extent of the displacement can sometimes be measured by means of the colour: where this was not possible the solution was treated with carbon dioxide and the acids produced were determined. In this way Conant and Wheland have been able to arrange in the order of their relative strengths a large number of hydrocarbons of the kind whose alkaline salts we have been discussing, beginning with phenyl isopropane (2-phenyl propane $CH_3—CH\Phi—CH_3$) as the weakest (though no doubt it is much stronger than the paraffins themselves) and ending with indene, phenyl acetylene, and (for comparison) acetophenone, which with its enol form is almost as acidic as alcohol. The displacement experiments were (with one unexplained exception) self-consistent, the sodium and potassium salts giving the same results. If we wished to express the results in terms of the dissociation constants we should start with pK = *ca.* 20 for acetophenone (K for alcohol is 7×10^{-20}), and the rest would all have higher pK values; but though their order is determined we have no real means of finding the magnitude of the steps.

In the table which follows, the acids are given in the order of their strengths, beginning with the weakest; the colour of the solution (which usually differs but little from that of the solid salt) is stated under each:

1



$\Phi(H_3C)_2C[M]$

Red

2

$\Phi_2C=CH—CH_2[M]$

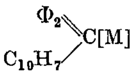
Red-brown

3

$\Phi_2CH[M]$

Orange

4



$\Phi_2(C_{10}H_7)C[M]$

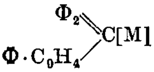
Green

5

$\Phi_3C[M]$

Orange-red

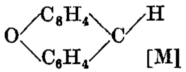
6



$\Phi_2(\Phi\cdot C_6H_4)C[M]$

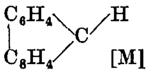
Purple

7



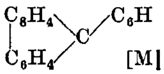
Orange-red

8



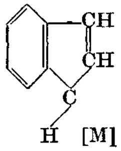
(Fluorene)
Yellow

9



(Phenyl fluorene)
Orange

10



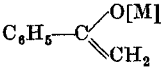
(Indene)
Light yellow

11

$C_6H_5\cdot C\equiv C[M]$

(Phenyl acetylene)
Colourless

12



$C_6H_5—C(O[M])=CH_2$

(Acetophenone)
Colourless

It will be seen that the order arrived at by Conant and Wheland agrees essentially with that indicated by the general behaviour of these compounds; that the acidity increases with the number of aromatic groups

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* There is reason to think that this is approximately true. It is of course true of the salts of all acids strong enough to be measured electrochemically; ammonium acetate in solution, so far as it is not hydrolysed, is as much ionized as potassium chloride; and among the salts of the triaryl methyls we have evidence of the same thing[475,485]; the sodium salts of triphenyl methane and of tri-*p*-nitrotriphenyl methane have the same conductivity though the strengths of the acids are very different.

attached to the acidic carbon atom; that it is especially marked with the derivatives of cyclopentadiene (indene and fluorene); and that it reaches a climax in the acetylenes, which are practically as highly ionized as hydroxyl compounds.

Structures of the Alkaline-Carbon Compounds

So far we have considered the facts, and said little about their causes. It is clear that the alkaline derivatives of acetylene and its mono-substitution products are fully ionized salts and that they are colourless, so that the presence of a negative 'Carbonium' ion $[-\overset{|}{\underset{|}{\mathrm{C}}}\ ]^-$ (valency group 2, $\underline{6}$) does not involve colour. Colourless alkaline derivatives appear also at the other end of the series, where ionization is least to be expected, in the simple alkyl and aryl compounds such as $NaCH_3$ and KC_6H_5; but the intermediate compounds, derived from hydrocarbons whose acidity is minute but not zero, are intensely coloured. The evidence both of the character of the parent hydrocarbons, and of the behaviour of the alkaline derivatives, which give conducting solutions in ether, supports the view that these coloured compounds are ionized, and to a fairly high degree; while the simple alkyl derivatives, which are non-conductors and contain hydrocarbon radicals which we know to be very reluctant to form anions, must be taken to be covalent compounds.

This view is strongly supported by the behaviour of the so-called 'penta-alkyl' compounds of nitrogen, which were discovered by Schlenk.[431,434] These are highly coloured, and closely resemble the coloured alkaline hydrocarbon derivatives; they all contain, in addition to the usual four simple alkyl groups, one hydrocarbon radical of the kind that can form a coloured conducting alkaline derivative, such as benzyl or triphenyl methyl: with these nitrogen compounds we have a further reason for thinking that the compound must be ionized, in that the covalency maximum of 4 for nitrogen makes a fifth covalency impossible. All efforts to obtain a 'penta-alkyl' nitrogen in which all five groups are of the simple alkyl type—i.e. of the kind which are found in the colourless sodium alkyls—have failed,[469] the products breaking up into a tertiary amine and a mixture of hydrocarbons: thus from tetraethyl ammonium iodide and lithium ethyl we get triethyl amine, ethane, and ethylene. The reason obviously is that a group like benzyl or triphenyl methyl can occur in the ionized form while methyl or phenyl cannot.

We may therefore conclude that the three classes of alkaline hydrocarbon derivatives are constituted thus:

I. Colourless compounds like sodium methyl: covalent, but highly associated.

II. Coloured compounds like sodium triphenyl methyl: ionized.

III. Colourless compounds like sodium phenylacetylene, or sodium carbide: ionized.

This leaves the following questions to be considered:

1. The cause of colour in Class II.
2. The difference in Class I compounds between the lithium compounds (soluble, fusible, volatile) and those of the other metals.
3. The cyclopentadiene derivatives.

[The cause of the acidity of the acetylenes is discussed under Carbon (IV. 508)].

1. *Colour of Class II Compounds*

The only possibilities for the link between the alkali metal and carbon would seem to be that it should be (1) ionized, or (2) covalent, or (3) a resonance hybrid between the two. The ionized $[M]\overset{|}{\underset{|}{C}}—$ link, as in the acetylene salts, is colourless; the covalent link is colourless in the simple alkyls, and in any case there is no reason why this covalent link should be coloured, any more than the links in the colourless beryllium dimethyl. Further, we have no evidence that when a link shows resonance between the covalent and the electrovalent form this of itself will cause colour: such resonance occurs in a high degree in hydrogen fluoride, which is not coloured. Evidently we must look for the cause of the colour elsewhere than in the link itself: it must be due to the conditions in the hydrocarbon radical which make the ionization possible. These consist in the presence of aromatic nuclei or conjugated double links: in fact it is obvious that the same peculiarities of structure favour both the formation of coloured alkaline salts and that of free radicals, though the latter are less easily produced. The essential point is that the structures should be able to assume a variety of resonance forms; in triphenyl methyl, for instance, owing to the presence of the adjacent aromatic structures the unsaturation (to put it crudely) may be on any one of the nineteen carbon atoms, and this high degree of resonance greatly increases the stability. A corresponding number of resonance forms must be available for the anion $[\Phi_3C]^-$ and its derivatives, and the same must be true for all the radicals occurring in the coloured alkaline salts (the case of the acetylene derivatives, which are colourless, is different, and is discussed below). It must then be the resonance which gives rise to the colour, and that is to be expected. A wide experience shows that when resonance affords several possible positions for an electric charge, colour is produced (as in the triphenyl methane dyes, or in ozone), and such possibilities are afforded here.* On the other hand, the resonance between C—M and C[M] does not involve any such shift of the charge, and so should not cause the production of colour.

2. *Difference in Class I between the Lithium Alkyls and the Rest*

This difference, which has already been pointed out, is considerable. The lithium alkyls, except lithium methyl, are either low-melting solids

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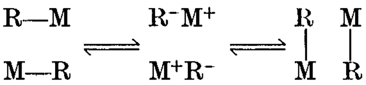
* See further under Carbon: free radicals (IV. 532).

or liquids, are readily soluble in benzene and in ligroin (being associated and non-conducting in the solution), and the ethyl compound at least can be distilled with only partial decomposition. The alkyl compounds of the other alkali metals are all solids which on heating decompose without melting; they are quite insoluble, even sodium octyl, in any solvent except zinc ethyl, with which they react. On the other hand, they agree with the lithium alkyls in being colourless, and agree also in their reactions, though the lithium compounds are on the whole less reactive. If the whole series are to be regarded as covalent compounds it would seem as if a reason ought to be given for these differences.

Now it is clear that the differences are what we should expect if the alkyls of the metals from sodium to caesium are more highly associated than those of lithium, and that such a difference in the degree of association would be sufficient to account for them; only in that case we ought to be able to explain why the association is so much less with lithium. Here, however, we come up against the fundamental difficulty that it is not possible at present to explain why metallic alkyls are associated at all. Lithium ethyl, as we have seen, is some 6 times associated in benzene solution. The alkyls of the other alkali metals are presumably more highly associated still. Nor is the phenomenon confined to these elements. All the alkyl derivatives of the elements of the first three periodic groups except those of boron, zinc, cadmium, and mercury (more than twelve elements in all) can be shown to be associated in the fused state or in solution. Now in all these metallic alkyls there are no unshared valency electrons, so that an attachment by co-ordination is impossible, and there is no other obvious method. The problem is at present unsolved, and as long as we do not know why any of these compounds are associated it is useless to ask why some are more associated than others. The cause of the association may possibly be a high dipole moment of the M—C link (dipole association), or some resonance scheme, for example:



$$\begin{matrix}R\text{—}M\\ M\text{—}R\end{matrix} \rightleftharpoons \begin{matrix}R^-M^+\\ M^+R^-\end{matrix} \rightleftharpoons \begin{matrix}R & M\\ | & |\\ M & R\end{matrix}$$

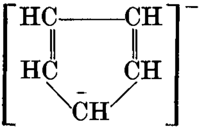
A difficulty here is the interatomic distances. The ions of the alkali metals are much smaller than the covalent atoms, the differences being

Li 0·55 Na 0·59 K 0·70 Rb 0·67 Cs 0·70 A.

Hence in passing from the covalent to the electrovalent state the metallic atom contracts by nearly one A.U., and it seems improbable that the carbon atom can expand by as much as this in acquiring a single negative charge, though the hydrogen atom does so in forming the hydrogen bond.

[illegible]. *The Cyclopentadiene Derivatives*

These hydrocarbons (cyclopentadiene, indene, and fluorene), though they belong to the general class of 'active methylene' compounds, are exceptionally high in the acidic series, and evidently have an arrangement of double links which makes the negative ion peculiarly stable. We can see why this is so; in the cyclopentadienyl ion we have a structure not



unlike the neutral benzene molecule: a perfectly symmetrical molecule with five similarly placed CH groups, and at the same time six more valency electrons than are required to maintain single links in the molecule—the 'aromatic sextet' which is found not only in the true aromatic hydrocarbons but also in such semi-aromatic substances as pyridine and pyrrol. If the arrangement of these electrons gives any one carbon atom a unique position, as in the ordinary symbol above, there must clearly be a complete resonance between five different but equivalent forms.

The increase of stability caused by attaching to the 5-ring one or two benzene rings (in indene and fluorene and their homologues) is to be expected, as further possibilities of resonance are thereby created.

NITROGEN COMPOUNDS

The alkali metals form two kinds of binary compounds with nitrogen; the salts of hydroazoic acid N_3H, which are definite salts, and the true nitrides M_3N; these are substitution products of ammonia, and along with them we have to consider the products in which the hydrogen is only partially replaced, the imides M_2NH and the amides MNH_2; finally there are what may be called the substitution products of ammonium, the 'alkali ammonias' MNH_3.

Nitrides, M_3N

The relative stabilities of these are remarkable; the lithium compound is formed from its elements even at the ordinary temperature, and rapidly above the melting-point, while none of the other metals will take up nitrogen at any temperature or pressure, even in the presence of an active catalyst such as iron.[493] None of these nitrides except the lithium compound has been obtained in the pure state.

Lithium nitride Li_3N, which is made from its elements in this way, is described as a black hygroscopic mass, which when it is heated is converted into a crystalline form containing some ruby-red crystals: these are presumably the pure nitride, the remainder being contaminated mainly with iron.[495-7] The crystal structure has been examined by Juza and

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[493] E. W. Guernsey and M. S. Sherman, *J.A.C.S.* 1925, **47**, 1933.

[494] See Wells, p. 425.

[495] L. Ouvrard, *C.R.* 1892, **114**, 120.

[496] A. Guntz, ib. 1896, **123**, 995.

[497] F. W. Dafert and R. Miklaus, *Mon.* 1910, **31**, 797.

Hahn[494] who find that each N has 2 Li at 1·94 A, and 6 more at 2·11; this seems to suggest the structure Li[Li—N—Li]; in any case the compound is presumably ionized in some way. It is not attacked by dry air in the cold, but is decomposed at once by water to the hydroxide and ammonia, and is readily oxidized by air on warming.

The other alkaline nitrides can be made by the action of an electric discharge on the metal in nitrogen, or by the partial dissociation of the azide. Fischer and Schröter[498] found that if an electric discharge is passed between electrodes of sodium, potassium, or rubidium in a liquid mixture of 10 per cent. nitrogen and 90 per cent. argon, a dark mixture of the nitride and the metal is produced, from which the nitride cannot be isolated; but it readily loses nitrogen on warming (sodium nitride even explosively) and gives ammonia with water. Suhrmann and Clusius[499] showed that if an alkaline azide is heated *in vacuo* a certain amount (20 per cent. with potassium azide, 40 per cent. with rubidium azide, 10 per cent. with caesium azide) remains behind as the nitride. It is remarkable that if the excess of rubidium is distilled away from its nitride, the residue is colourless and very stable to heat. (On colour see below.)

Both these methods of preparation have been repeated and extended by Wattenberg.[500] He showed that the action of active nitrogen (or nitrogen in presence of an electric discharge) on a sodium film is to give first the nitride and then on further action the azide; with potassium and rubidium at the ordinary temperature the stability of the nitride is so small as compared with that of the azide that only the latter is formed; but at 200° or in presence of potassium vapour the nitride can be obtained. The preparation of the nitride by decomposition of the azide is much improved if an intimate mixture of the azide with the metal (got by the evaporation of a solution of the metal and the azide in liquid ammonia) is used; the metal catalytically lowers the decomposition temperature of the azide. This is the best way of getting sodium nitride. Potassium azide behaves in the same way, but the temperature of decomposition is nearer to the explosion temperature of the azide.

Sodium nitride obtained in this way will not dissolve in any solvent without decomposition, and is too unstable to heat to be purified by sublimation; hence it is contaminated by azide and free metal, which cannot be removed. It is a crystalline substance, which undergoes a remarkable change of colour with temperature:

Temperature . . .	−180°	+20°	+100°	+300°
Colour . . .	Orange	Cinnabar	Dark red	Black

Sodium nitride begins to lose nitrogen at 150°, and at 350° the dissociation is complete in a few minutes. Its chemical behaviour is very like that

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[498] F. Fischer and F. Schröter, *Ber.* 1910, **43**, 1465.

[499] R. Suhrmann and K. Clusius, *Z. anorg. Chem.* 1926, **152**, 52.

[500] H. Wattenberg, *Ber.* 1930, **63**, 1667.

of metallic sodium. It is very sensitive to moisture, which at once turns it white with liberation of ammonia; with alcohol it behaves in the same way. Hydrogen gas reduces it at 120° to the hydride and ammonia. Dry oxygen gas has no action on it in the cold, but it burns in oxygen on warming.

These alkaline nitrides are of peculiar interest as being probably among the few salts of the trivalent nitrogen anion N^{---}. But their colour suggests that they are not fully ionized.

Imides, Amides, and Ammonia Compounds

Imides M_2NH

Only one of these is known, lithium imide Li_2NH (another sign of the abnormally strong affinity of lithium for nitrogen); it is made by heating the amide $LiNH_2$ *in vacuo* almost to its melting-point (374°), and finally to 450°.[509] It is a colourless crystalline very reactive substance; it is insoluble in indifferent organic solvents, and does not melt below 600°, where it begins to decompose.

Amides MNH_2

Amides MNH_2 are formed by the action of ammonia on all the alkali metals, and the more easily, the heavier the metal; with liquid ammonia the times of reaction of the metals under comparable conditions were found to be[523]: caesium 15 min.; rubidium 30 min.; potassium 60 min.; sodium and lithium several days They are white crystalline substances, insoluble in the ordinary organic solvents, but at once decomposed by

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[501] E. C. Franklin and C. A. Kraus, *Amer. Chem. J.* 1900, **23**, 306.

[502] O. Ruff, *Ber.* 1901, **34**, 2604.

[503] O. Ruff and E. Geisel, ib. 1906, **39**, 828.

[504] A. Joannis, *Ann. Chim. Phys.* 1906, [8] **7**, 41.

[505] C. A. Kraus, *J.A.C.S.* 1907, **29**, 1557.

[506] O. Ruff and J. Zedner, *Ber.* 1908, **41**, 1948.

[507] C. A. Kraus, *J.A.C.S.* 1908, **30**, 1197.

[508] Id., ib. 1323.

[509] O. Ruff and H. Goerges, *Ber.* 1911, **44**, 502.

[510] C. A. Kraus, *J.A.C.S.* 1914, **36**, 864.

[511] B. Emmert, *Ber.* 1914, **47**, 2598.

[512] G. E. Gibson and W. L. Argo, *J.A.C.S.* 1918, **40**, 1327.

[513] L. Wöhler and F. Stang-Lund, *Z. Elektrochem.* 1918, **24**, 261.

[514] C. A. Kraus, *J.A.C.S.* 1921, **43**, 749.

[515] J. M. McGee, ib. 1921, **43**, 586.

[516] F. Benoit, *Bull. Soc. Chim.* 1923 [iv], **33**, 908.

[517] C. A. Kraus and W. W. Lucasse, *J.A.C.S.* 1923, **45**, 2551.

[518] E. Weitz and W. Vollmer, *Ber.* 1924, **57**, 1015.

[519] N. W. Taylor and G. N. Lewis, *Proc. Nat. Acad. Wash.* 1925, **11**, 456; N. W. Taylor, *J.A.C.S.* 1926, **48**, 854.

[520] C. A. Kraus and W. C. Johnson, ib. 1925, **47**, 725.

[521] G. E. Gibson and T. E. Phipps, ib. 1926, **48**, 312.

[522] C. A. Kraus, E. S. Carney, and W. C. Johnson, ib. 1927, **49**, 2206.

[523] R. Juza, *Z. anorg. Chem.* 1937, **231**, 121.

water, the caesium compound catching fire in the process. They have rather high melting-points:

	$LiNH_2$	$NaNH_2$	KNH_2	$RbNH_2$	$CsNH_2$
M.pt.	374°	208°	338°	309°	261°

and at higher temperatures can usually be sublimed or distilled with some decomposition. It is quite clear that they are ionized (and are among the few salts of the NH_2' ion); the conductivities in the fused state are[513] $NaNH_2$ 0·593 at 215°; KNH_2 0·389 at 340°. McGee[515] gives rather higher values.

Alkali-ammonias, -amines, and -ammoniums

It has long been known that the alkali metals have a singular power of dissolving in liquid ammonia to give a blue solution. On evaporation of the ammonia a copper-coloured solid separates, which loses ammonia continuously until the metal is left behind, usually in a crystalline condition.[502] The more recent experimental work on this subject is that of Ruff and especially of Kraus.

The nature of the process is not yet clear. Earlier workers claimed to have isolated definite solid compounds,[504,516] but this has not been confirmed. Ruff[503,506] showed that if the red solid is pressed with a cooled glass rod, a blue liquid can be squeezed out of it; he considered that it is a spongy mass of finely divided metal with absorbed liquid. The observation of Joannis[504] that the dissociation tension of the solid is the same as that of the liquid, if it is correct, certainly supports this view.

As regards the liquid, all the five alkali metals can dissolve in liquid ammonia. The solubilities at 0° of the first three of them were found by Ruff and Geisel[503] to be:

	Li	Na	K
Ats. M to 100 mols. NH_3 . . .	25·4	17·0	21·1
g. M to 100 g. NH_3	9·41	18·7	32·7

Kraus[507] found from the vapour pressures that the molecular weight of the sodium in ammonia was not more than 23. The observation of Taylor and Lewis[519] that sodium in ammonia solution is paramagnetic strongly supports this. The solution is a good conductor of electricity, and perhaps contains solvated sodium ions $[Na(NH_3)_n]^+$; the difficulty is to see what the anions can be. The transport and conductivity measurements of Kraus[501,508,510,514,517,522] indicate that in concentrated solution the mobility of the anion is enormously greater than that of the cation (up to 280 times as great[510]), from which he concludes that the anion is a more or less solvated electron, which must be supposed to have a kind of Grotthus conductivity (like the hydrogen ion in water).

These conclusions are in agreement with the spectroscopic results of Gibson and Argo.[518] They showed that solutions of lithium, sodium, and potassium gave identical absorption spectra in liquid ammonia, the absorption being proportional to the concentration (Beer's law); in liquid methylamine the absorptions were different and no longer proportional to the concentration. They assume that the absorption is that of the negative ions $[e(NH_3)_n]^-$ (e = electron), and that these are wholly dissociated, but that the corresponding methylamine ions are only partially so. In a later paper[521] Gibson and Phipps obtained conductivity measurements which entirely supported these conclusions.

The behaviour of these solutions has been discussed from the theoretical side by L. Farkas,[524] and his conclusions though physically more precise are on the whole in accord with what has been said above. The work of Kraus and of Gibson[520] shows that the equivalent conductivity of a solution of sodium in ammonia falls as the concentration rises from low values to about decinormal; then with a further increase of concentration the conductivity rises, reaching abnormally high values, and finally when saturation is reached (at about 8 times normal) attaining a value comparable (in specific conductivity) with that of metallic mercury; at the same time the contribution made by the sodium ions to the carriage of the current diminishes rapidly and becomes insignificant.

The supposed equilibrium between electrons, neutral NH_3 molecules, and NH_3 anions will not account for the magnitude of the rise in conductivity. Farkas gives a quantum-mechanical discussion of the problem, and gets a fair agreement with observation on the assumption that the conductivity is the result of quantum-mechanical transitions of electrons between the sodium atoms in the solution. This really makes the general mechanism of the conductivity very like that of a metal.[526]

The sodium solution gives a eutectic at 13 per cent. sodium, m.pt. −110°. The solid has been said to be superconducting at −200°, but this has not been confirmed.[526a]

This power which the alkali metals have of combining in some sense with bases is not limited to ammonia. Primary alkylamines will behave in the same way,[505] although the power falls off rapidly with an increase in the size of the alkyl and in the atomic weight of the metal; thus lithium will not dissolve in propylamine nor sodium in ethylamine; and secondary and tertiary bases have no solvent power. Further, as we have seen, the electrolytic dissociation of the product appears to be more complete with ammonia than with methylamine.

It has also been known since 1870 that sodium acts on pyridine, α-picoline, and quinoline to give dark masses from which various decomposition products have been isolated, including α-, α′-dipyridyl. The nature of the primary product in this reaction was made known by the investiga-

[524] *Z. physikal. Chem.* 1932, **161**, 355.

[525] See summaries in C. A. Kraus, *Properties of Electrically Conducting Systems*, New York, 1922; W. C. Johnson and A. W. Meyer, *Chem. Reviews*, 1931, **8**, 273.

[526] See further: S. Freed and N. Sugarman, *J. Chem. Phys.* 1943, **11**, 354.

[526a] A. J. Birch and D. K. C. MacDonald, *Trans. Far. Soc.* 1947, **43**, 792.

tions of Emmert.[511] He showed that sodium dissolves in pure pyridine in an atmosphere of nitrogen to give a solution which is at first red, and as it becomes stronger goes dark green and finally black: no hydrogen is evolved. If two molecules of pyridine are used to one atom of sodium, the product is dry: if excess of either component beyond this is taken, either liquid or metallic sodium is left over. The product is extremely reactive; it catches fire at once in air.

If a large excess of pyridine is used, and the excess carefully distilled off, the product has the composition $Na(C_5H_5N)_2$: it is dark green, and in air at low pressure it forms sodium peroxide Na_2O_2. α-Picoline behaves in the same way: the product has the composition $Na(picoline)_2$, and is dark blue and spontaneously inflammable. The pyridine compound (like the solution of sodium in liquid ammonia) reacts with nitric oxide to give the hyponitrite $Na_2N_2O_2$.[518]

Zintl and his collaborators[527] have made use of these ammonia solutions for the examination of intermetallic compounds. For example, lead, which is quite insoluble in ammonia, will dissolve in the sodium solution to give green solutions, from which on evaporation the compounds Na_2Pb or $NaPb_2$ can be obtained.

OXIDES

The alkali metals can form oxides of four types of the compositions M_2O, M_2O_2, M_2O_3, and M_2O_4; the existence of suboxides M_4O has not been confirmed. The affinity for oxygen, and especially the tendency to form the higher oxides and their stability when formed, increase markedly with the atomic weight of the metal, as the following list of the oxides formed by each element shows.

	M_2O	M_2O_2	M_2O_3	M_2O_4
Li . .	+	+	0	0
Na . .	+	+	0	0
K . .	+	+	?	+
Rb . .	+	+	+	+
Cs . .	+	+	+	+

In the same way the highest oxides that can be formed by heating the metal in oxygen are Li_2O, Na_2O_2, K_2O_4, Rb_2O_4, and Cs_2O_4.

Monoxides M_2O. These can all be made by the action of oxygen on the metal, but with all except lithium the action is liable to go too far; with potassium, rubidium, and caesium a defect of oxygen must be used, and the excess of metal distilled off *in vacuo*; with sodium the monoxide can be made by the remarkable method[528] of heating sodium azide with sodium nitrate at 280°:

$$5\ NaN_3 + NaNO_3 = 3\ Na_2O + 8\ N_2.$$

These oxides all have a fluorite lattice.[528-30]

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[527] e.g. E. Zintl, J. Goubeau, and W. Dullenkopf, *Z. physikal. Chem.* 1931, **154**, 1.

[528] Na_2O: E. Zintl and H. H. v. Baumbach, *Z. anorg. Chem.* 1931, **198**, 88.

[529] Li_2O: J. M. Bijvoet and A. Karssen, *Rec. Trav.* 1924, **43**, 680.

They have a tendency to be coloured, increasing with the atomic weight of the metal and the temperature, which is characteristic of this whole group of oxides. Lithium and sodium monoxide are colourless; K_2O is white when cold but yellow when hot; rubidium monoxide Rb_2O is pale yellow when cold, golden yellow at 200°, and reddish at higher temperatures; caesium oxide Cs_2O forms orange-red needles, which go purple at 100° and nearly black at 250°. The lithium compound alone of these oxides will not take up more oxygen in the gas, even under 12 atmospheres at 480°.

All these oxides combine readily with water to form the hydroxides MOH, the later ones, especially the rubidium and caesium compounds, with inflammation and almost explosively.

'*Dioxides*' M_2O_2. Lithium dioxide Li_2O_2 is the only one of these that cannot be made by the direct action of oxygen on the metal or the monoxide; but if lithium hydroxide LiOH is treated with hydrogen peroxide in alcohol, a compound of the composition Li_2O_2, H_2O_2, $3\,H_2O$ separates; and when this is heated[531] or dried over phosphorus pentoxide[532] it is converted into the dioxide Li_2O_2, which is not very stable, and if heated *in vacuo* at 300° loses oxygen and gives the pure monoxide.[532] The other peroxides can be made by the direct action of oxygen on the metal either dry or dissolved in ammonia, and the peroxides of the heavier metals can also be made by the partial dissociation of the higher oxides. They show the same deepening of the colour with the rise of atomic weight of the metal as the monoxides; for example, in the cold the colours are:

Li_2O_2	Na_2O_2	K_2O_2	Rb_2O_2	Cs_2O_2
White	Pale yellow	Orange	Dark brown	Yellow (black if fused)

As before, the colour deepens on heating: thus potassium peroxide goes olive-brown at 100°.

'*Trioxides*' M_2O_3. The supposed sodium sesquioxide Na_2O_3 has not been confirmed,[533-4] and the potassium 'compound' K_2O_3 behaves like a mixture of the dioxide and the tetroxide.[535-6] Rubidium and caesium sesquioxides Rb_2O_3 and Cs_2O_3 can be obtained as solid phases by the oxidation of the metal or a lower oxide, or by the partial decomposition of the tetroxide.[537]

'*Tetroxides*' M_2O_4. These are the highest products of the direct oxidation of potassium, rubidium, and caesium, and can be made directly from

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[530] K_2O: E. Zintl, A. Harder, and B. Dauth, *Z. Elektrochem.* 1934, **40**, 589.

[531] R. de Forcrand, *C.R.* 1900, **130**, 1465.

[532] P. Pierron, *Bull. Soc. Chim.* 1939 [v], **6**, 235.

[533] R. de Forcrand, *C.R.* 1898, **127**, 364.

[534] C. A. Kraus and E. F. White, *J.A.C.S.* 1926, **48**, 1786.

[535] A. Helms and W. Klemm, *Z. anorg. Chem.* 1939, **241**, 97.

[536] S. I. Reichstein and I. A. Kazarnovski, *J. Phys. Chem. Russ.* 1938, **11**, 743.

[537] E. Rengade, *C.R.* 1906, **142**, 1149; 1907, **144**, 920; *Ann. Chim. Phys.* 1907. [8] **11**, 348.

these elements; with potassium (at 180-200°) the conversion is not complete, unless the metal is in a very thin layer such as can be formed by the evaporation of its solution in liquid ammonia,[538] but in the cold the stability of potassium tetroxide is so great that it is formed by the spontaneous decomposition of the hydrated dioxide:

$$3\ (K_2O_2,\ H_2O) = K_2O_4 + KOH + H_2O.$$

Some of the physical properties of these compounds are:

Compound	K_2O_4	Rb_2O_4	Cs_2O_4
Colour	Orange-yellow	Dark orange	Reddish-yellow
M. pt.	380°	412°	515°
Diss. tens. of O_2 = 30 mm. at	471°	600°	900°

They are very hygroscopic, and are violently decomposed by water with the formation of hydrogen peroxide and the evolution of oxygen; on heating they lose oxygen more readily the lighter the alkali metal.

The structures are fairly clear of all these oxides except the trioxide. The monoxide M_2O is obviously the ionized salt $M_2[O]^{--}$. The dioxides M_2O_2 must be the salts of hydrogen peroxide (like barium peroxide) having the divalent anion $O—O^{--}$; the formation of hydrogen peroxide when the dioxide is treated with water is good evidence for this. The trioxide M_2O_3 is still somewhat obscure; it may well be a crystal aggregate of the dioxide and the tetroxide.

The 'tetroxides', which are usually written M_2O_4 (the conventional names are all derived from formulae M_2O_n), have been examined in detail, and shown to have only half this formula, being of the type $M[O_2]$, with the 'odd' monovalent ion $[O—O]^-$. The X-ray study of potassium tetroxide[539] shows the crystal to be made up of potassium ions and O_2' ions, the O—O distance in the anions being 1·28±0·07 A.U. (the normal value for the single O—O link is 1·32 A.U.). The salt is paramagnetic,[540] though that is equally compatible with the presence of O_4'' ions.[541] Helms and Klemm in 1939[535] have reinvestigated all three compounds KO_2, RbO_2, and CsO_2; they show that they are all of the same type; they confirm both the X-ray results and the paramagnetism (amounting for each compound to nearly 2 Bohr magnetons; for spin only of one electron it should be 1·73), and find that the lattice is essentially the same as that of calcium carbide $Ca[C_2]$. There can therefore be no doubt that the salt has the simpler formula of MO_2, with an odd-numbered anion of the structure $[O^8—O^7]^-$.

[538] C. A. Kraus and E. F. Parmenter, *J.A.C.S.* 1934, **56**, 2384.

[539] V. Kasatotchkin and S. Kotov, *J. Phys. Chem. Russ.* 1936, **8**, 620.

[540] E. W. Neuman, *J. Chem. Phys*, 1934, **2**, 31.

[541] W. Klemm and H. Sodomann, *Z. anorg. Chem.* 1935, **225**, 273.

SULPHIDES, SELENIDES, AND TELLURIDES

All the alkali metals form compounds of the M_2X type with sulphur, selenium, and tellurium. Poly-derivatives are formed with sulphur up to M_2S_3, and in a less degree with selenium and tellurium. The mono-derivatives M_2X are usually prepared by the combination of the elements (excess of the metal being used, and this excess distilled off *in vacuo* at about 300°), or by the dehydration of the hydrates, or (with sulphur in particular) by the reduction of the sulphates with carbon. The solid compounds have some tendency, but much less than the monoxides, to become coloured as the metal gets heavier or the temperature higher; in the cold they are all colourless except caesium telluride Cs_2Te, which is pale yellow, but rubidium sulphide becomes orange at 300°[542]; in air, however, they readily become discoloured through oxidation. They all have the fluorite lattice, so far as is known.[543-6] The melting-points that have been observed are as follows[547]:

	Na	K	Rb	Cs
Sulphide . .	1180°[a]	840°	530° decpn.	510–520° decpn.
Selenide . .	875°+	. .	640° decpn.	600° decpn.
Telluride . .	953°	. .	690° decpn.	680° decpn.

a = [548]

The salts are hygroscopic, and some, especially caesium monosulphide, react with water violently, with the formation of polysulphides. The sulphides and especially the selenides often form hydrates with large amounts of water, more particularly those of the lighter metals: thus we have Li_2Se, 9 aq.; Na_2S, 9, 6, etc., aq.; Na_2Se, 16, 10, 9, etc., aq.; K_2S, 5, 2 aq.; K_2Se, 19, 14, 9 aq.; Rb_2S 4, 2 aq. They are readily oxidized by atmospheric air, and the more so, the heavier either component; thus caesium selenide catches fire in the air if it is warm.

There are no signs that the higher sulphides are less readily formed by the lighter metals, as are the oxides.

Rengade found that caesium oxide was able to take up more of the metal at a low temperature, though no definite suboxide was isolated. Bergmann[547] has examined the behaviour of caesium sulphide selenide and

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[542] E. Rengade and N. Costeanu, *C.R.* 1913, **156**, 792; 1914, **158**, 946; *Bull. Soc. Chim.* 1914 [4], **15**, 720.

[543] Li_2S, Na_2S: A. Claassen, *Rec. Trav.* 1925, **44**, 791.

[544] Li_2Se, Li_2Te: C. D. West, *Z. Krist.* 1934, **88**, 115.

[545] K_2S, K_2Se, K_2Te: E. Zintl, A. Harder, and B. Dauth, *Z. Elektrochem.* 1934, **40**, 593.

[546] Rb_2S: K. May, *Z. Krist.* 1936, **94**, 412.

[547] A. Bergmann, *Z. anorg. Chem.* 1937, **231**, 269.

[548] G. Courtois, *C.R.* 1939, **208**, 199.

telluride from this point of view. He shows that the caesium compounds can all take up caesium vapour at temperatures from 30° to 150°, becoming coloured (the sulphide and selenide violet, and the telluride olive-green) and also conductors of electricity in the process. The quantity taken up by the sulphide may amount to nearly 2 per cent. This is too much to be due to a mere surface action, and the caesium atoms must penetrate the lattice. A remarkable point is that the rubidium compounds show no such effect; they do not acquire either colour or conductivity in presence of rubidium vapour.[547]

HALIDES

The alkaline halides M(hal) are typical salts; so far as can be ascertained they are completely ionized under all conditions. This is proved for the crystalline state by the form of their lattices, in which each ion is symmetrically surrounded by 6 (or 8) ions of the other kind, and is equally related to all of them. It is shown in the fused salts by their high conductivities:

Salt	LiCl	NaCl	KCl	RbCl	CsCl
Spec. conductivity[a] .	5·87	3·50	2·24	1·50	1·54
Mol. conductivity[b] .	166	133	103	78·2	66·7
Temp. . .	620°	850°	776°	733°	660°

$a = {}^{549}$; $b = {}^{550}$

and in dilute aqueous solution by the agreement of the observed conductivities with those calculated by Debye and Hückel for a completely ionized salt. In the gaseous state the molecules are present as ion-pairs [M](hal); this is proved by their behaviour on photodissociation[551] and by the magnitude of their electrical dipole moments as measured by the beam method.[552]

The crystalline forms of these halides are of two kinds, a 6:1 (sodium chloride) and an 8:1 (caesium chloride) lattice. It can be shown by geometry that in an AB crystal formed of spherical A and B ions the 6:1 lattice gives the closest packing when the ratio of the radii of A and B is less than $\sqrt{3}-1 = 0{\cdot}73$, and the 8:1 when it is more than this. The change over from a 6:1 to an 8:1 lattice in the series of alkaline halides does not come exactly at this place, but near it, as the following table shows. The diagonal line indicates the point at which the change should theoretically occur; those salts (CsCl, CsBr, and CsI) which have the 8:1 lattice at the ordinary temperature and pressure are enclosed in frames, and those which can be made to assume it by a suitable rise of pressure or temperature in dotted frames.

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[549] W. Biltz, *Z. anorg. Chem.* 1924, **133**, 312.

[550] W. Biltz and W. Klemm, ib. 1926, **152**, 267.

[551] H. Sponer, *Z. Elektrochem.* 1928, **34**, 483.

[552] KCl 8·0; KBr 9·1; KI 9·24 D: W. H. Rodebush, L. A. Murray, and M. E. Bixler, *J. Chem. Phys.* 1936, **4**, 372; corrected by R. G. J. Fraser and J. V. Hughes ib. 730. See also H. Scheffers, *Phys. Z.* 1934, **35**, 425.

The reason why the change of form does not occur exactly at the calculated point is obviously that the electrostriction leads to a deformation of the ions which the geometrical calculation has not taken into account. In the same way the thallous halides TlCl, TlBr, TlI all have 8:1 lattices, though the radius of the thallous ion is the same (1·49 A) as that of the rubidium ion. (See III. 483.)

Ratio of the Ionic Radii A/B

	Li (0·78)	Na (0·98)	K (1·33)	Rb (1·49)	Cs (1·65)
F (1·33) . .	0·59	0·74	1·00	1·12	1·24
Cl (1·81) . .	0·43	0·54	0·73	0·82	$\boxed{0{\cdot}91}$
Br (1·96) . .	0·40	0·50	0·68	0·76	$\boxed{0{\cdot}84}$
I (2·20) . .	0·35	0·45	0·61	0·68	$\boxed{0{\cdot}75}$

Some of the halides which come near the dividing line can be made to change their lattices by a suitable change of temperature or pressure. Caesium chloride (8:1) goes over at 445° into a second modification with a 6:1 lattice,[553-4] and rubidium chloride bromide and iodide (all of which are 6:1) can be made to go over into the closer packed 8:1 form by high pressures,[555-6] the pressures in atmospheres required at 50°, and the compression produced, being: rubidium chloride 5525, 14·6 per cent.; rubidium bromide 4925, 11·3 per cent.; rubidium iodide 4050, 10·7 per cent. That the new modifications have the caesium chloride lattice was proved by X-ray analysis.[553]

The melting- and boiling-points and the interatomic distances[557] are given in the following table.

Melting- and Boiling-points

	Li		Na		K		Rb		Cs	
	M.pt.	*B.pt.*	*M.pt.*	*B.pt.*	*M.pt.*	*B.pt.*	*M.pt.*	*B.pt.*	*M.pt.*	*B.pt.*
MF	840°	1,670°	992°	1,705°	846°	1,498°	775°	1,408°	684°	1,253°
MCl	606°	1,382°	803°	1,430°	768°	1,411°	717°	1,383°	638°	1,303°
MBr	535°	1,310°	740°	1,393°	748°	1,376°	681°	1,350°	627°	1,300°
MI	450°	1,189°	653°	1,300°	693°	1,330°	638°	1,305°	621°	1,280°

[553] G. Wagner and L. Lippert, *Z. physikal. Chem.* 1933, B **21**, 471: 1936, B **31**, 263.

[554] C. D. West, *Z. Krist.* 1934, **88**, 94.

[555] J. C. Slater, *Proc. Amer. Acad.* 1925, **61**, 147.

[556] P. W. Bridgman, *Z. Krist.* 1928, **67**, 363.

[557] W. H. Zachariasen, ib. 1931, **80**, 137.

Interatomic Distances in Crystals

[8:1 crystals in brackets.]

LiF	NaF	KF	RbF	CsF
2·04	2·31	2·66	2·82	3·00
LiCl	NaCl	KCl	RbCl	[CsCl]
2·57	2·81	3·14	3·29	3·56
LiBr	NaBr	KBr	RbBr	[CsBr]
2·75	2·98	3·29	3·43	3·71
LiI	NaI	KI	RbI	[CsI]
3·03	3·23	3·53	3·66	3·95

The solubilities of these halides in water are discussed in the next section, along with those of other salts.

ALKALINE SALTS

The best known of the salts of nearly all acids are those formed by the alkali metals. Many of them will be discussed later under the elements from which their anions are derived, but a few general remarks may be made about them here.

In water the salts of the alkalies are as a rule more soluble than those of the metals of any other periodic group; in ordinary analysis the alkalies remain in solution after all the other metals have been precipitated. A comparison of the solubilities in water of the salts of the different alkalies shows that in general there is a continuous change from lithium to caesium, though the number of (mostly small) departures from this order is not inconsiderable, owing partly to changes in crystal structure, and partly to the formation of hydrates, whose solubility is necessarily less than that of the anhydrous salt at the same temperature, but we cannot as a rule calculate how much less. Disregarding such small irregularities we find in almost every case a very simple but peculiar effect of the rise of atomic number of the alkali metal on the solubility: of the salts of a strong acid the lithium salt is the most soluble, and of the salts of a weak acid it is the least. The following table gives some quantitative evidence of this: the solubilities are expressed in grammes of anhydrous salt to 100 g. of water at a temperature near 25°.[558] Where the solid in contact with the solution is known to be hydrated (this is almost confined to the lithium and sodium salts) the solubility is marked +. Of the salts given here the first four MOH, M_2CO_3, MF, and the azides MN_3 show an increase of solubility with a rise of atomic weight of the metal, and the rest a fall.

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[558] The values are taken mainly from A. Seidell, *Solubilities*, New York, vol. i, 1920, vol. ii, 1928; Landolt-Börnstein, *Tabellen*, and Gmelin, *Handbuch*, ed. 8 (Alkali metals 1926–39). Also for the sodium salts (at 25°) from J. E. Ricci, *J.A.C.S.* **1944, 66, 1015.**

Solubilities of Alkaline Salts in g. anhydrous salt to 100 *g. water at ca.* 25°

Salt	Li	Na	K	Rb	Cs
MOH	13·0+	108·3+	112·8	197·6 (30°)	385·6 (15°)
M_2CO_3	1·33	21·4+	112·7	222·7	261·5
MF	0·133	4·13+	96·5+	130·6	366·5
MCl	80·8+	35·9	34·4	91·2	185·8
MBr	163+	94·1	65·0	108·3	123·4
MI	165·3	184·1	144·6	156·4	69·9
$MClO_3$	440·5+	100·4	7·16	5·36	6·28
$MBrO_3$	152·5+	38·3	6·89	2·93	3·66
MIO_3	80·3	9·10	8·1	2·1	2·61
$MClO_4$	56+(3 aq.)	209·8	1·67	1·28	1·97
MNO_3	72·4+	91·8	31·6	53·4	23·0
MN_3	66·4	41·6	49·7	114·1	307·4
M_2SO_4	34·8+	61·3	11·1	48·1	179·1
M alum	(none)	23·0	13·5	2·27	0·619

There are many other series of alkaline salts where the data, though incomplete and often only qualitative, are sufficient to show in which direction the solubility is changing. These are included in the following table, and are divided into three groups: (I) those in which the lithium salts are the most soluble and the caesium salts the least; (II) a small number of doubtful series, in which the lithium and caesium salts are both more soluble than the potassium; and (III) finally those in which the caesium salt is the most soluble and the lithium salt the least. When we look at the table as a whole, it is obvious that the strong acids (the complex acids in which the central atom has attained its maximum effective

I. Li > Cs		II. *Doubtful*	III. Li < Cs
MI	$MOsO_3N$	MCl	MF
$M(hal)_3$	$M_2OsO_4(OH)_2$	MBr	MOH
$MClO_3$	$M_2OsO_4F_2$	M_2SO_4	M_2CO_3
$MBrO_3$	$M_2Ir(OH_2)Cl_5$	MNO_2	MN_3
MIO_3	$M_3IrCl_2(NO_2)_4$		M_2SeO_4
$MClO_4$	$M_3IrCl_2(NO_2)_2C_2O_4$		M_3PO_4
MNO_3	$M_3IrCl_2(C_2O_4)_2$		M_2SbO_2
M alum	$M_2Ir(py)Cl_5$		$M[V'''F_4aq_2]$
M_2CrO_4	M_3IrCl_6		$M_2[TaF_7]$
$M_2Cr_2O_7$	M_2PdCl_6		$M_2S_2O_8$
M_2TeCl_6	M_2PtCl_4		Formates
M_2TeBr_6	M_2PtCl_5		Acetates
M_2TeI_6	M_2PtCl_6		Oxalates
M_2RuCl_6	M_2PtBr_6		
M_2OsCl_6	$MCuS_4$		
$M_2OsO_2(C_2O_4)_2$	$MAuCl_4$		

covalency are all strong) come in group I, and the weak acids in III, although in the latter group there are one or two acids that it is surprising to find there, such as selenic.*

The hydration of these salts is discussed in the following section, under the complex compounds.

COMPLEX COMPOUNDS

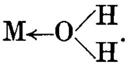
The complex compounds of an element are those which it forms by means of co-ordinate links, either as an acceptor or as a donor, but in the earlier groups as an acceptor only. A simpler definition which covers nearly every case is that a complex compound is one in which the covalency of the element is greater than its valency.

The alkali metals ionize more readily than any other elements, and are correspondingly reluctant to form covalent compounds of any kind, including complexes. The complexes which they do form may be divided into complexes of the ions and those of the neutral atoms.

Complexes of the Alkaline Ions

These occur in the solvated—hydrated and ammoniated—salts. It is obvious, as was pointed out by Fajans,[559] that the alkaline cations with their single charges have a relatively small tendency to form complexes but that this tendency will be stronger with the smaller ions of the lighter elements, although the number of links which they can form is less (this is limited to 4 for lithium, 6 for sodium and potassium, and 8 for rubidium and caesium, though these higher values are seldom or never realized in fact). The degree of solvation of the ions in solution is a matter of doubtful argument. That it diminishes as we go from lithium to caesium is obvious from the order of the ionic mobilities, which increase with the radii of the monatomic ions, the values at 25° being:

	Li	Na	K	Rb	Cs
Mobility . .	39·6	51·4	75·6	77·3	79·9
Radius . .	0·78	0·98	1·33	1·48	1·67 A

The water of crystallization in the hydrated salts, though it need not be the same as, and is presumably often much less than, the water combined with the salt in solution, gives us a rough measure of the co-ordinating power of the ions, and we know that the hydration of solid salts is mainly due to the cation, which forms the link  $M\leftarrow O\begin{smallmatrix}H\\H\end{smallmatrix}$. A comparison of all the known alkaline salts of some 30 of the commoner inorganic acids shows

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* The ferrocyanides do not seem to fit in, as the acid is (at least in its first and second dissociation constants) strong, while the solubilities increase from Li to Cs. Possibly the rule does not apply to tetrabasic acids; see VIII. 1335.

[559] K. Fajans and G. Joos, *Z. Phys.* 1924, **23**, 1; K. Fajans, *Naturwiss.* 1923, **11**, 165; *Z. Krist.* 1924, **61**, 18.

that of the lithium salts 76 per cent. form solid hydrates; of the sodium salts 74 per cent.; of the potassium salts 23 per cent.: while of the rubidium and caesium salts in the list only one of each is hydrated, in both cases the ferrocyanide. It is quite possible that with the last three elements the cation is never hydrated in the solid, and that the water of crystallization that is found is attached to the anion; this view is supported by the observation of Lembert[560] that when the potassium salt of an acid is hydrated, the ammonium salt of that acid (in which the cation, being co-ordinately saturated, can scarcely take up water) is hydrated too, as the following list shows:

	Mols. of water of cryst.	
	Ammonium	*Potassium*
Carbonate	1	3/2, 2
Oxalate	1	1
Acid oxalate	1/2, 1	1, 2
Pentasulphide	1	(K_2S_4:8)
Sulphite	1/2, 1, 4/3	1, 2
Thiosulphate	1/3	1
Iodate	1/2	? 1/2
Periodate	2, 3	4
Dithionate	1/2	0
Orthophosphate	1	0

As evidence of the covalency limit it is to be noticed that the lithium salts, in spite of their strong tendency to hydration, never form hydrates with more than $4\,H_2O$ except the bromide, iodide, and hydroxide, at temperatures well below zero; these exceptions may be due to hydration of the anion, to the presence of double water molecules (as was suggested by Werner) or to the formation of crystal aggregates of molecules of different kinds.

Another series of co-ordinated ions is found in the ammoniates, the solid compounds of the salts with ammonia and amines. They have been investigated by Biltz[561–2] by measuring the dissociation tension over a range of composition of the system solid salt+ammonia gas. Some of them are of considerable stability, such as LiI, $4\,NH_3$, which has a dissociation tension of 100 mm. at +60·5°, but in others the tension is not much less than that of solid ammonia at the same temperature. The results in general show, as we should expect, that the stability of the ammines falls off in the order Li > Na > K. With the halides of the same alkali it is found to fall off in the order I > Br > Cl; the problem is of course complicated by the influence of the crystalline forces and the change in the lattice energy. The stability of the tetrammines of the lithium salts is especially marked.[563]

[560] M. E. Lembert, *Z. physikal. Chem.* 1923, **104**, 101.

[561] W. Biltz and W. Hansen, *Z. anorg. Chem.* 1923, **127**, 1.

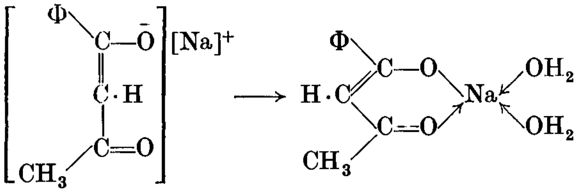
[562] W. Biltz, ib. **130**, 93.

[563] F. Ephraim, *Ber.* 1919, **52**, 236.

The ammonia in these compounds can be replaced by alkylamines (primary, secondary, and tertiary) but the products are much less stable.[564-5] In the same way a series of alcoholates, corresponding to the hydrates, is known.[566]

Neutral Alkaline Complexes

An acceptor naturally forms a co-ordinate link more easily when it has a positive charge, and so complexes are less readily produced by neutral atoms of the alkali metals than by their ions. We should expect the neutral complexes to be formed, if at all, especially as chelate derivatives of β-diketones and β-keto-esters, and this is so. The hydroxylic hydrogen in the enolic forms of these diketones is of course readily replaced by an alkali metal. The products are usually salts: when they are heated they char without melting, and they dissolve in hydroxylic solvents but not in hydrocarbons. They can, however, be made to assume the covalent form,[567-8] but only when a further co-ordination converts the metal into the more stable 4- or 6-co-ordinated form (completes its valency octet or duodecet). Thus sodium benzoylacetone has all the properties of a salt, and as such is insoluble in benzene or toluene; but if it is recrystallized from 96 per cent. alcohol, it takes up two molecules of water from the solvent, and the resulting 'dihydrate' is perceptibly soluble in toluene. It is evident that the water molecules have attached themselves to the sodium ion, and the salt has then gone over into the covalent chelate form, which is not stable in the anhydrous compound where it would give the sodium a covalency of only 2, but becomes so when the co-ordinated water raises the covalency to 4:



The stability of the product is proved by the fact that the necessary water is withdrawn from its dilute solution in alcohol, and the covalent character by its solubility in toluene.

The necessary increase in the covalency can also be attained by adding to the enol salt a second molecule of the same or another enol, which can form a chelate addition compound. Thus Hantzsch showed[569] that sodium ethylate reacts with salicylaldehyde ($C_7H_6O_2$) to give a compound of the composition $C_7H_5O_2Na, C_7H_6O_2$, and that this 'acid salt' is so stable that

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[564] A. Simon and R. Glauner, *Z. anorg. Chem.* 1929, **178**, 177.

[565] A. Simon and H. Kimmerle, ib. 1931, **202**, 385.

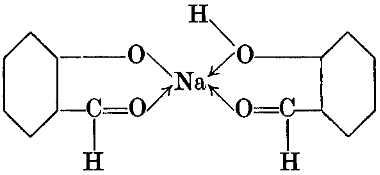
[566] Lithium: Gmelin, pp. 234–5: sodium, Gmelin, pp. 858–61.

[567] N. V. Sidgwick and F. M. Brewer, *J.C.S.* 1925, **127**, 2379.

[568] F. M. Brewer, ib. 1931, 361.

[569] A. Hantzsch, *Ber.* 1906, **39**, 3089.

it is not decomposed by excess of sodium ethylate. The structure is evidently this:



If a second molecule of a chelating compound is added in the same way, a molecule with a 6-covalent alkali atom is formed. By these methods a series of 4- and 6-covalent compounds have been made, containing all the alkali metals.[567-8] Various chelate groups were employed: acetylacetone, benzoyl acetone, aceto-acetic ester, salicylaldehyde, methyl salicylate, *o*-nitrophenol, *o*-nitrocresol, and quinizarine (α-dihydroxyanthraquinone). The 4-co-ordinated compounds are either monochelate with two water molecules (which, as we should expect from the hydration of the salts, are found only with the lighter alkali metals), or dichelate: the 6- are monochelate with four water molecules, or tri-chelate. The covalency with lithium never exceeds 4: all the other elements give derivatives in which they have covalencies of 4 and 6. The following are examples of the compounds of this kind that have been prepared.[567-71]

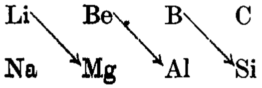
Neutral Complex Alkaline Compounds

Abbreviations: HA acetylacetone; HB benzoylacetone; HQ ½(quinizarine); HS salicylaldehyde; HNp *o*-nitrophenol.

Metal	4-*covalent*	*Ref.*	6-*covalent*	*Ref.*
Lithium	LiB, 2 H_2O	567	None	. .
	LiS, HS	568		
Sodium	NaB, 2 H_2O	567	NaB, 4 H_2O	570
	NaNp, HS	567	NaQ, 2 HS	567
Potassium	KA, 2 H_2O	567	KQ, 2 HS	567
	KS, HS	569	KS, 2 HS	568
Rubidium	RbS, HS	568	RbS, 2 HS	568
Caesium	CsS, HS	568	CsS, 2 HS	568

APPENDIX: *Peculiarities of Lithium*

Lithium, like every 'typical' element, differs in many ways from the other members of the group, and in most of these differences shows a resemblance to magnesium. This is an example of the 'diagonal' relationships observed in the Periodic Table, which are largely explained by the Fajans theory. In such a series of elements as these:



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[570] C. Weygand and H. Forkel, *J. prakt. Chem.* 1927, **116**, 293.
[571] See also O. L. Brady and W. H. Bodger, *J.C.S.* 1932, 952.

the deforming power of the cation is increased as we move to the right, owing to the increase in the ionic charge, and is diminished when we move downwards, owing to the increase in the atomic radius. If we make both movements (as indicated by the arrows) and go from lithium to magnesium, from beryllium to aluminium, or from boron to silicon, the two changes will more or less compensate one another, and we shall reach an atom of about the same deforming power, and so far of similar properties to the one from which we started.

The resemblances between lithium and magnesium are numerous, and they are all points in which lithium differs from the other alkali metals. The most important are the following: the relative inertness, high melting-point, and hardness of the metal; the instability of the higher oxides, the refusal to form an oxide higher than M_2O by the direct action of oxygen, and the absence of any oxide with more than two oxygen atoms to two equivalents of the cation; the relative instability of the carbonate*; the ready combination of the metal with carbon and with nitrogen; lithium and magnesium can be used indifferently to remove nitrogen in the isolation of the rare gases. Another difference is in the low melting-points and easy solubility in hydrocarbons of the lithium alkyls, in which they are sharply distinguished from the alkyls of the other alkalies, but resemble those of beryllium and magnesium.

The stronger hydration of the lithium ion is a result of its smaller radius, and a similar effect is produced in magnesium by its double charge. The solubilities of the lithium salts in water also show many resemblances to magnesium: the high solubilities of the chlorides, bromides, and iodides, and the relatively low values for the fluorides, hydroxides, carbonates, phosphates, and oxalates. Another point of similarity is the enormous solubility of the perchlorates of lithium (but not those of the other alkalies except to some extent sodium) and of the alkaline earths, especially in organic solvents. The following are the values in moles of perchlorate to 100 moles of solvent at 25° in water, alcohol, acetone, and ethyl acetate[572]:

	Li	Na	K	Rb	Cs	Mg	Ba
Water	9·5	30·8	0·216	0·130	0·153	8·03	10·6
Ethyl alcohol	64·8	5·52	0·0040	0·0024	0·0022	4·94	17·0
Acetone	74·4	24·5	0·065	0·030	0·037	11·1	21·5
Ethyl acetate	78·4	6·93	0·00095	0·00076	0	27·9	29·6

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* The dissociation pressures of the alkaline carbonates in mm. at 1,000° are roughly:

Li_2CO_3	Na_2CO_3	K_2CO_3	Rb_2CO_3	Cs_2CO_3
90	19	8·3	11	43 mm.

A pressure of 90 mm. would be reached by magnesium carbonate at about 500°, and calcium carbonate about 650°.

[572] The solubilities in organic solvents are from H. H. Willard and G F. Smith, *J.A.C.S.* 1923, **45**, 293.

It will be seen that, as in some other properties, sodium follows lithium to a certain extent, and that there is a second large change between sodium and potassium.

The cause of these high solubilities in organic solvents is obscure. Among the alkaline salts (apart from the perchlorates) it is most marked on the one hand in the iodides, and on the other in the salts of lithium; it is entirely absent in the fluorides, sulphates, and nitrates. Now the lithium ion has the highest deforming power of all the alkaline cations, and among the anions the deformability of the sulphate, nitrate, and fluoride is very small, but in the halides it rises rapidly in the order $F < Cl < Br < I$. So far the results suggest that for some reason it is the salts with highly deformed anions that are readily soluble in organic solvents, and this conclusion is supported by the behaviour of many highly deformed salts of other metals, such as the iodides of magnesium, zinc, and cadmium. But the high solubility of the perchlorates in these solvents must be due to some other cause, since the perchlorate anion ClO_4 is remarkable for its small deformability, as is shown by the persistence with which perchloric acid remains fully dissociated in solvents of low dielectric constant, in which nitric and even hydrochloric acid do not.

GROUP I (3)

COPPER, SILVER, GOLD

THE contrast between the two subdivisions of this group is perhaps greater than obtains in any other, even in Group VII. The alkali metals form the most closely related series we know; their differences are practically all in degree and not in kind, and the properties change regularly with the atomic numbers; they are all strictly confined to the group valency of 1, and the metals pass into the ionized state more readily than any others. The 'coinage' metals of Group I. B show few regular graduations of properties: silver cannot be said to be in any chemical sense intermediate between copper and gold. Each of them has at least two states of valency, which are not the same in all of them, and which differ enormously in relative stability according to the metal; finally, these metals pass into the ionic state with more difficulty than any others, and the more so the higher the atomic number, while of the alkali metals caesium ionizes the most easily.

A study of the properties of this subgroup shows the truth of Fajans's fourth rule, that the inert gas form of cation has less deforming power than any other. In these B metals, in which the outermost electronic group of the ion is a complete or incomplete 18, the simple rules that apply to a cation with an outermost group of 8, like sodium, no longer hold. The deforming power, which leads to covalency formation, has little relation here to the size of the ion; the radii of these ions are Cu^+ 1·0, Ag^+ 1·13, Au^+ probably less than 1·2: that is, they are all of about the same size and come between Na^+ 0·98 and K^+ 1·33 A; but the change in the principal quantum number of the outer electron group in the ion as we go from one period to the next, from 3 in copper to 4 in silver and 5 in gold, has a great effect on the properties, and in ways we do not yet fully understand; even the stable numbers of the valency groups in the complexes—the co-ordination numbers—are different.

Each of these elements has two different states of valency. When this happens with an element, the compounds belonging to the two states have quite independent properties, and form groups as distinct from one another as the compounds of two different metals. At the same time the range of their existence is limited by the possibility of one valency passing over into the other, and this limitation is of particular importance with these three elements.

The established valencies are: copper 1 and 2; silver 1 and 2; gold 1 and 3. In the monovalent condition, where they have the group valency, they are of course comparable with the alkali metals, though the resemblance scarcely extends beyond the value of the valency. In particular, the cuprous, argentous, and aurous compounds have a far stronger tendency to pass over into the covalent state, and this tendency on the whole increases with the atomic number, which is the opposite to what happens in the alkali metals of Group I. A.

In their polyvalent states these elements belong to the transitional class, which is defined as having the outer electronic group of the ion greater than 8 and less than 18; in Cu^{++} and Ag^{++} it is 17, and in Au^{+++} 16; their nearest analogues are to be found among the members of the preceding triads. They accordingly show the characteristic properties of transitional elements; while the cuprous and argentous compounds are colourless and diamagnetic, the cupric and argentic are coloured and paramagnetic. In the auric compounds the combined effects of the triple charge and of the increased tendency to covalency formation which accompanies the rise of atomic number make the covalent state so much more stable that the ion does not practically exist at all. Indeed the effects go beyond this. Not only are all the auric compounds covalent, but they are all, so far as can be made out, complexes which have increased their covalency by co-ordination to 4.

The Elements Copper, Silver, and Gold

None of these elements is common on the earth, copper being about twentieth in the order of abundance, and gold amongst the rarest of known elements; the amount in the earth's crust in g. per ton are[573]: copper 100; silver 0·1; gold 0·005.

Copper

This is probably the most technically important metal after iron. It boils at 2,310° and melts at 1,083°; this is the melting-point of the pure element; if air is not excluded in its purification cuprous oxide is produced, which forms a solid solution with the metal, and this may depress the melting-point as much as 20°.[574] This trace of oxide, which has a bad effect on the mechanical properties of the metal, cannot be removed by heat alone, as the oxygen is not all given off until a temperature is reached at which the copper begins to volatilize; it can be removed by carbon monoxide at temperatures above 800°, or by hydrogen, which last, however, renders the metal very brittle.[575]

At high temperatures (from 450° upwards) hydrogen will diffuse through the metal.[576] The rate of diffusion through copper that is spectroscopically free from oxygen has been measured by Ham,[577] who finds that it is proportional to the square root of the hydrogen pressure even as low as 450°. At a red heat metallic copper will take up nitrogen from ammonia (see below, p. 116, under the compounds of copper with nitrogen).

Copper is readily attacked by sulphur, selenium, and the halogens. Its

[573] V. M. Goldschmidt, *J.C.S.* 1937, 656.
[574] E. Heyn, *Z. anorg. Chem.* 1904, **39**, 11.
[575] C. E. Ransley, *J. Inst. Met.* 1939, **65**, 147.
[576] J. H. Simons and W. R. Ham, *J. Chem. Phys.* 1939, **7**, 899.
[577] W. R. Ham, ib. 903.

reaction with chlorine has been investigated by Frommer and Polanyi[578] at 470°, and also at 750° where the halide evaporates at once and the metallic surface remains clean. The pressure of the chlorine was from 0·04 to 0·002 mm. The heat of activation was found to be very small (about 2 k.cals.), and the yield per impact was at 470° 0·3 (the product being over 70 per cent. cupric chloride).

Copper occurs to a minute extent, between 3 and 12 mg./ton,[579] in sea-water, and has even been supposed to be the cause of its blue colour, but it is too little for this.

Copper and its salts are highly toxic to the lower organisms, much more than to man; it is, however, an essential constituent of certain proteins.

Copper, like other metals of a transitional character, is very important as a catalyst, especially in oxidations, as in Deacon's process

$$4\,HCl + O_2 = 2\,Cl_2 + 2\,H_2O$$

in the oxidation of organic dyes, the production of formaldehyde from methyl alcohol and air, and the dehydrogenation of ethyl alcohol to acetaldehyde. It is also used in the Gattermann and Sandmeyer reactions, and in many others.

Silver

M. pt. 960·5°: B. pt. 1,927°[580]; for the magnetic moment of the atom see Gerlach and Stern.[581]

Silver is intermediate in hardness between copper and gold; next to gold it is the most extensible of metals. It is unaffected by water or by atmospheric oxygen, but is blackened by ozone with the formation of the monoxide Ag_2O, and also by sulphur and many of its compounds: a solution of hydrogen sulphide blackens it at once in the cold. The tarnishing of silver in the air is due to the formation of a film of sulphide by the reduction of sulphur compounds (probably sulphur dioxide) which the air contains.

Concentrated nitric acid dissolves silver (and copper) but not gold. Fused alkalies dissolve silver if the air has access to the mixture but not otherwise. Potassium cyanide attacks it at once, especially in presence of air.

Gold

Metallic gold is remarkable for its ductility, and for the thinness to which it can be reduced. Ordinary gold-leaf has a thickness of about 1/10,000 mm. (10^{-5} cm.: about 350 atoms) and transmits a characteristic green light.

Gold melts at 1,063° and boils at 2,200°. Its chief chemical characteristic is its extreme inactivity, in which it resembles the platinum metals

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[578] L. Frommer and M. Polanyi, *Z. physikal. Chem.* 1928, **137**, 201.

[579] H. Kalle and H. Wattenberg, *Naturwiss.* 1938, **26**, 630.

[580] E. Baur and R. Brunner, *Helv. Chim. Acta*, 1934, **17**, 958.

[581] W. Gerlach and O. Stern, *Z. Phys.* 1921, **8**, 110.

more than silver or copper; it is not attacked by the strongest acids, nor of course by oxygen; halogens at the ordinary temperature only act superficially if at all, and all its compounds are very readily decomposed, nearly always with separation of the metal.

Its tendency to ionization is so small that in the reactions

$$2\,\mathrm{Au} + 2\,\mathrm{H}^+ = 2\,\mathrm{Au}^+ + \mathrm{H}_2$$

and

$$2\,\mathrm{Au} + 6\,\mathrm{H}^+ = 2\,\mathrm{Au}^{+++} + 3\,\mathrm{H}_2$$

only a minute concentration of gold ions can be reached, even with the strongest acids. The removal of gold ions by complex formation cannot raise the concentration of the hydrogen H_2 to the point at which the gas is evolved, and so enable the reaction to proceed; in a centinormal potassium cyanide solution, in spite of the formation of the very stable $[Au(CN)_2]^-$ ion, only 0·2 mg. of gold will dissolve per litre. If the solution is to proceed, the hydrogen concentration must also be reduced. In the presence of potassium cyanide this can be effected by the addition of oxygen itself, or better of sodium peroxide, as is done in the cyanide process for the extraction of gold.[582] Otherwise gold will only dissolve in presence of the strongest oxidizing agents, especially those which contain chlorine, and so form the stable complex halide anions.

Gold occurs in sea-water, but in much smaller quantity than was formerly believed. According to Caldwell[583] the amount is from 0·1 to 0·2 mg. per ton.

Later work by Stark[584] gives rather higher values: 0·02, 0·4, and 2·0 mg. per ton in the waters of the Adriatic, the Mediterranean, and the Atlantic respectively.*

Compounds of Univalent Copper, Silver, and Gold

The range of existence of the cuprous, argentous, and aurous compounds is limited in two ways. With every element that has more than one valency we have to reckon with the possibility of the atom being oxidized or reduced from one state to another by its surroundings (of which in the salts the anions forms a part). But there is also a further limitation, the possibility of the ions of lower valency reacting with one another to form ions of higher valency and the free metal:

$$\begin{aligned} 2\,\mathrm{Cu}^+ &= \mathrm{Cu}^{++} + \mathrm{Cu} \\ 2\,\mathrm{Ag}^+ &= \mathrm{Ag}^{++} + \mathrm{Ag} \\ 3\,\mathrm{Au}^+ &= \mathrm{Au}^{+++} + 2\,\mathrm{Au}. \end{aligned}$$

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* This shows that the extraction of gold from sea-water is not likely to be a commercial success. We may compare its value per ton of sea-water with those of the bromine and the magnesium, which are extracted on the large scale; they are bromine 100 g. worth about 5*d.*; magnesium 1·3 kg. worth 1*s.*; gold, say 1 mg., 1/15th of a penny. [Prices taken to be gold 170*s.* per oz.; bromine 1*s.* per lb.; $MgCO_3$ 4*d.* per lb.]

[582] See G. Bodländer, *Ahrens Sammlung*, 1899.

[583] W. E. Caldwell, *J. Chem. Educ.* 1938, 15, 507.

[584] W. Stark, *Helv. Chim. Acta*, 1943, 26, 424.

This is of special importance in this subgroup because here the metallic state is exceptionally stable, as is shown by the small tendency of the metal to ionize; also the metal is of course almost insoluble, which promotes its separation. It is obvious that the monovalent form can only exist so far as this reaction does not take place, and therefore we have to inquire into its nature and its extent.

With copper the conditions of the reaction are known with some accuracy. The equilibrium between the two ions in presence of the metal has been determined by measuring the amount of cuprous salt present in a cupric solution which is in contact with metallic copper.[585–6] The measurements are difficult because the amount of cuprous salt is so small, and special care has to be taken to exclude atmospheric air. At equilibrium we have

$$\frac{[\mathrm{Cu}^{++}].[\mathrm{Cu}]}{[\mathrm{Cu}^{+}]^2} = k.$$

The value of [Cu], the minute solubility of metallic copper in water, is of course unknown, but it can be taken to be constant, and so we may write

$$\frac{[\mathrm{Cu}^{++}]}{[\mathrm{Cu}^{+}]^2} = K.$$

The mean value of this constant at 20° (the proportion of cuprous salt rises with the temperature) is found to be 1×10^6. Hence copper will dissolve in a molar solution of cupric ions until the cuprous concentration is 10^{-3} normal (63 mg. Cu′ per litre), and in a hundredth molar cupric solution until it is 10^{-4}. We can also see that the cuprous ion cannot reach the concentration of the cupric as long as the latter exceeds 10^{-6}.

Hence a cuprous compound can only exist in any quantity so long as it does not ionize. This explains the curiously limited number of cuprous compounds that are known. The oxide, sulphide, and the halides (except the fluorides) can be prepared, because they are so insoluble in water that the ionic concentration never reaches its very low limit. A soluble cuprous compound may be prepared if it is prevented from forming cuprous ions, either by not letting it ionize at all, or by causing the ions to form complexes. Thus cuprous sulphate $\mathrm{Cu_2SO_4}$ can be made by the action of dimethyl sulphate on cuprous oxide, but it is at once decomposed by water to metallic copper and cupric sulphate $\mathrm{CuSO_4}$. Cuprous oxide will also dissolve in ammonium sulphate solution in presence of ammonia to form the complex salt $\mathrm{[Cu(NH_3)_2]_2SO_4}$: similar complex anions are formed when cuprous chloride dissolves in hydrochloric acid or sodium chloride solution, and complex cations in aqueous ammonia; in the same way cuprous nitrate can be obtained as the stable complex $\mathrm{[Cu(CH_3{\cdot}CN)_4]NO_3}$.[587]

When we come to the silver salts, it is clear that the reversible reaction

$$2\,\mathrm{Ag}^{+} \rightleftharpoons \mathrm{Ag}^{++} + \mathrm{Ag}$$

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[585] F. Fenwick, *J.A.C.S.* 1926, **48**, 860.

[586] E. Heinerth, *Z. Elektrochem.* 1931, **37**, 61.

[587] See further J. E. B. Randles, *J.C.S.* 1941, 802.

is possible, but that the equilibrium is very far over to the left-hand side. The divalent argentic ion has so strong a tendency to give up half its charge to its surroundings—to act as an oxidizing agent—that its salts can only exist if the ion is stabilized by co-ordination, and even then the co-ordinated groups must be very firmly attached, or the anion must be incapable of further oxidation; the known argentic salts, apart from the oxide AgO which is doubtful, and perhaps the fluoride AgF_2 which may not exist as such, and anyhow has an unattackable anion, are all co-ordination compounds which either, as in the persulphate $Ag(py)_4S_2O_8$ have exceptionally stable anions, or have exceptionally stable co-ordinating groups, as in the nitrate or chlorate of the complexes with dipyridyl or ortho-phenanthroline.

The behaviour of gold is more like that of copper: the monovalent ion goes over with great readiness into metallic gold and the auric form. The position is complicated by the enormously strong tendency of gold, especially in the auric state, to form complexes. This makes it impossible to determine the equilibrium between the ions, but it is found that all aurous salts that are not complex are decomposed by water with separation of metallic gold.

Thus the stability of the polyvalent as compared with the monovalent ion is much greater with copper and gold than it is with silver; the electronic group of 18 is much less easily broken down in silver than in either of the other two elements. This is in accordance with the structures of the elements preceding these three in their respective periods of the table.

The elements of the middle series (which includes silver) have a much stronger tendency than the others to retain electrons in the large penultimate group (see Table, p. xxv), and this is clearly reflected in the reluctance with which silver loses an electron from this group to become divalent.

We have next to compare the monovalent compounds of these elements with one another, and with those of the alkali metals. We may begin with the solubility in water, although the data, apart from the nearly insoluble oxides, sulphides, and halides, are practically confined to the silver salts; all the aurous compounds must be omitted, as they are decomposed by water, and all the more soluble cuprous compounds for the same reason.

The only freely soluble silver salts—giving a more than normal solution in water at 25°—are the fluoride, nitrate, and perchlorate. A few others, such as the chlorate, sulphate, and acetate, have solubilities between normal and centinormal; the rest are relatively insoluble, the oxide, sulphide, chloride, bromide, and iodide especially so. The corresponding salts of sodium, the alkali metal whose ionic radius (0·98 A) comes nearest to that of silver (1·13 A), are all very soluble. One point is worth notice. We know that the structure of the argentous ion gives it a greater deforming power (as compared with an alkaline ion) than corresponds to its size. Since the lithium ion (radius 0·78 A) is much smaller than the silver ion, we might expect that this difference in size would to some extent compensate for the difference in structure, and that in the solubilities of its salts silver would resemble lithium rather than sodium. But there is no sign of this. Lithium fluoride is abnormally insoluble, while silver fluoride is abnormally soluble (about 1,400 times as soluble as lithium fluoride at 25°); the chloride and bromide of lithium are far more soluble than those of sodium, but silver bromide and chloride are almost insoluble. Again, it is characteristic of lithium, as we have seen, that its salts with weak acids are less soluble than those of strong, but there is no sign of this with silver, where the acetate, for example, is among the more soluble salts. Again the lithium ion has the strongest tendency to hydration of any alkaline ion, and practically all its salts are hydrated, which is plausibly explained by the Fajans theory as being due to its large deforming power. On the other hand, silver, which certainly has a greater deforming power than lithium, has scarcely any salts that form hydrates; almost the only salts that do so are the fluoride and the perchlorate, which are exceptional in other ways too.

These facts illustrate the general principle that in an ionized molecule the two ions in spite of the deformation remain essentially distinct, and the properties of the salt can be regarded as depending on two factors, the deforming power and the deformability; but that in covalent molecules the strength of the link depends on the particular affinity of the two component atoms for one another, which is not necessarily the same for any two equally deforming or equally deformable atoms. Accordingly in their covalent compounds the relations between different elements are much more selective than they are in the salts. This is well exemplified by the coinage metals. Their most obvious characteristic is a relative indifference, especially in silver and gold, to oxygen, but a strong tendency to combine with sulphur. Again among the co-ordination compounds of their monovalent atoms we shall find a much stronger affinity for nitrogen as donor than for oxygen: this is illustrated by the readiness with which silver compounds co-ordinate with ammonia while they refuse to hydrate, and it no doubt explains why the less stable states of these elements are 'protected' by co-ordination to nitrogen, but not to water.

It is thus of fundamental importance to be able to ascertain whether a given link is predominantly ionized or covalent. Among the methods used for determining this two of the more important are the crystal structure for the solid and photodissociation for the vapour. The characteristic crystal structures for an ionized compound of the formula AB (i.e. a binary compound with equal numbers of the two kinds of atoms in the molecule) are, as we have seen in the alkaline halides, the close-packed 6:1 (sodium chloride) and 8:1 (caesium chloride) lattices. For a covalent AB compound when the sum of the valency electrons of A and B is 8, the forms are nearly always either the zinc blende, wurtzite, or diamond lattice[588]; this is found, for example, with the compounds AgI, CdTe, InSb, and SnSn or metallic tin. These three types of lattice are open structures, in which each atom has four nearest neighbours of the other kind, at the points of

[588] H. G. Grimm and A. Sommerfeld, *Z. Phys.* 1926, **36**, 36.

a regular tetrahedron of which it is at the centre. It is evident that such a crystal forms a continuous molecule—a 'giant' molecule; by a kind of co-ordination each atom has 4 of the 8 electrons and behaves like a carbon atom, the covalent links extending from atom to atom through the crystal as they do in diamond, which in fact is a typical crystal of this class. The formation of one of these 4:1 lattices is good evidence of a covalent structure.

All the four cuprous halides, with the possible exception of the fluoride, crystallize in the zinc blende form, so that they are clearly covalent. Silver fluoride, chloride, and bromide have sodium chloride lattices, and are therefore ionized in the crystal. Silver iodide crystallizes in three forms, which have many peculiarities, but the more important are a low-temperature γ-form which has a zinc blende lattice, and a regular form with a sodium chloride lattice, which must be ionized. These conclusions are supported by the interatomic distances, which are as follows:

Interatomic Distances

Compound	*Calcd. covt.*	*Obsd.*	*Calcd. ionic*	*Conclusion*
CuF	1·99	1·85*	2·33	Cov.
CuCl	2·34	2·34	2·81	Cov.
CuBr	2·49	2·46	2·96	Cov.
CuI	2·68	2·62	3·20	Cov.
Cu_2O	2·01	1·85	2·32	Cov.
AgF	2·17	2·46	2·46	Ionic
AgCl	2·52	2·77	2·94	Ionic
AgBr	2·67	2·88	3·09	Ionic
AgI	2·86	3·05 2·83	3·33	Ionic Cov.
Ag_2O	2·19	2·04	2·45	Cov.

* This result is not certain: see below under cuprous fluoride, p. 119.

The two oxides are added because the distances establish their covalent character; but their crystal structures are of course necessarily different from those of the AB compounds.

In the vapour state the covalent molecules can be detected by the fact that one of the two neutral atoms into which they break up on photo-dissociation is electronically active. By this test it has been shown that silver chloride, bromide, and iodide are covalent in the vapour.[589] It is not surprising that a molecule which is ionized in the crystal should become covalent in the gas; the deformation is likely to be greater when the ion-pair is isolated than when it is packed into the crystal.[590]

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[589] J. Franck and H. Kuhn, *Z. Phys.* 1927, **43**, 164 (AgI); **44**, 607 (AgBr).

[590] See A. Sommerfeld, *Z. Elektrochem.* 1928, **34**, 518.

We can therefore sum up the conclusions as follows:

		F	Cl	Br	I	O
Copper	Gas	..	Cov.	Cov.	Cov.	..
	Crystal	Cov.	Cov.	Cov.	Cov.	Cov.
Silver	Gas	..	Cov.	Cov.	Cov.	..
	Crystal	Ion.	Ion.	Ion.	Ion. Cov.	Cov.

These results indicate that copper has a stronger tendency than silver to assume the covalent state, which is opposed to the usual rule, since it has the smaller atomic number; this is another example of the exceptional position of silver in the series, since in gold the co-ordinating power is much stronger again. That the iodide should more readily form a covalent link than the other halides is in accordance with Fajans's theory, since the iodide anion is the largest and most deformable; so too is the covalency of the links in the oxides owing to the double charge on the oxygen in the ionized form.

We may now consider some of the individual compounds of the monovalent metals.

Copper and Hydrogen: Copper Hydride CuH

The formation of a brown solid supposed to be cuprous hydride CuH when copper sulphate is warmed with hypophosphorous acid H_3PO_2 was discovered by Wurtz in 1844. The product certainly contains hydrogen, and evolves it on warming, but it is insoluble and cannot be purified.

The more recent work of Hüttig and Brodkorb[591] indicates that the product undoubtedly contains cuprous hydride, but that it is mixed with copper, copper oxide, and water. It is very unstable; it is oxidized slowly by air in the cold, and on heating it gives off hydrogen, at first slowly, and then at 110-120° the whole of the rest of the hydrogen comes off at once[591]; it is also liable to decompose explosively.[592] It thus has two main reactions:

$$4\,CuH + 3\,O_2 = 4\,CuO + 2\,H_2O$$
$$2\,CuH = 2\,Cu + H_2.$$

Hüttig and Brodkorb[591] found the lattice to be identical in type with that of metallic copper, but expanded, the distance between two neighbouring copper atoms being 3·06 A instead of 2·70 as in the pure metal. This suggests that like other hydrides of a metallic character copper hydride may have a metallic structure, in which CuH molecules take the place of the Cu atoms in the metal itself. The radius of the CuH molecule, regarded as a sphere, would be (3·06—2·70)/2 = 0·18 A greater than that of the copper atom in the metal; the normal 'radius' of a covalent hydrogen atom, for example in the halogen hydrides or in the C—H group, is about 0·30 A.U.

[591] G. F. Hüttig and E. Brodkorb, *Z. anorg. Chem.* 1926, **153**, 235.

[592] O. Neunhöffer and F. Nerdel, *J. prakt. Chem.* 1935, (2) **144**, 63.

The spectrum of copper vapour in hydrogen at 1,400° indicates the presence of a hydride CuH (presumably the same compound), with a heat of dissociation of about 65 k.cals.[593]

Silver and Hydrogen

A solid hydride of silver formed from the elements has been described[594]; but it seems very doubtful, especially since Steacie and Johnson[595] have measured the absorption of hydrogen by silver in complete absence of oxygen, and shown that this does not exceed about 1 atom of hydrogen to 2,400 of silver.

Farkas[593] obtained evidence of the formation of a gaseous hydride of silver from the loss of weight when the metal is heated in hydrogen at 1,100°. For half a mole of gas this was 2·7 mg. with nitrogen and 3·2 mg. with hydrogen, the difference presumably being due to the hydride AgH.[596] The results give a heat of dissociation of 57 ± 6 k.cals.

Aurous Hydride. Similarly Farkas[593] found with gold at 1,400° a loss of weight per half-mole of gas of 11·1 mg. with hydrogen, 0·9 with nitrogen, and 1·4 with helium; from his results he gets a heat of dissociation of 72 k.cals., while the spectrum gives 75·6.

Compounds with Carbon

These are of two kinds, (*a*) substitution products of hydrocarbons, especially acetylene and benzene, and (*b*) addition products of unsaturated hydrocarbons like ethylene, and of carbon monoxide. Class (*b*) are complex compounds, and so will be considered later.

Acetylides

Cuprous acetylide Cu_2C_2. Acetylene, or any of its derivatives that still contain the $C{\equiv}C$—H group, when treated with an ammoniacal solution of a cuprous salt will give a precipitate of a cuprous compound. With acetylene the product has been shown[597] to have the composition Cu_2C_2, H_2O after drying over calcium chloride in the cold; at 80–100° over calcium chloride, or in a current of dry carbon dioxide, it loses the water and Cu_2C_2 remains. The reaction is quantitative and can be used for the estimation of copper, the ammoniacal solution being reduced with hydroxylamine[598]; a visible precipitate is formed at a dilution of 1 in 1,100,000, so that the solubility of the acetylide is less than 1·1 mg. per litre. It is reddish-brown, insoluble in all inactive solvents, but explodes violently at 120° or in contact with nitric acid, sulphuric acid, chlorine, or bromine.[599]

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[593] A. Farkas, *Z. physikal. Chem.* 1929, B **5**, 474.

[594] E. Pietsch and F. Seuferling, *Naturwiss.* 1931, **19**, 573.

[595] E. W. R. Steacie and F. M. G. Johnson, *Proc. Roy. Soc.* 1928, **117**, 662.

[596] For the band spectrum of the hydride AgH see L. Gerö and R. Schmid, *Z. Phys.* 1943, **121**, 459.

[597] J. Scheiber and H. Reckleben, *Ber.* 1911, **44**, 210.

[598] J. Scheiber, *Z. anal. Chem.* 1909, **48**, 529.

[599] H. Rupe, *J. prakt. Chem.* 1913, (2) **88**, 79.

It regenerates acetylene on treatment with dilute hydrochloric acid or potassium cyanide solution.

The only mixed derivative for which there is much evidence is

$$Cu_2C_2,\ CuCl,\ H_2O,$$

obtained by Manchot[600] as a dark violet powder by the action of acetylene on a solution of cuprous chloride in hydrochloric acid. With ammonia it produces copper acetylide Cu_2C_2, and with hydrochloric acid it evolves acetylene.

The structures of these compounds are uncertain. The formula $Cu_2CH\cdot CHO$ suggested for the hydrate is disproved by the fact[597] that when treated with acids it gives acetylene and no trace of aldehyde. The formula $H\cdot C\equiv C—Cu—Cu—OH$ is incompatible with the fact that cuprous copper consists of a single monovalent and not two divalent atoms.

If the anhydrous compound is covalent $Cu—C\equiv C—Cu$, its non-volatility and insolubility show that it must be highly associated, presumably in the same obscure way as the alkaline alkyls.

Silver acetylide, Ag_2C_2. This is similar to the cuprous compound, and is obtained in a similar way, but it is more explosive, and never seems to have been got quite free from oxygen and water. It is purer and less explosive when it is formed from an ammoniacal solution of silver nitrate.[605] It is also formed by the action of a hot silver nitrate solution on sodium acetylene-dicarboxylate $Na_2(O_2C—C\equiv C—CO_2)$[602]; the cuprous compound seems to be formed in a similar way.[601] Since the pure substance can give no volatile product on explosion, forming only carbon and silver, the force of the explosion must be due to the effect of the heat evolved (which, according to Berthelot, is 87 k.cals. per mole) on the surrounding air. Eggert[603-4] exploded it electrically in an exhausted glass globe; there was a flame, and the glass became covered with a deposit of silver and carbon, but with the pure material (but only with this) the globe was not broken.

The pure acetylide is more sensitive to a blow even than mercury fulminate, and it explodes when heated to 120-140°, but not when brought in contact with nitric or sulphuric acid, which regenerate acetylene.

Aurous acetylide, Au_2C_2. This is said to be formed in the same way as the copper and silver derivatives, and to be explosive.[606]

Alkyl and Aryl Compounds

These are very imperfectly known; their stability is small, and falls off rapidly in the order aryl > alkyl, and Cu > Ag > Au. No alkyl com-

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[600] W. Manchot, *Ann.* 1912, **387**, 270.

[601] A. v. Baeyer, *Ber.* 1885, **18**, 2273.

[602] W. Lossen, *Ann.* 1893, **272**, 140.

[603] J. Eggert and H. Schimank, *Ber.* 1918, **51**, 454.

[604] J. Eggert, *Z. Elektrochem.* 1918, **24**, 150.

[605] A. Stettbacher, *Z.f.d. ges. Schiess- u. Sprengstoffwesen*, 1916, **11**, 1 [*Chem. Centr.* 19, II, 126].

[606] J. A. Mathews and L. L. Watters, *J.A.C.S.* 1900, **22**, 108.

pounds of any of the elements have been isolated, and no gold compounds of either kind.

Cuprous Alkyls

Cuprous iodide will dissolve in an ethereal solution of ethyl magnesium bromide at −18° to give a green solution, which behaves as if it contained cuprous ethyl Cu·Et, but is extremely unstable, and rapidly decomposes at any temperature above −50°.[607]

Cuprous Aryls

Cuprous phenyl, $Cu \cdot C_6H_5$.[607-9] If a solution of phenyl magnesium bromide in ether is treated with cuprous iodide in an atmosphere of nitrogen, a green solution is formed, from which a grey precipitate separates, of the composition CuC_6H_5; an 86 per cent. yield can be obtained.[607] It is unstable; on warming it suddenly decomposes at 80° to copper and diphenyl; on standing in a vacuum in the cold it completely decomposes within two days to a black mass. It is slowly hydrolysed by water to benzene and cuprous oxide. It is practically insoluble in benzene, carbon tetrachloride, or chloroform, but dissolves readily (probably with reaction) in pyridine, benzonitrile, and benzaldehyde. With benzoyl chloride it forms benzophenone, and many similar replacements can be effected.

Cuprous aryls can also be obtained in solution[610] by the action of copper powder on diazonium borofluorides at about 80°; the aryls (phenyl, *p*-tolyl, and *o*- and *p*-nitrophenyl) were identified by their reactions (e.g. with butyl bromide and with water) but were isolated only in the form of the phenyl and nitrophenyl pyridine complexes $Ar \cdot Cu, py_4$.

Argentous alkyls. Semerano and Riccoboni[611] claim to have made silver methyl, ethyl, and *n*-propyl by the action of lead tetra-alkyl on alcoholic silver nitrate at −60° to −80°. The products are precipitated as solids from the solution; they decompose rapidly at temperatures from −35° to −60°. This was confirmed by Theile.[612]

Argentous Aryls

Silver phenyl, $Ag \cdot C_6H_5$. An addition product of the composition $(Ag \cdot C_6H_5)_2, AgNO_3$ was obtained by Krause and Schmitz[613] as an unstable bright yellow powder by treating the ethyl-triphenyl compound of lead or tin $MEt(C_6H_5)_3$ (but not the tetra-phenyl) with silver nitrate. Challenger and Allpress[614] prepared it by the action of silver nitrate solution on bismuth triphenyl. The aryl silver itself was made by Krause and Wendt[615]

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[607] H. Gilman and J. M. S. Straley, *Rec. Trav.* 1936, **55**, 821 [*B.C.A.* 1936, 1528].

[608] R. Reich, *C.R.* 1923, **177**, 322.

[609] W. M. Whaley and E. B. Starkey, *J.A.C.S.* 1946, **68**, 793.

[610] F. A. Bolth, W. M. Whaley, and E. B. Starkey, ib. 1943, **65**, 1456.

[611] G. Semerano and L. Riccoboni, *Ber.* 1941, **74**, 1089.

[612] H. Theile, *Z. Elektrochem.* 1943, **49**, 426.

[613] E. Krause and M. Schmitz, *Ber.* 1919, **52**, 2150.

[614] F. Challenger and C. F. Allpress, *J.C.S.* 1921, **119**, 916.

[615] E. Krause and B. Wendt, *Ber.* 1923, **56**, 2064.

by treating silver chloride suspended in ether with phenyl magnesium bromide; it forms a dark slightly soluble product of the composition $Ag \cdot C_6H_5$. If it is exposed to the air, it decomposes violently as soon as the ether has dried off, evolving clouds of diphenyl vapour; this decomposition into silver and diphenyl is good evidence of its structure. Reich[608] made the compound in the same way from silver bromide. Gilman, who made it from silver iodide and the Grignard reagent at $-18°$,[607] found that the yield was much smaller than with copper.

The formation and decomposition of these silver aryls were made use of by Gardner[616–17] for the preparation of a number of diaryls and dialkyls (such as diphenyl, ditolyl, dibenzyl, octane, and unsymmetrical compounds like anisyl benzene) by adding the appropriate Grignard reagent to silver bromide suspended in ether, and boiling; he did not isolate the intermediate silver compounds, but it is clear that they must have been formed.

Gold Aryls

These are the most unstable of all the aryls and have never been isolated; but Kharasch and Isbell[618] have shown that they are formed, and obtained a solution of one of them.

They showed that an ethereal solution of the carbonyl $AuCl \cdot CO$ reacts with a Grignard reagent thus:

$$2\,R \cdot MgBr + 2\,AuCl \cdot CO = 2\,Au + R \cdot R + 2\,MgClBr + 2\,CO.$$

The more electronegative R is, the slower is the precipitation of gold, indicating the intermediate formation of $R \cdot Au$; and with α-naphthyl magnesium bromide CO is evolved and a clear red solution left which does not deposit gold until it is heated.

It is evident that all the alkyls and aryls of this subgroup that actually exist are highly polymerized.

Cyanides

Cuprous cyanide, CuCN. This forms colourless crystals which melt with decomposition at 473°.[619] Like the iodide it is formed from a cupric salt, the cupric cyanide $Cu(CN)_2$ which is first precipitated on addition of potassium cyanide soon breaking up into cuprous cyanide CuCN and cyanogen (in other words, the cupric cation being reduced by the anion). According to Barber[620] it can be made in almost quantitative yield from copper sulphate, potassium cyanide, and sodium bisulphite at 60°. It is insoluble in water and dilute acids; it dissolves in potassium cyanide solution to form the double cyanide $K[Cu(CN)_2]$, but this is a rather weak complex, and is decomposed by water with precipitation of cuprous cyanide; the stability of these cyanide complexes increases with the atomic number of the central atom.

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[616] J. H. Gardner and P. Borgstrom, *J.A.C.S.* 1929, **51**, 3375.

[617] J. H. Gardner, L. Joseph, and F. Gollub, ib. 1937, **59**, 2583.

[618] M. S. Kharasch and H. S. Isbell, ib. 1930, **52**, 2919.

[619] W. Truthe, *Z. anorg. Chem.* 1912, **76**, 144.

[620] H. J. Barber, *J.C.S.* 1943, 79.

Argentous cyanide, AgCN. This is a colourless compound which melts with decomposition between 320° and 350°.[619] It is very slightly soluble in water; the saturated solution at 20° is $1{\cdot}6 \times 10^{-6}$ normal (0·22 mg. per litre).[621] It has been said to be dimorphic, but this is not so.[622] Its crystalline structure is of peculiar interest,[623] especially in view of the dispute as to whether it was a cyanide or an isocyanide. The crystal is made up of endless parallel rectilinear chains $-Ag-C{\equiv}N-Ag-C{\equiv}N-$, etc. (a structure which must be linear), the Ag···Ag distance being 5·26 A. The calculated distance for this formula is 5·68 A; the shortening of 0·42 A, or 7·4 per cent., is presumably due to resonance. Thus the compound is covalent, and is at once a cyanide and an isocyanide.

Silver cyanide is soluble in concentrated but not in dilute acids. It is also soluble in ammonia and in alkaline cyanides; the complexes formed with the latter are more stable than those of copper, and do not appear to break up in water (see later under complexes). The solid absorbs about 1 mole of ammonia from the gas at 1 atmosphere in the cold. Its reaction with alkyl halides is familiar, but remarkable; it gives mainly the isonitrile, whereas an alkaline cyanide gives mainly the nitrile, presumably because the Ag—C link is stronger than the Ag—N; the mercuric cyanide behaves like the silver compound.

Aurous cyanide, AuCN. Yellow crystals. This compound like the iodide is formed when we should expect an auric compound, by the action of prussic acid on auric hydroxide. It can also be made by the decomposition of auric cyanide, or by heating the double cyanide $K[Au(CN)_2]$ with hydrochloric acid to 50°. The crystal structure is the same as that of silver cyanide.[624]

Aurous cyanide is apparently more stable than the cuprous and argentous compounds. On heating it breaks up at a red heat, leaving metallic gold. It is even less soluble in water than aurous iodide, and it has a stronger tendency to complex formation than any of the aurous halides (see below, p. 134).

Nitrogen Compounds

Of the binary nitrogen compounds, apart from the highly explosive azides MN_3, only cuprous nitride is at all well known.

Cuprous nitride, Cu_3N, can be made by heating copper to redness in ammonia, or more conveniently[625] by passing ammonia over anhydrous cupric fluoride at 280°. It is a dark green powder which is stable in air when cold, and if heated in a vacuum does not change until it reaches 450°, where it decomposes completely into its elements. An X-ray examination of its crystal structure showed[626] it to be anti-isomorphous

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[621] W. Böttger, *Z. physikal. Chem.* 1903, 46, 559.

[622] O. Schmitz-Dumont, *Ber.* 1939, 72, 298.

[623] C. D. West, *Z. Krist.* 1935, 90, 555.

[624] G. S. Shdanov and E. Schugam, *Acta phys. chem. U.R.S.S.* 1945, 20, 253.

[625] R. Juza and H. Hahn, *Z. anorg. Chem.* 1939, 241, 172.

[626] Id., ib. 1938, 239, 282.

with rhenium trioxide ReO_3, the copper atoms being at the middle of the edges. The C—N distance of 1·90 A (theory Cu—N 2·05; Cu[N] 2·7 A) suggests a covalent linkage, although each nitrogen is surrounded by six copper atoms. It is dissolved by acids with the formation of cupric salts and the precipitation of metallic copper. It is an endothermic compound, being formed from the metal and gaseous nitrogen with absorption of 17·8 k.cals. per Cu_3N.[625]

A compound Cu_3N, perhaps the same, is formed by treating a solution of copper nitrate in liquid ammonia with potassamide KNH_2, and heating the green precipitate that is formed (which may be cuprous amide $CuNH_2$) *in vacuo* to 160°.[627]

Argentous nitride, Ag_3N, is said to occur in Berthollet's explosive silver, which is made by heating a solution of silver oxide in ammonia.[628]

Aurous nitride, Au_3N. Raschig[629] treated aurous oxide with ammonia, and obtained an explosive compound of the composition Au_3N, NH_3 as one of a series of compounds that could not be purified.

Phosphides, Arsenides, etc.

Of these compounds little is known, except of the phosphides of copper. Haraldsen[630] has examined the system Cu+P in detail, by thermal analysis, X-ray analysis, measurement of dissociation tensions, etc.; he finds that there are only two definite compounds, Cu_3P and CuP_2. Cu_3P is got from the elements at 1,000°; it is silvery-white, hard, metallic, friable, and readily soluble in nitric acid. Its existence is proved by its constant dissociation tension (e.g. 100 mm. at 762°). It forms solid solutions with phosphorus up to the composition $CuP_{0·38}$.

CuP_2 is similar: it is metallic, and like Cu_3P diamagnetic. It also forms solid solutions with phosphorus, almost up to the composition CuP_3. Its crystal structure is extremely complicated.

Oxides

Cuprous oxide, Cu_2O. (A suboxide Cu_4O has been described, but there is no good evidence for it.) Cuprous oxide or cuprite is shown by its crystal structure[631] to be a covalent compound. It melts above 1,230°. Its supposed paramagnetism has been shown,[632] as we should expect, to be an error, due probably to the presence of cupric oxide; pure cuprous oxide has the magnetic susceptibility (per gramme) $-0·18 \times 10^{-6}$.

The colour of cuprous oxide varies according to the method of preparation, and is variously described as yellow, orange, red, or even dark brown. It has been supposed that there are two forms of the oxide, yellow and

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[627] F. F. Fitzgerald, *J.A.C.S.* 1907, **29**, 656.

[628] F. Raschig, *Ann.* 1886, **233**, 93.

[629] Ib. 1886, **235**, 349.

[630] H. Haraldsen, *Z. anorg. Chem.* 1939, **240**, 337.

[631] P. Niggli, *Z. Krist.* 1922, **57**, 253. For further references see R. W. G. Wyckoff, *Structure of Crystals*, 2nd ed. 1931, p. 236.

[632] W. Klemm and W. Schüth, *Z. anorg. Chem.* 1931, **203**, 104.

brown, and it is often assumed that the red is the true oxide Cu_2O and the yellow the hydroxide CuOH. But the X-ray measurements of Straumanis and Cirulis[633] have proved that both forms have the same crystal lattice and so are the same substance; the X-ray lines are fewer and less sharp with the yellow specimens, which is a sign that their particle-size is smaller.

Cuprous hydroxide, CuOH. The light yellow colour of the precipitate formed on treating cuprous chloride with alkali suggests that it is a hydroxide; but no definite compound of this composition has been isolated.

Argentous oxide, Ag_2O. G. N. Lewis has shown[634] that in the system $Ag—O_2$ the only stable phases are Ag, Ag_2O, and O_2, so that Ag_4O, if it occurs at all, must be metastable.

Argentous oxide, Ag_2O, is almost black in colour; it separates from solution in ammonia in violet crystals. It has the cuprite lattice, and the Ag—O distance (see above, p. 110) shows that the molecule is covalent.[635] It is difficult to remove the last traces of water from it without its dissociating to some extent.[636] It begins to evolve oxygen at 160°, and does so rapidly at 250°. It readily absorbs carbon dioxide from the air. It is decomposed by light; it reacts with hydrogen peroxide and with ozone to give silver and oxygen; in its reaction with ozone it was shown by Strutt[637] that at low pressures practically every ozone molecule which hits the silver oxide surface is decomposed.

The use of 'moist silver oxide' in organic chemistry to replace halogens by hydroxyl is familiar. The basic character of the oxide is shown in many ways, as in its power of absorbing carbon dioxide. An aqueous suspension of silver oxide has a distinct alkaline reaction, though the solubility is minute ($2{\cdot}2 \times 10^{-4}$ normal, or 27 mg. per litre at 25°). But the hydroxide is amphoteric, with a very minute tendency to dissociate into AgO^- and H^+, the ratio $(AgO^-)/(Ag^+)$ being, according to Laue,[638] about 10^{-4}. It is more soluble in alkaline hydroxide solution than in pure water (about 25 times as soluble in 6·5 normal sodium, potassium, or barium hydroxide), from which it can be calculated that the acid dissociation constant of silver hydroxide is $7{\cdot}9 \times 10^{-13}$.[639] This is about the same as the third dissociation constant of phosphoric acid.

Aurous oxide, Au_2O, can be made by precipitating the aurobromide $K(AuBr_2)$ with alkali. Its solubility in water is 0·04 mg. per litre at 25°. It is a pale grey-violet solid which can be dried at 200°, but gives off oxygen a few degrees above this, and rapidly at 250°. Like silver oxide it is some-

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[633] M. Straumanis and A. Cirulis, *Z. anorg. Chem.* 1935, **224**, 107.

[634] *Z. physikal. Chem.* 1906, **55**, 449.

[635] V. M. Goldschmidt, *Geochem. Vertheilungs. ges.* viii. Oslo, 1927.

[636] See H. B. Baker and H. L. Riley, *J.C.S.* 1926, 2527: the purest oxide they could prepare contained 0·3 per cent. of water.

[637] R. J. Strutt, *Proc. Roy. Soc.* 1912, **87**, 302.

[638] E. Laue, *Z. anorg. Chem.* 1927, **165**, 315.

[639] H. L. Johnston, F. Cuta, and A. B. Garrett, *J.A.C.S.* 1933, **55**, 2311.

what amphoteric; when freshly precipitated it dissolves in alkali, but the solution rapidly deposits gold.

The higher oxides of copper, silver, and gold are described later (pp. 150, 174, 179).

Sulphides, etc.

The sulphides can all be made by heating the elements together, and they are all extremely insoluble in any solvent that does not decompose them.

Cuprous sulphide, Cu_2S, is dimorphic, occurring in a rhombic and a regular form, of which the first is a fairly good conductor of electricity, and the second has a fluorite lattice. The heat of formation from copper and rhombic sulphur is 18·3 k.cals.[640]

Argentous sulphide, Ag_2S, is formed by the direct combination of the elements even in the cold; this is the cause of the tarnishing of silver in the air. The heat of formation from silver and rhombic sulphur is 7·6 k.cals. at 25°.[641] It is decomposed by mercury, especially in presence of sodium chloride, into mercuric sulphide and silver (Mexican 'amalgamation' process for extracting silver); it is probably the least soluble of all the compounds of silver.[642]

Aurous sulphide, Au_2S, is a dark brown solid, whose solubility product is less than 10^{-13}. Dilute acids have no action upon it, but it dissolves in aqua regia, in sulphide solutions, especially polysulphides, and in potassium cyanide.

The system Ag—Te has been examined by Koern, who found[643] that only two compounds were formed, argentous telluride Ag_2Te, and a compound $Ag_{12}Te_7$ both of which are dimorphic.

Halides

With the possible exception of two of the fluorides (CuF, AuF), all the mono-halides of these elements are known, and we have in addition the very singular silver subfluoride Ag_2F. It is convenient to deal with the halides of each metal separately.

Cuprous Halides

Cuprous fluoride, CuF. It is doubtful whether this compound exists in the pure state. Poulenc's supposed preparation from cuprous chloride and gaseous hydrogen fluoride[644] is not accepted by Ruff.[645]

Ebert and Woitinek[646] passed fluorine mixed with chlorine over metallic

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[640] I. A. Korschunov, *J. Phys. Chem. Russ.* 1940, **14**, 134.

[641] A. F. Kapustinski and I. A. Korschunov, ib. 131.

[642] P. Rahlfs, *Z. physikal. Chem.* 1936, B **31**, 157, determines the X-ray structure of Ag_2S, Ag_2Se, and Ag_2Te; they all seem to have ionic lattices, though the oxide (p. 118) is covalent.

[643] V. Koern, *Naturwiss.* 1939, **27**, 432.

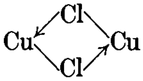
[644] C. Poulenc, *C. R.* 1893, **116**, 1446.

[645] O. Ruff, *Das Fluor*, Berlin, 1920, p. 124.

[646] F. Ebert and H. Woitinek, *Z. anorg. Chem.* 1933, **210**, 269.

copper, and considered that the red layer next to the metal was cuprous fluoride; they examined this with X-rays and concluded that it had a zinc blende lattice; this would be of great interest as showing that the cuprous fluoride had a covalent structure. But the recent work of v. Wartenberg[647] throws great doubt on this. He shows that cupric fluoride CuF_2 melts (not sharply) at about 950°, and the fused mass then loses fluorine, and at 900-1,200° contains about 70 per cent. of cuprous fluoride. But when it solidifies, however suddenly it is quenched, this goes over into metallic copper and cupric fluoride; condensation of the vapour gave nothing but cupric fluoride. Once only a melt on chilling formed a deep red transparent solid composed of 60 per cent. CuF and 40 per cent. CuF_2, which, however, changed over in a few days to a mixture of cupric fluoride and the metal. This certainly suggests that cuprous fluoride is ionized in the solid (fluorine has of course a stronger tendency to ionize than any other halogen), and that accordingly the cuprous ions undergo the normal change to cupric ions and metallic copper.

Cuprous chloride, CuCl, is a colourless substance, usually made by reducing a cupric solution with metallic copper in presence of excess of hydrochloric acid. M.pt. 430°; b.pt. 1,367°. It is polymerized in the vapour to Cu_2Cl_2 even at very high temperatures; the vapour density at 1,700° indicates that it consists almost entirely of double molecules[648]; this conclusion is supported by the absorption spectrum[649]; the structure is presumably



(see below, p. 125). In solvents like pyridine the molecular weight is nearly normal, but such solvents do not contain cuprous chloride but a co-ordination complex.

In the solid state, especially when heated, cuprous chloride is a good conductor of electricity. Frers[650] finds that at 170° the conductivity is almost wholly metallic, but at 200° it is as much as 10 per cent. electrolytic, the only mobile ion being monovalent copper.

Cuprous chloride is almost insoluble in water, the saturated solution at 25° being $1{\cdot}1 \times 10^{-3}$ normal (0·11 g. per litre), but it is readily soluble in hydrochloric acid, in solutions of alkaline chlorides, and in ammonia, owing to the formation of complexes such as $H[CuCl_2]$ and $[Cu(NH_3)_2]Cl]$, which are ionized and soluble (see later under complexes).

Cuprous bromide, CuBr. Pale greenish-yellow; melts at 483° and boils at 1,345°. The saturated aqueous solution at 25° is $2{\cdot}0 \times 10^{-4}$ normal (0·029 g. per litre). It is very similar in every way to the chloride The vapour pressure has been measured statically by v. Wartenberg[651] and

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[647] H. v. Wartenberg, *Z. anorg. Chem.* 1939, **241**, 381.

[648] H. Biltz and V. Meyer, *Z. physikal. Chem.* 1889, **4**, 267.

[649] J. Terrien, *Ann. Phys.* 1938, [xi] **9**, 477.

[650] J. N. Frers, *Ber.* 1927, **60**, 864.

[651] H. v. Wartenberg and O. Bosse, *Z. Elektrochem.* 1922, **28**, 384.

gravimetrically by transport by Jellinek[652]; their results taken together give the molecular weight at 910-1,100° as that of the double molecule Cu_2Br_2. By the same methods it was shown that at these temperatures the iodide is not associated, but is CuI.

Cuprous iodide, CuI, is pure white; it melts at 588° and boils at 1,293°; as we have seen, it is not associated in the vapour. The saturated solution in water at 25° is $2 \cdot 2 \times 10^{-6}$ normal (0·42 mg. per litre). (For a comparison of the solubilities of the cuprous halides with those of the other metals see below, p. 125.) The iodide is very similar (apart from the association) to the other halides, but it differs from them in being formed directly from a cupric salt by warming with potassium iodide:

$$2\,CuSO_4 + 4\,KI = 2\,K_2SO_4 + 2\,CuI + I_2$$

(a reaction used for the quantitative estimation of copper). The iodine ion is so readily oxidized to the neutral iodine atom that it removes a charge from the cupric ion and reduces it to cuprous. Cupric iodide is actually formed in this reaction, but it cannot be isolated, and rapidly loses iodine to give cuprous iodide. The cyanide behaves similarly.

Argentous Halides

We may begin by considering silver subfluoride Ag_2F, which is quite anomalous, and in which it is difficult to say what the valency of the silver is.

Silver subfluoride, Ag_2F. Chemical literature contains a large number of 'sub' compounds, especially subhalides, in which an element, usually a metal, appears with only half its normal valency; examples are K_2Cl, CaCl, CdCl, Cu_4O, and Ag_2Br. All these have been found when fully investigated to be non-existent in any chemical sense*; some of them can live long enough in a vacuum tube to give an absorption spectrum; many prove to be mixtures of the normal compound with excess of the metal. The one member of this group whose existence is beyond doubt is silver subfluoride, Ag_2F. It is made by leaving silver fluoride solution in contact with metallic silver for some time, best at 50° to 90°; dust and light must be carefully excluded.[653-5] It is also formed at the cathode in the electrolysis of silver fluoride solutions with low current density.[656] It forms small but good crystals with a bronze reflex. It is a good conductor of electricity. On heating it begins to decompose into silver and argentous fluoride AgF at 100°, and is completely converted by 200°; it is decomposed by water into silver and silver fluoride. Its crystal structure has been found by Terrey and Diamond[657] to show that it contains neither free silver nor free

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* See, for example, Ag_2Cl (p. 122): Ag_2Br (p. 123).

[652] K. Jellinek and A. Rudat, *Z. physikal. Chem.* 1929, **143**, 58.
[653] A. Guntz, *C.R.* 1890, **110**, 1337; 1891, **112**, 861.
[654] L. Wöhler, *Z. anorg. Chem.* 1912, **78**, 239.
[655] O. Ruff, *Das Fluor*, 1920, p. 38.
[656] A. Hettich, *Z. anorg. Chem.* 1927, **167**, 67.
[657] H. Terrey and H. Diamond, *J.C.S.* 1928, 2820.

argentous fluoride; there are successive layers of silver, silver, and fluorine; the two silver atoms are united to one another, since their distance apart is 2·86 A, which is very nearly twice the normal radius (1·53 A) of the silver atom in the covalent and in the metallic state: the Ag···F distance is 2·46 A, which is the same as that in ordinary (ionized) silver fluoride.

Pauling[658] considers this to be intermediate between a salt and a metal, the bonds between the silver layers being metallic, and those between the silver and the fluorine ionic-covalent (in resonance).

Argentous fluoride, AgF, is peculiar in many ways. It is colourless and melts at 435°; it dissolves in its own weight of cold water, the saturated solution at 25° being 14-normal, and containing 64·2 per cent. of anhydrous salt. It forms hydrates with $4\,H_2O$ stable from $-14°$ to $+18·7°$, and $2\,H_2O$ stable to 39·5°.[659] This is very unlike the usual behaviour of silver salts, which are scarcely ever hydrated, and is in strong contrast to the other silver halides, which are all very insoluble. Fused silver fluoride conducts electricity well, apparently by metallic conduction. It forms acid fluorides AgF_2H and AgF_4H_3,[660] the first no doubt Ag(F···H—F): the other can be formulated in a similar way.

Aqueous silver fluoride has a neutral reaction (both hydrofluoric acid and silver hydroxide are rather weak electrolytes), but it dissolves silver oxide and becomes alkaline. It has been suggested that this is due to the formation of a base $(Ag_2F)OH$, which in view of the linkage of the two silver atoms to one another in silver subfluoride is not impossible.

Silver chloride. AgCl (horn silver). This white crystalline solid melts at 449° to an orange-yellow liquid, which boils at 1,554°. The saturated solution in water at 25° is only $2·1 \times 10^{-4}$ normal (30 mg. per litre). It appears to be less associated in the vapour than cuprous chloride; H. Biltz and V. Meyer[661] found the density at 1,735° only 20 per cent. greater than corresponds to AgCl, but at a lower (unspecified) temperature it was some 50 per cent. higher than this.

Silver chloride is soluble in solutions of many salts, such as potassium cyanide, sodium thiosulphate, concentrated solutions of potassium chloride or hydrochloric acid, and in ammonia, in every case through the formation of complexes.

Silver subchloride, Ag_2Cl, has been described,[662] but the supposed arrest in the E.M.F. curve for the system Ag—AgCl ,which was believed to show its existence, has been found to be due to an error.[663]

Silver bromide, AgBr, m. pt. 419°; saturated solution in water at 25° $2·9 \times 10^{-5}$ normal (5·5 mg. per litre). It resembles silver chloride in every way.

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[658] *Chem. Bond*, 1st ed. 401; 2nd ed. (1942), 421.

[659] W. Jahn-Held and K. Jellinek, *Z. Elektrochem.* 1936, **42**, 608.

[660] A. Guntz, *Bull. Soc.* 1895, [3] 13, 114.

[661] *Z. physikal Chem.* 1899, **4**, 268.

[662] A. Guntz, *C.R.* 1891, **112**, 861.

[663] See E. Baur, *Z. physikal. Chem.* 1903, **45**, 613; H. Weiss, ib. 1906, **54**, 305.

Solid silver bromide has a relatively high electrical conductivity when heated. Tubandt and Lorenz[664] showed that the specific conductivity is 0·44 reciprocal ohms in the solid state at 410° and 2·76 when melted at 422°. This was explained by Frenkel[665] by supposing that the argentous ions can leave their places in the lattice (which can then be filled up by other argentous ions) and occupy intermediate positions. A study of the density and lattice constants of the salt at 410^c supports this conclusion.[666]

Silver bromide is of great importance from its use in photography. The nature of the reduction product which makes the silver bromide grains more easily reduced to metal has been much disputed. It has been shown by E. J. Hartung[667–9] not to be a subhalide. Later work, especially on the physics of the solid phase (see Mott[670–1] and Huggins[672]), has indicated that the change is physical rather than (in the ordinary sense) chemical.

Silver iodide, AgI. This compound has remarkable properties in the solid state.[673–4] It is trimorphic. The liquid solidifies at 555° to the dark brown α-form, which is regular (cubic). This gets paler on cooling, and changes at 146° to the greenish-yellow hexagonal β-form. This can remain in the metastable state down to much lower temperatures, but below 137° the stable form is the γ, which like the α is cubic. There is a remarkable contraction on going from β to α; the densities at 145·8° are α 6·00, β 5·68.[673] According to Wilsey[675] the γ-form has a zinc blende lattice and the β a wurtzite. The later examination of the β-form by Helmholz[674] shows that at $-180°$ C. it has an almost exact wurtzite lattice, but at ordinary temperatures there is probably a random distribution of silver atoms among 4 positions which surround tetrahedrally the ideal wurtzite positions, the Ag$\cdots$I distances being 2·74 and 3·03 A (theory Ag—I 2·86, Ag[I] 3·33).

The structure of the α (high-temperature cubic) form is equally remarkable. According to Strock[673] it consists essentially of a body-centred cubic lattice of iodine atoms 2·18 A apart: in the 30 largest gaps in this structure the silver atoms are placed at random. The Ag$\cdots$I distances depend on the co-ordination numbers of the silver (the number of iodine atoms at this distance from it) thus:

Co-ord. No. . . .	2	3	4
Distance . . .	2·52	2·67	2·86 A.U.

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[664] C. Tubandt and E. Lorenz, ib. 1914, **87**, 513.

[665] J. Frenkel, *Z. Phys.* 1926, **35**, 652.

[666] C. Wagner and J. Beyer, *Z. physikal. Chem.* 1936, B **32**, 113.

[667] *J.C.S.* 1924, **125**, 2198 ($Ag+Br_2$).

[668] Ib. 1925, **127**, 2691 ($Ag+Cl_2$).

[669] Ib. 1926, 1349 ($Ag+I_2$).

[670] R. W. Gurney and N. F. Mott, *Proc. Roy. Soc.* 1938, **164**, 151.

[671] N. F. Mott, *Phot. J.* 1938, **78**, 286 [*B.C.A.* 38 i. 318].

[672] M. L. Huggins, *J. Chem. Phys.* 1943, **11**, 412, 419.

[673] L. W. Strock, *Z. physikal. Chem.* 1934, B **25**, 441.

[674] L. Helmholz, *J. Chem. Phys.* 1935, **3**, 740.

[675] R. B. Wilsey, *Phil. Mag.* 1923, **46**, 487.

This structure explains the high conductivity of the solid, and the way silver atoms diffuse into and out of it.

Silver iodide is extremely insoluble in water; the saturated solution at 25° is $2{\cdot}4 \times 10^{-7}$ normal (0·056 mg. per litre). Its solubility in ammonia is much less than that of the chloride or the bromide; the tendency to complex formation is not strong enough to overcome the effect of the extremely small solubility product. Silver iodide is moderately soluble in sodium thiosulphate and in concentrated hydrochloric acid.

Aurous Halides

Aurous fluoride, AuF. Moissan claimed to have obtained this compound, but Lenher[676] was unable to repeat the work, and Ruff[677] considers that up to 1920 no definite fluoride of gold had been obtained. The instability of aurous fluoride is probably due to the same cause as that of cuprous fluoride, the strong tendency of the fluorine to ionize, and the great instability of the aurous as of the cuprous ion.

Aurous chloride, AuCl, is formed by heating auric chloride $AuCl_3$ to 200°, but it decomposes a little above that temperature. It is unstable and even when dry slowly changes in the cold into auric chloride and gold; this change is at once brought about by water. From the dynamics of the reversible reaction between chlorine gas and gold at 500–900° Biltz[678] showed that at these temperatures the vapour was essentially Au_2Cl_2. He got no evidence of the formation of a dichloride $AuCl_2$ (as with copper and silver) or of a complex salt of this with potassium chloride.[679]

Aurous bromide, AuBr. Obtained by warming bromauric acid $HAuBr_4$ until it is converted into auric bromide, and then carefully heating this to 115°. A little above this temperature it decomposes into its elements. Water decomposes it to auric bromide and metallic gold.

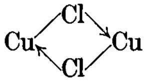
Aurous iodide, AuI. This compound is markedly endothermic (−5·52 k.cals.), but it is more easily made than the other halides. It is formed from auric iodide at the ordinary temperature: from auric oxide and hydriodic acid: by the action of potassium iodide solution on auric chloride, or of iodine on gold at 50°.

Aurous iodide is more slowly acted on by water than the other halides; water and dilute acids decompose it only on warming. This is no doubt due to its smaller solubility.

It will be seen that the order of solubilities of the monovalent halides, as observed for copper and silver, and inferred for gold, is the same for all of them Cl > Br > I. The measured solubilities of the halides of copper and silver are as follows:

Compound	*Normality* $\times 10^4$	*Mg./L.*	*Compound*	*Normality* $\times 10^4$	*Mg./L.*
CuF	. .	. .	AgF	140,000	1,800,000
CuCl	11·0	110	AgCl	2·0	30
CuBr	2·0	29	AgBr	0·29	5·5
CuI	0·022	0·42	AgI	0·0024	0·056

There is an evident tendency for the monovalent halides of these metals to form double molecules in the vapour. This is common among the covalent halides (other than the fluorides) of metals and semi-metals of groups I, II, and III. It is clearly due to co-ordination with the halogen atom as donor and the metal as acceptor. This involves for a double molecule a structure of the type with angles of 90° on the average, in which the metal has a quartet of shared electrons. We have evidence that with such a quartet the natural angle of the valencies is 180° (see, for example, $M[Ag(CN)_2]$), but also that it is very easily deformed,* so that this structure does not seem to involve an excessive strain.



Derivatives of Oxy-acids

As we have already seen, the tendency of cuprous and aurous ions to go over into the polyvalent state with separation of the metal greatly limits their power of forming salts. Practically no simple aurous salts are known, and the only cuprous salts are those in which the cation is complex. A few (probably covalent) cuprous derivatives of carboxylic acids are known. On the other hand, the argentous salts of most of the oxyacids have been prepared.

The silver salts of oxy-acids show curious changes of colour. It was suggested by Pitzer and Hildebrand[680] that the colour of a compound formed from colourless ions is proportional to the degree of covalent character in the links between them. This view, which is supported by a comparison of the colours and bond lengths in a series of binary iodides, has been applied by Helmholz[681-2] to the silver derivatives of oxy-acids; he gives the following table† (theory for ionic [Ag]O 2·45, for covalent Ag—O 2·19 A):

Compound	*Mean dist.* Ag···O	*Colour*
$AgClO_3$	2·54 A	Colourless
Ag_2SO_4	2·50	Colourless
$KAgCO_3$	2·42	Colourless
Ag_3PO_4	2·34	Yellow
Ag_3AsO_4	2·34	Deep red
Ag_2CO_3	2·30	Yellow
Ag_2O	2·06	Black

* For evidence of this see $Hg(C_6H_5)_2$, II. 309.

† For reference see [682].

[676] V. Lenher, *J.A.C.S.* 1903, **25**, 1136.

[677] O. Ruff, *Das Fluor*, 1920, p. 125.

[678] W. Blitz, W. Fischer, and R. Juza, *Z. anorg. Chem.* 1928, **176**, 125.

[679] W. Blitz and W. Fischer, ib. 81.

[680] K. S. Pitzer and J. H. Hildebrand, *J.A.C.S.* 1941, **63**, 2472.

[681] L. Helmholz and R. Levine, ib. 1942, **64**, 354.

[682] J. Donohue and L. Helmholz, ib. 1944, **66**, 295.

Carboxylic Acid Derivatives

Formates

Cuprous formate $Cu \cdot O \cdot CHO$ is made by dissolving cuprous oxide in excess of formic acid, and precipitating with alcohol; air must be carefully excluded.[683] It forms colourless crystals which are stable when dry, but are at once hydrolysed by water with the separation of cuprous oxide, and on treatment with aqueous formic or sulphuric acid are converted into the cupric salt and metallic copper. We should expect that the formate like the acetate would be volatile on heating, but this point was not investigated.

The argentous and aurous formates do not seem to have been made.

Acetates

Cuprous acetate, $Cu \cdot O \cdot CO \cdot CH_3$. When cupric acetate is heated *in vacuo* to temperatures above 220° a sublimate of cuprous acetate is formed, while carbon dioxide, acetic acid, and other decomposition products are evolved.[686]

Cuprous acetate is a colourless crystalline compound which very easily volatilizes, and is at once hydrolysed by water with precipitation of yellow cuprous oxide Cu_2O.

Silver acetate, $Ag \cdot O \cdot CO \cdot CH_3$, is a perfectly stable compound, of which 1·12 g. dissolve in 100 g. of water at 25° C.[688] It seems to behave completely as a salt, and to be non-volatile.

Aurous acetate is unknown.

Oxalates

According to Daniels[689] cuprous oxalate $Cu_2C_2O_4, H_2O$ can be made by the action of oxalic acid on cuprous oxide or sulphite, and is a brown substance which on heating turns first grey and then greenish-blue, and explodes feebly. His material was probably impure.

Argentous oxalate is a colourless crystalline substance which on heating undergoes the exothermic reaction[690]

$$Ag_2C_2O_4 = 2\,Ag + 2\,CO_2 + 29{\cdot}5 \text{ k.cals.}$$

The reaction begins about 140° and easily becomes explosive. The silver is obtained in an extremely bulky form, partly as a grey smoke.[691] The salt is almost insoluble in water, of which 100 g. dissolve 3·79 mg. at 21°.[692]

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[683] A. Angel, *J.C.S.* 1906, **89**, 345.

[686] A. Angel and A. V. Harcourt, ib. 1902, **81**, 1385.

[688] J. Knox and H. R. Will, *J.C.S.* 1919, **115**, 853.

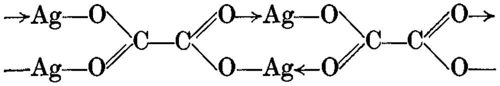
[689] Ll. C. Daniels, *J.A.C.S.* 1915, **37**, 1169.

[690] C. Hoitsema, *Z. physikal. Chem.* 1896, **11**, 143.

[691] V. Kohlschutter and E. Eydmann, *Ann.* 1913, **398**, 9.

[692] G. S. Whitby, *Z. anorg. Chem.* 1910, **67**, 108.

The crystal structure of silver oxalate has been examined by Griffith.[693] It consists of a series of chains



held together in sheets by cross Ag—O links. In the chain the Ag—O distances are 2·17 and 2·30 (theory Ag—O 2·19); between the chains in the sheet 2·58 and 2·61; between the sheets 2·93 and 3·00. The distance between the two Ag atoms in the chelate ring is 3·56 A (in the metal Ag···Ag is 2·88 A).

Aurous oxalate is not known.

Salts of oxy-acids of elements of the 5th, 6th, and 7th periodic groups are numerous with silver, but the corresponding cuprous and aurous derivatives have not been prepared.

Oxy-salts of Nitrogen

Silver hyponitrite, $Ag_2N_2O_2$, is a pale yellow anhydrous salt scarcely more soluble in water than silver chloride; it is made by adding silver nitrate to the sodium hyponitrite solution obtained by reducing sodium nitrite with sodium amalgam.

Silver nitrite, $AgNO_2$, forms pale yellow hair-like crystals. It is relatively unstable and at 100° or above decomposes reversibly according to the equation

$$2\,AgNO_2 \rightleftharpoons Ag + AgNO_3 + NO,$$

the decomposition evolving 13·4 k.cals. per g.-atom of silver.[694] 100 g. of water at 25° dissolve 0·414 g. of the salt.[695] This salt is of course used for the preparation of aliphatic nitro-compounds; for example, ethyl iodide reacts with it to give about equal quantities of ethyl nitrite and nitroethane, whereas with potassium nitrite it gives only the nitrite. This has been explained by supposing that the silver compound is derived from H—NO_2 and the potassium salt from H—O—N═O; but of course the nitrite ion has the same structure ($\bar{\text{O}}$—N═O) whether it is derived from one form or the other.

Silver nitrite forms a series of double salts such as $Cs[Ag(NO_2)_2]$, which are discussed below, p. 138.

Silver nitrate, $AgNO_3$. This familiar salt melts at 208·6°, and forms no hydrates down to its cryohydric point of −7·5°.[696] It is dimorphic with a transition point of 159·8°[697]; its solubility in water can be followed up to its melting-point.[698–9] It is very soluble not only in water where it gives

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[693] R. L. Griffith, *J. Chem. Phys.* 1943, **11**, 499.

[694] M. Randall, G. G. Manov, and O. L. I. Brown, *J.A.C.S.* 1938, **60**, 694.

[695] H. J. M. Creighton and W. H. Ward, ib. 1915, **37**, 2333.

[696] W. Middelberg, *Z. physikal. Chem.* 1903, **43**, 313.

[697] J. v. Zawidzki, ib. 1904, **47**, 721.

[698] D. J. Hissink, ib. 1900, **32**, 543.

[699] A. N. Campbell and M. L. Boyd, *Canad. J. Res.* 1943, **21 B**, 163.

an abnormally small depression of the freezing-point, suggesting association,[700] but also in alcohols, the lower esters, amines, and nitriles, as is shown by the following list (from Seidell[701]), which gives the solubilities in moles of silver nitrate to 100 moles of solvent at 25° or 20°:

Water 27·2 (72 per cent. salt at 25°).

Alcohols, etc.: Methyl alcohol 0·679; ethyl 0·566; isopropyl 0·678; isoamyl 0·343. Ethyl acetate 1·38; acetone 0·215.

Nitrogen compounds: Aniline 9·77; pyridine 21·3; quinoline 3·66; acetonitrile 41·6; benzonitrile 9·16.

The large effect of the nitrogenous solvents (which is no doubt due to solvation of the silver) is obvious.

Oxy-salts of Sulphur

Silver sulphite, Ag_2SO_3, is a white solid, very slightly soluble in water. It is unstable, and sensitive to light; it is decomposed by boiling water into silver, silver sulphate, and sulphur dioxide.

Silver sulphate, Ag_2SO_4: sol^{y}* 0·83/25°.[702] From acid solutions an acid sulphate can be obtained.

Silver thiosulphate, $Ag_2S_2O_3$, is insoluble in water. It slowly decomposes to silver sulphide and sulphuric acid, and forms numerous complex salts.

Oxy-salts of the Halogens

Silver chlorite, $AgClO_2$: yellow; sol^{y} 0·45/25°, 2·13/100°.[703] It explodes at 105°.

Silver chlorate, $AgClO_3$: melts at 230° and decomposes into silver chloride and oxygen at 270°. Sol^{y} 20 at ordinary temperature. The bromate and iodate are known; their solubility in water falls off rapidly, being for the bromate 0·204/25°,[704] and for the iodate 0·024/75°.[705] Silver bromate gives a double salt AgBrO, $NaBrO_3$, which forms solid solutions with it.

Silver perchlorate, $AgClO_4$, is one of the most remarkable of salts. Unlike nearly all other silver salts it forms a hydrate: it is abnormally soluble in almost all solvents, even hydrocarbons: it forms solid compounds with benzene and toluene: in benzene solution it is highly polymerized, and at extreme dilution it has the large dipole moment of a salt (10·7 D.). Its properties are considered in detail under perchloric acid (Gp. VII. 1230).

Silver periodate. Various salts with complicated formulae are known; they are nearly all derived from the acid H_5IO_6, the simplest being Ag_5IO_6.

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* This symbol is used throughout the book to mean grammes of anhydrous salt to 100 g. of water (or other solvent if specified) in a saturated solution at the temperature given.

[700] See N. V. Sidgwick and E. K. Ewbank, *J.C.S.* 1924, **125**, 2273.

[701] A. Seidell, *Solubilities*, 2nd ed., New York, 1920.

[702] E. L. Simons and J. E. Ricci, *J.A.C.S.* 1946, **68**, 2194.

[703] G. R. Levi, *Atti R.* 1923, [5] **32**, i. 623.

[704] J. E. Ricci and J. J. Aleshnick, *J.A.C.S.* 1944, **66**, 980.

[705] W. P. Baxter, ib. 1926, **48**, 615.

Silver permanganate, $AgMnO_4$ (1 g. of which will dissolve in 100 g. of cold water), is peculiar in having in solution a much greater oxidation potential than an alkaline permanganate[706–7]; the cold solution absorbs hydrogen far more readily than potassium permanganate; silver salts, especially the nitrate, increase this, and the reactivity is greater to organic substances as well. This effect may be due to the presence of undissociated silver permanganate, or to the catalytic influence of the silver ion, as in oxidations with persulphates. In pyridine solution, where the complex cation is that of $[Ag(py)_2]MnO_4$, the reactivity is less.

Silver perrhenate, $AgReO_4$ is colourless; it melts at 430°[707a]; its sol^y is 0·32/20°, less than that of the permanganate.[708]

COMPLEX DERIVATIVES OF UNIVALENT COPPER, SILVER, AND GOLD

These three elements, even in the univalent state, have a great tendency to form complex compounds by co-ordination, as might be expected from their high deforming power and low position in the electrochemical series.

The complexes formed by an element are of importance as showing how that element behaves when the restriction imposed on the covalency by the number of valency electrons is removed. The two fundamental points to notice about the complexes are the number of links which the atom forms (its co-ordination number) and the nature of the atoms (nitrogen, oxygen, halogens, etc.) with which it forms them.

The stability of a complex group XA_n will be determined by that of the X—A link, together with the influence on this of the number of such links that are formed, and no doubt that of the resulting charge if any on the complex. On all these points we have very little *a priori* knowledge, and this makes it the more important to collect and compare the known facts about complex formation.[709]

The corresponding compounds of the three metals in their monovalent state are sufficiently similar to be treated together. They include both open-chain and ring complexes, but the latter are few with these monovalent elements, and confined to those that are linked through oxygen or sulphur or both. The complexes are classified by the nature of the donor atoms, which can be carbon, nitrogen, phosphorus, arsenic, oxygen, sulphur, or the halogens.

1. *Donor atom Carbon*

These include addition compounds of ethylene and its derivatives; of carbon monoxide; of the CN group; and of isonitriles.

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[706] F. Hein and W. Daniel, *Z. anorg. Chem.* 1929, **181**, 78.

[707] F. Hein, W. Daniel, and H. Schwedler, ib. 1937, **233**, 161.

[707a] D. Vorländer and G. Dalichau, *Ber.* 1933, **66**, 1534.

[708] J. and W. Noddack, *Z. anorg. Chem.* 1929, **181**, 25.

[709] See further N. V. Sidgwick, *J.C.S.* 1941, 433.

1. (*a*) *Ethylene derivatives*

Berthelot[710] observed that ethylene dissolves in a solution of cuprous chloride in dilute hydrochloric acid. Manchot and Brandt[711] showed that if ethylene is passed into water containing cuprous chloride in suspension, both the gas and the chloride dissolve, the amount of gas reaching one molecule per copper atom ($CuCl,C_2H_4$), or nearly so, at 0° under 1 atmosphere pressure. The compound will not separate out, being far more highly dissociated than the corresponding carbon monoxide compound (p. 131) in spite of the fact that ethylene is about six times as soluble in water as carbon monoxide. The addition of concentrated hydrochloric acid or a rise of temperature breaks up the complex.

Solid cuprous chloride also can take up ethylene under pressure.[712] According to Gilliland and his colleagues[713] solid cuprous chloride will absorb (mostly under pressure) ethylene, propylene, and isobutylene, the first two up to one molecule per copper atom, the dissociation tensions being about 1 atmosphere at the temperatures: CuCl, ethylene $-8{\cdot}3°$; propylene $-11{\cdot}5°$; butylene $-6{\cdot}0°$. Cuprous bromide forms a compound with ethylene which has a dissociation tension of 17·5 atmospheres at 0°.

Argentous complexes of ethylene derivatives are also known, though so far only in solution. Lucas and his colleagues[714-15] have established their existence by determining the partition of unsaturated hydrocarbons (and certain unsaturated oxygen compounds) between carbon tetrachloride and an aqueous solution of (*a*) potassium nitrate, (*b*) silver nitrate, (*c*) a mixture of the two salts, the total ionic concentration being kept at 1-normal. If we call the unsaturated hydrocarbon B, it was found that the equilibrium constant

$$K = \frac{[B \cdot Ag^+]}{[B] \cdot [Ag^+]}$$

remained constant when the concentration of the silver ion was changed. A large number (7) of unsaturated hydrocarbons with one or two* double links were examined. The values of K vary from about 900 to 13 (at 25°). They seem to fall steadily as more of the hydrogen atoms in the ethylene are replaced by alkyl groups. Thus we have the values

$RHC{=}CH_2$	$R_2C{=}CH_2$	$RHC{=}CHR$	$R_2C{=}CHR$
925	62	63	13
860		79 (cy)	

* Where there are two double links the constant should obviously be halved.

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[710] M. Berthelot, *Ann. Chim. Phys.* 1901, **23**, 32.

[711] W. Manchot and W. Brandt, *Ann.* 1909, **370**, 286.

[712] H. Tropsch and W. J. Mattox, *J.A.C.S.* 1935, **57**, 1102.

[713] E. R. Gilliland, J. E. Seebold, J. R. Fitz-Hugh, and P. S. Morgan, ib. 1939, **61**, 1960.

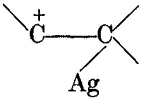
[714] W. F. Eberz, H. J. Welge, D. M. Yost, and H. J. Lucas, *J.A.C.S.* 1937, **59**, 45.

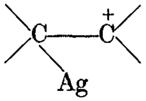
[715] S. Winstein and H. J. Lucas, ib. 1938, **60**, 836.

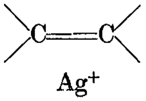
(cy = cyclohexene); when there are two double links which are conjugated, the constant is very much reduced; thus for $H_2C{=}CH \cdot CH_2 \cdot CH_2 \cdot CH{=}CH_2$ it is 1,850 (2 × 925), whereas for $H_2C{=}CMe \cdot CMe{=}CH_2$ it is only 22·5.

The constants for cyclohexene and trimethylethylene were determined at 0° and 25°, and the results showed that the heat of linkage of the double C=C link to the silver is about 6·0 k.cals. (6·01 and 5·80 for these two hydrocarbons); for the amine ion $[Ag(NH_3)_2]^+$ it is found to be 2 × 6·7 k.cals.

The authors suggest that the structure of the complex is that of a resonance hybrid between the three forms



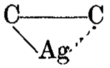




a view which is supported by the Raman spectra of the products.[716]

This is effectively a 3-ring; but they point out that the strain due to this contraction of the valency angle must be less than a third of that in cyclopropane, since only one angle is concerned, and this is larger than 60° owing to the greater size of the silver atom: the strain should therefore be less than the resonance energy, which they estimate at about 10 k.cals.

Now if we take the radii of the atoms concerned as 0·77 for carbon and 1·35 for silver, the angle



will be 65° 34′, and so the Baeyer strain or deflection of the valency angle 44°, compared with 49° 30′ in cyclopropane. As a rough approximation the strain is proportional to the square of the angular contraction, and it should therefore be $(44/49{\cdot}5)^2$ or 0·790 of the strain on one carbon atom of the 3-ring. Now the total strain energy in cyclopropane is almost the same per molecule as in ethylene, 17·2 k.cals., or 5·73 k.cals. per angle. Hence the strain in one angle of the silver-ethylene complex should be 5·73 × 0·790 or 4·53 k.cals., and much less than the resonance energy, if that is about 10 k.cals.

No corresponding aurous compounds are known.

1. (*b*) *Carbon Monoxide Complexes*

It has long been known that solutions of cuprous chloride, for example in ammonia, will absorb carbon monoxide, and this fact is used in gas analysis. W. A. Jones[717] isolated a solid compound; on re-examining this, Manchot and Friend[718] found that cuprous chloride dissolved in dilute or concentrated hydrochloric acid or ammonia, or suspended in water, absorbs carbon monoxide, and at 0–12° very nearly one molecule per atom of copper; on heating, the solution loses its carbon monoxide again below

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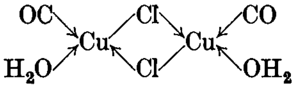
[716] H. J. Taufen, M. J. Murray, and F. F. Cleveland, *J.A.C.S.* 1941, **63**, 3500.

[717] *Amer. Chem. J.* 1899, **22**, 287.

[718] W. Manchot and J. A. N. Friend, *Ann.* 1908, **359**, 100.

100°. From the cold solution a compound $CuCl,CO,H_2O$ separates in colourless crystals, which lose carbon monoxide slowly in air; no addition product with hydrogen chloride can be made to separate, even from concentrated hydrochloric acid. When the solid product is treated with either strong sulphuric acid or alcohol (i.e. with a dehydrating agent) a rapid evolution of carbon monoxide takes place. Cuprous bromide and iodide behave in the same way, but the compounds were not analysed.

Cuprous chloride in contact with, or dissolved in, organic bases such as aniline, piperidine, or pyridine will absorb carbon monoxide in the same way, but it will not do so in the dry state except under high pressure[719]; this is the more remarkable since ethylene is absorbed by the dry salt, although no ethylene complex can be isolated. This seems to show that a co-ordinated molecule of water or a base is a necessary constituent of the carbon monoxide (but not the ethylene) complex. If we suppose that in this as in most other carbon monoxide complexes the central atom has the effective atomic number of an inert gas (36 for copper), this would explain why such a further co-ordinated molecule is required; the complex is presumably dimeric, being derived from the Cu_2Cl_2 molecule, in which the copper atom has $29+3 = 32$ electrons. In such a molecule as



the necessary four extra electrons per copper atom are added.

The carbon monoxide complex is oxidized by oxygen or by the cupric ion with separation of carbon dioxide; hence a solution of cuprous halide in ammonia will absorb carbon monoxide and oxygen from a mixture of carbon monoxide and air, oxidizing it to carbon dioxide, and so forming ammonium carbonate[720]; the chloride is much the most efficient halide for this purpose.[721]

Evidence for the existence of a copper carbonyl has been got by passing halogen-free carbon monoxide over heated copper. A metallic mirror is formed in the hotter parts of the tube.[723]

No corresponding silver compounds have been isolated, but Manchot[722] has shown that a solution of silver sulphate in sulphuric acid, especially fuming, absorbs carbon monoxide rapidly and largely (up to 9·6 litres/Ag at 0°, i.e. 0·86 mol. CO per Ag_2SO_4); the reaction is reversible, and the carbon monoxide is expelled on warming; the solution remains colourless.

A similar (but anhydrous) aurous compound AuCl,CO was made by Manchot and Gall[724] by the action of carbon monoxide on solid aurous

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[719] O. H. Wagner, *Z. anorg. Chem.* 1931, **196**, 364.

[720] K. Leschewski, H. G. Tolkmitt, and H. Möller, ib. 1938, **235**, 369, 385.

[721] H. Möller and K. Leschewski, ib. 1939, **243**, 185.

[722] W. Manchot J. König, and H. Gall, *Ber.* 1924, **57**, 1157.

[723] H. Bloom, *Nature*, 1947, **159**, 539.

[724] W. Manchot and H. Gall, *Ber.* 1925, **58**, 2175.

chloride at 90°; it can be made more easily by passing carbon monoxide into a solution of auric chloride in tetrachloroethylene at 100-140°[725]; in this latter reaction the auric chloride is first converted by the carbon monoxide into aurous chloride and phosgene $COCl_2$. The complex AuCl,CO forms colourless crystals which are soluble in benzene and ether; the molecular weight was found cryoscopically in benzene to be 230: the simple formula AuCl,CO requires 260, but the substance may have contained a little phosgene. It is extraordinarily sensitive to water, evolving carbon monoxide and precipitating metallic gold: even moist air brings about this change. It is decomposed in the same way by alcohol, but not by acetic acid. It reacts with the Grignard reagent R·MgBr like cuprous chloride, giving metallic gold, magnesium halide, and the hydrocarbon R_2. Kharasch and Isbell (loc. cit.) have obtained evidence that at least when R is aromatic, an intermediate aurous aryl is formed (see above, p. 115).

1. (*c*) *Cyanide Complexes*

All three metals in the monovalent state have a strong tendency to form complexes with cyanide groups. Such complex cyanides are very numerous over the whole periodic table; they might be supposed to have the metal attached either to carbon or to nitrogen. Their structure is discussed later under the cyanides (V. 671) and it is concluded that the M—C—N formula is correct.

Complex Cuprous Cyanides. The tendency of this element to form cyanide complexes is so strong that copper will dissolve in concentrated potassium cyanide solution with evolution of hydrogen. Solid salts of three simple types have been obtained[726-7]; $M[Cu(CN)_2]$, $M_2[Cu(CN)_3]$, and $M_3[Cu(CN)_4]$. E.M.F. measurements have shown[728] that the solution contains mainly $[Cu(CN)_4]'''$ ions, but some $[Cu(CN)_3]''$, especially in higher dilutions; practically the whole of the copper is in complex forms, a solution in which the potassium cyanide is normal and the cuprous concentration decinormal having a concentration of free cuprous ions of 5×10^{-29} (one single atom in 33,000 litres). The 4-covalent ion is unusually stable, its dissociation constant (to $Cu^+ + 4CN^-$) being 2×10^{-27},[728] so that it is far more stable than any of the complex cuprous halides.

The tendency for the co-ordination number to reach 4 is more marked with the cyanides than with any other group of cuprous complexes.

Complex Argentous Cyanides. The tendency to complex formation is very strong here too. For the dicovalent complex $K[Ag(CN)_2]$ it is found that the equilibrium constant

$$K = \frac{[Ag(CN)_2^-]}{[Ag^+]\cdot[CN]^2} = 2{\cdot}63 \times 10^{18},$$

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[725] M. S. Kharasch and H. S. Isbell, *J.A.C.S.* 1930, **52**, 2919.

[726] H. Grossmann and P. v. d. Forst, *Z. anorg. Chem.* 1905, **43**, 94.

[727] J. Brigando, *C.R.* 1942, **214**, 908.

[728] F. Kunschert, *Z. anorg. Chem.* 1904, **41**, 359.

so that in a decinormal solution of this salt the concentration of silver ions is $1{\cdot}6 \times 10^{-6}$. It is on the stability of this complex that the use of cyanides in electroplating depends. The effect is a double one: at the lower concentration of silver ions a more coherent deposit is obtained, and also the danger of direct electro-chemical deposition of silver by the corrosion of the electrode is avoided.

The stable cyano-complexes are the 2- and 3-covalent, $M[Ag(CN)_2]$ and $M_2[Ag(CN)_3]$. The 4-co-ordinated complex is not stable with silver as it is with copper. See further Brigando.[727]

In the $[Ag(CN)_2]^-$ ion it has been shown[729] by X-ray analysis that the atoms N—C—Ag—C—N are in a straight line, the Ag···N distance being 3·29 A.U. (calculated 3·45).

Complex Aurous Cyanides. The ion $[Au(CN)_2]^-$ is formed with great readiness, so that gold will dissolve in potassium cyanide solutions in presence of oxidizing agents, among which atmospheric air is included, as Faraday first pointed out. In the original cyanide process for extracting gold, which first came into use in Australia in 1888, the oxidizing agent was the dissolved oxygen in the solution, but as there is very little of this, it was necessary to use very dilute solutions; it was subsequently found that by adding sodium peroxide much stronger solutions of cyanide could be used. According to Bodländer[730] the E.M.F. measurements show that even if we assume that aurous chloride is completely dissociated the equilibrium constant has the enormous value

$$K = \frac{[Au(CN)_2^-]}{[Au^+]\cdot[CN^-]^2} = 2{\cdot}5 \times 10^{29}.$$

Bodländer also shows that gold will precipitate silver from the argenticyanide $K[Ag(CN)_2]$ solution until the ratio of gold to silver in the solution (i.e. of their complex ions) is 820:1. The free acid $H[Au(CN)_2]$ is unstable, and loses hydrocyanic acid at once.

Although the dicovalent ions $[Au(CN)_2]^-$ are more stable than the corresponding cuprous and argentous complexes, they do not seem to be able to take up a third CN group as the others can. They are converted by the halogens into the 4-covalent auric complexes $K[Au(CN)_2(hal)_2]$,[731] 4 being the invariable covalency of the auric compounds.

1. (*d*) *Co-ordination Complexes of Isonitriles*

These are formed by monovalent copper and silver, but not gold.

Guillemard[732] found that compounds of the type CuCN,R·NC (where R = ethyl, propyl, isobutyl) can be made by the direct combination of their components. They are all colourless crystalline solids which dissociate very readily.

[729] J. L. Hoard, *Z. Krist.* 1933, **84**, 231.

[730] G. Bodländer, *Ber.* 1903, **36**, 3933.

[731] C. G. Lindbom, *Ber.* 1877, **10**, 1725; *Bull. Soc. Chem.* 1878, [2] **29**, 416.

[732] H. Guillemard, *Ann. Chim. Phys.* 1908, [8] **14**, 424 (C. 08. II. 583).

The isonitrile compounds of silver are at least as numerous as those of copper. As early as 1869 Gautier showed[733] that methyl iodide reacts with 2 molecular proportions of silver cyanide in a sealed tube at 100° to give silver iodide and a compound of the composition of $AgCN,CH_3NC$, which must be presumed to be an addition product of an isonitrile, since it liberates an isonitrile on heating. The reaction is, however, somewhat complicated, for it was found by Hartley[734] that methyl iodide and silver cyanide combine in the cold to form a compound $2\ AgCN,CH_3I$, which at 40° takes up more methyl iodide to form $AgCN,CH_3I$. The double salt $K[Ag(CN)_2]$ will not react with methyl iodide.

A series of complexes of this type $AgCN,R\cdot NC$ were made by Guillemard[732] by the direct combination of the components. They are colourless crystalline substances (methyl, m.pt. 75°; ethyl 96°; propyl, isobutyl, isoamyl also made) which have a strong smell of isonitrile. They are insoluble in water and most organic solvents, but easily soluble in alcohol; strong acids and boiling aqueous alkalies decompose them. On heating, a mixture of the nitrile and the isonitrile comes off.

No aurous isonitrile complexes are known.

2. *Donor atom Nitrogen*

2. (*a*) *Co-ordination Compounds of Nitriles*

Cuprous compounds of this kind are known, and some argentous, but no aurous.

Cuprous nitrile compounds such as $CuCl,CH_3CN$ can be made by the action of a simple nitrile on the solid cuprous halide or its solution in hydrochloric acid,[735] or by dissolving copper powder in a solution of cupric chloride or bromide in acetonitrile.[736] These compounds are nearly all 1:1 except the derivative of succinonitrile, which, having 2 CN groups, takes up 2 CuCl. They are soluble in the nitrile but not in water, which slowly decomposes them. It is singular that if the compound is treated with ferric chloride the copper is at once oxidized to the cupric state, and the nitrile liberated[735]; it would seem that the power that copper has of co-ordinating with nitriles is limited to the cuprous state.

A saturated solution of cuprous chloride in hydrochloric acid will absorb both prussic acid and cyanogen, giving with the first of these the solid 2 CuCl, HCN, 2 H_2O (colourless crystals easily oxidized by air) and with the second pale yellow crystals of $2\ CuCl,(CN)_2$,[735] perhaps the cupric compound Cu(CN)Cl.

These halide nitrile complexes are presumably not ionized. A different type of complex is formed from the nitrate. If copper powder acts on a solution of silver nitrate in acetonitrile the silver is precipitated and the

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[733] A. Gautier, *Ann. Chim. Phys.* 1869, [iv] **17**, 203.
[734] E. G. J. Hartley, *J.C.S.* 1916, **109**, 1296.
[735] C. Rabaut, *Bull. Soc.* 1898, [3] **19**, 786 (C. 98. ii. 859).
[736] H. H. Morgan, *J.C.S.* 1923, **123**, 2901.

copper takes its place. On evaporating off the excess of nitrile a colourless crystalline residue of the composition $[Cu(CH_3 \cdot CN)_4]NO_3$ is left. This is stable in acetonitrile solution even in contact with air; but if an inert gas is passed over the solid, so that some of the nitrile is removed, it at once begins to decompose, turning green and separating metallic copper, even if the greatest care is taken to exclude air and moisture.[142] This is the characteristic reaction of the cuprous ion: its occurrence here shows that the nitrile, though it is not very firmly attached, is able to protect the ion from the reaction. The fact that the deposition of copper begins as soon as the nitrile content is reduced below 4 molecules suggests that the only complex formed by the cuprous ion contains these 4 molecules.

Argentous compounds form similar complexes with nitriles, though few of them have been isolated. Silver nitrate is very soluble in acetonitrile, 1·5 g. dissolving in the cold in 1 g. of the liquid (about 2 $AgNO_3$ to 3 $CH_3 \cdot CN$) with considerable evolution of heat, and the solution has a high conductivity, as great as that of many salts in water.[737] This is no doubt due to the formation of a complex salt $[Ag(CH_3 \cdot CN)_n]NO_3$. Silver nitrate can combine to form solid compounds of the 1:1 type with bromoacetonitrile and iodoacetonitrile $BrCH_2 \cdot CN$ and $ICH_2 \cdot CN$, and even with methylene iodide CH_2I_2; the compounds are decomposed by water but otherwise are reasonably stable; the methylene iodide compound $AgNO_3,CH_2I_2$ melts at 80°.[738] So too Middelberg has shown[739] from a phase rule study of the system $AgNO_3$—Succinonitrile (SuN) that the solid phases (1) 4 $AgNO_3$, SuN; (2) 2 $AgNO_3$, SuN; (3) $AgNO_3$, SuN; (4) $AgNO_3$, 2 SuN,H_2O are formed; but their properties have been little investigated.

2. (*b*) *Co-ordination compounds of Azoparaffins*

These[740] are rather like the nitrile complexes. If the diacetate of hydrazomethane $CH_3 \cdot NH \cdot NH \cdot CH_3$ is treated with copper sulphate a dark red solid is formed, which hydrochloric acid or sodium chloride converts into the red compound $CH_3 \cdot N{=}N \cdot CH_3$, 2 CuCl. An isopropyl compound containing water, $(CH_3)_2CH \cdot N{=}N \cdot CH(CH_3)_2$, CuCl, 2 H_2O was also prepared, but this was very unstable.

No argentous or aurous analogues of these complexes seem to be known.

2. (*c*) *Ammines*

Cuprous Ammines. These are formed with great readiness; for example, cupric sulphate in concentrated ammonia solution is reduced by copper gauze in the cold in a few days with the separation of a colourless soluble salt $[Cu(NH_3)_2]_2SO_4,H_2O$, which in solution is readily oxidized by air, and is decomposed by dilute acids with the separation of metallic copper.[741]

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[737] P. Dutoit and L. Friderich, *Bull. Soc.* 1898, [3] **19**, 321.

[738] R. Scholl and W. Steinkopf, *Ber.* 1906, **39**, 4393.

[739] W. Middelberg, *Z. physikal. Chem.* 1903, **43**, 306.

[740] O. Diels and W. Koll, *Ann.* 1925, **443**, 262.

[741] F. Foerster and F. Blankenberg, *Ber.* 1906, **39**, 4428.

Other amino-derivatives behave in the same way. Alkylamines (which always have less co-ordinating power than ammonia) do not seem to have been used, but there is an analogous series of pyridine compounds, and a hydrazine complex has been described.[742] The ammonia and pyridine complexes contain 1, 2, and 3 molecules of the base; more than 3 do not seem to be found, and Biltz's measurements of the dissociation tensions of the ammines[743] give no indication of their occurrence. Abegg[744] gives a list of these salts, which contains 4 mono-, 6 di-, and 2 triammines. Werner[745] points out that the co-ordination number 3 is especially characteristic of cuprous and argentous complexes.

Argentous Ammines. These are very like the cuprous. Solid silver chloride will absorb gaseous ammonia up to the composition $AgCl,3\ NH_3$, and will dissolve in aqueous ammonia owing to the formation of an ammine salt. A variety of complex salts of this kind have been isolated, the great majority of which contain either 2 or 3 NH_3 to 1 Ag, and none more than 3. The arrangement in the $[H_3N\rightarrow Ag\leftarrow NH_3]$ ion is linear (Hoard). From the solubility measurements of the sulphate, bromate, and iodate in aqueous ammonia, Vosburgh and McClure[746] derived the constants in water at 25°:

$$\frac{[Ag^+]\cdot[NH_3]}{[Ag\cdot NH_3^+]} = 4{\cdot}3\times10^{-4}$$

$$\frac{[Ag^+]\cdot[NH_3]^2}{[Ag(NH_3)_2^+]} = 6{\cdot}2\times10^{-8}$$

Ammonia acts on silver cyanide to give the doubly complex salt

$$[Ag(NH_3)_2]\cdot[Ag(CN)_2].^{747}$$

Other amines can combine in the same way. In a few compounds the co-ordination number seems to reach 4: Weinland mentions complexes with 4 aniline or toluidine molecules, such as $[Ag(C_6H_5NH_2)_4]NO_3$,[748] but he gives no references and no further data.

Aurous Ammines. The aurous halides when put into liquid ammonia combine with the solvent; the ammines which are stable at the ordinary temperature are $[Au(NH_3)_3]Cl$, $[Au(NH_3)_2]Br$, and $[Au(NH_3)]I$[749,750]; this is the usual order of stability of the different halides. The formation of aurous halide complexes cannot be studied in water, because water decomposes the halides.

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[742] T. Iredale and C. E. Mallen, *J.C.S.* 1930, 395.

[743] W. Biltz and W. Stollenwerk, *Z. anorg. Chem.* 1920, **114**, 174.

[744] *Handbuch*, ii. 1, p. 538 [1908].

[745] *N.A.*, ed. 5 [1923], p. 49.

[746] W. C. Vosburgh and R. S. McClure, *J.A.C.S.* 1943, **65**, 1060.

[747] R. Lucas, *Z. anorg. Chem.* 1904, **41**, 193.

[748] *Komplexverbindungen*, 1919, p. 71.

[749] F. Herrmann, *Ber.* 1905, **38**, 2813.

[750] F. Meyer, *C.R.* 1906, **143**, 280.

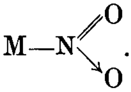
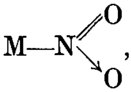
Herrmann[749] also prepared non-ionized monammines such as

$$H_3N{\rightarrow}Au{-}Cl,$$

which can be made by treating aurous chloride with aqueous ammonia, and evaporating down the solution. It is colourless, insoluble in water, but soluble in aqueous ammonia (perhaps through the formation of $[Au(NH_3)_2]Cl$); on heating it decomposes without melting at 150-200°.

This presumably belongs to the class of 2-covalent aurous complexes, of which the phosphine and arsine compounds, such as $Et_3P{\rightarrow}Au{-}Cl$ (described below), are the best known.

2. (*d*) *Nitro-complexes*

The complex nitrites can be formulated in two ways, with an oxygen link as $M{-}O{-}N{=}O$ or with a nitrogen link as  $\mathrm{M{-}N}\begin{smallmatrix}\nearrow\!\!\!\!\nearrow O\\ \searrow O\end{smallmatrix}$. Isomeric compounds have in some cases (for example, with cobalt) been obtained. According to Werner[751] when M is a transitional element the stable form is always the true nitro-compound  $\mathrm{M{-}N}\begin{smallmatrix}\nearrow\!\!\!\!\nearrow O\\ \searrow O\end{smallmatrix}$, and we may suppose that it is so also when M is an element of Group I. B, even in the monovalent state, owing to the small affinity of these elements for oxygen as compared with nitrogen.

The only complex nitrites known in this subgroup are those of silver. Jamieson has described[752] a complex nitrite $Cs[Ag(NO_2)_2]$, $2H_2O$. He also obtained a series of salts of the general composition $Cs_3M''[Ag(NO_2)_6]$, $2H_2O$, where M = strontium, barium, or lead; but as 6-co-ordinated argentous complexes are otherwise entirely unknown, we may suspect (in the absence of X-ray data) that these double salts are not true complexes.

3. *Phosphorus and Arsenic Complexes*

Monovalent copper silver and gold form complexes with various compounds of trivalent phosphorus and arsenic: phosphine and arsine and their trialkyl derivatives, and also (at least with phosphorus) the trichloride and the ester $P(OAlk)_3$. The phosphorus and arsenic compounds are similar to one another, and may be treated together.

Cuprous Complexes

If an acid solution of a cuprous halide in alcohol is treated with phosphine PH_3, an addition compound is formed, containing one or two molecules of phosphine to one atom of copper.[753] The products have the compositions $CuCl,PH_3 : CuBr,PH_3 : CuI, 2\,PH_3$; they seem to be similar to the ammines but less stable, losing phosphine easily *in vacuo*, and readily

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[751] *N.A.*, ed. 3 (1913), pp. 131, 339.

[752] G. S. Jamieson, *J.A.C.S.* 1907, **38**, 614.

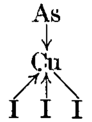
[753] R. Scholder and K. Pattock, *Z. anorg. Chem.* 1934, **220**, 250.

changing into cuprous phosphide Cu_3P. The order of stability in the ammines is $Cl > Br > I$, and this seems to hold here too, as far as the chloride and bromide are concerned, since the bromide has the higher dissociation tension of phosphine: but it is curious that the iodide, which should give the least stable compound, is alone in taking up two molecules of phosphine.

The co-ordination compounds formed by cuprous iodide with the tertiary phosphines and arsines have been examined by Mann, Purdie, and Wells.[754-5]

The compounds are made by the action of the phosphine or arsine on a solution of cuprous iodide in concentrated potassium iodide solution. They are colourless compounds, which are reasonably stable; they are obviously not salts, since they are insoluble in water but dissolve readily in organic solvents such as benzene. The melting-points of the higher homologues are low, being for $(R_3P—CuI)_n$, with R = ethyl 238°; *n*-propyl 207°; *n*-butyl 75°; *n*-amyl 27°; and for the arsenic compounds $(R_3As—CuI)_n$: ethyl (decomposes); *n*-propyl 208°; *n*-butyl 61·5°; *n*-amyl, liquid. The molecular weights of these compounds by the boiling-points in acetone and benzene, and cryoscopically in benzene and ethylene dibromide gave values of n between 3·5 and 4·2. They clearly all form a stable fourfold complex. The X-ray analysis of the triethyl arsine compound[756] showed that the 4 cuprous atoms occupy the points of a regular tetrahedon, with the 4 iodine atoms at the centre of each face, but above its plane. The arsenic lies on the line joining the centre of the tetrahedron to the copper produced, and its 4 valencies are tetrahedrally arranged.

The copper atom is thus 4-covalent, being attached to an arsenic atom and 3 iodines. It is monovalent with a complete octet, and its valencies, like those of the arsenic, are tetrahedrally disposed.



The tributyl arsine compound was found to have a dipole moment of 1·60 D. in benzene at 25°; whether this is due to flexibility or to abnormal atomic polarization was not determined; the molecule in its undisturbed state is symmetrical.

Argentous Complexes

Arbusov[757] has obtained addition compounds of the silver halides with triethyl phosphite, such as $AgCl,P(OEt)_3$, m.pt. +5°; $AgBr,P(OEt)_3$, m.pt. 40°; $AgI,P(OEt)_3$, m.pt. 82°. No other properties are described.

[754] F. G. Mann, D. Purdie, and A. F. Wells, *J.C.S.* 1936, 1503.

[755] See also G. J. Burrows and E. P. Sanford, *Proc. Roy. Soc. N.S. Wales*, 1936, **69**, 182.

[756] For details of the measurements see A. F. Wells, *Z. Krist.* 1937, **94**, 447.

[757] A. Arbusov, *Ber.* 1905, **38**, 1171.

The silver halide compounds of the trialkyl phosphines and arsines[758] are very similar to the cuprous compounds. They are made in the same way by the action of the base on a solution of silver iodide in concentrated potassium iodide solution; their molecular weights as determined both by boiling-points and by freezing-points show them to be fourfold polymers, and the molecular structures are found by X-ray analysis to be the same as those of their cuprous analogues. Their melting-points are somewhat irregular (perhaps on account of a change in the crystalline form); they are given below along with those of the aurous compounds.

Aurous Complexes

Various types of addition complexes formed by aurous compounds with compounds of trivalent phosphorus and arsenic are known. If phosphorus trichloride is added to a solution of auric chloride in ether, the solution loses its yellow colour (a sign of reduction) and on evaporation a compound $AuCl,PCl_3$ is obtained; this is insoluble in water, which decomposes it with the formation of phosphorous acid, while alcohol converts it into the phosphite ester compound $AuCl,P(OEt)_3$.[759] This last compound can be made directly by reducing auric chloride with the alkyl phosphite in alcohol. In the same way triphenyl phosphine reduces an alcoholic solution of auric chloride with the formation of the compound $\Phi_3P,AuCl$[760]: $(CH_3O)_3P\rightarrow AuCl$ and $(C_6H_5)_3P\rightarrow AuCl$ were found cryoscopically to be monomeric in benzene, unlike Mann's cuprous and argentous compounds.

The aurous compounds of trialkyl phosphine and trialkyl arsine have also been examined by Mann, Wells, and Purdie.[758] The aurous compounds differ markedly from the cuprous and argentous in being monomeric (2- and not 4-covalent), as Levi-Malvano found in his complexes, and in having as one might expect lower melting-points. The following table gives the melting-points (the mean when a range is given) and the average value of *a*, the association factor, for these substances.

	Cuprous				*Argentous*				*Aurous*			
	$R_3P\rightarrow CuI$		$R_3As\rightarrow CuI$		$R_3P\rightarrow AgI$		$R_3As\rightarrow AgI$		$R_3P\rightarrow AuI$		$R_3As\rightarrow AuI$	
	M.pt.	*a.*	*M.pt.*	*a.*	*M.pt.*	*a.*	*M.pt.*	*a.*	*M.pt.*	*a.*	*M.pt.*	*a.*
$R = CH_3$	..	..	..	..	..	..	..	..	..	..	177°	1·1
Ethyl	238°	3·5	Decp.	3·9	208°	3·7	184°	3·8	67°	1·1	77°	1·1
n-Pr.	207°	3·6	209°	3·9	262°	3·6	220°	3·5	..	..	..	..
n-Bu.	75°	3·5	62°	3·9	43°	3·9	..	..	..	..	..	..
n-Am.	27°	3·6	Liquid		..	..	..	..	..	..	..	..

	$R_3P\rightarrow AuCl$		$R_3As\rightarrow AuCl$		$R_3As\rightarrow AuCNS$	
	M.pt.	*a.*	*M.pt.*	*a.*	*M.pt.*	*a.*
$R = CH_3$	..	..	Decp.	1·1	127·8°	1·1
Ethyl	78°	1·2	94·5°	1·1	..	..
n.-Pr.	40°	1·15	..	..	..	..

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[758] F. G. Mann, A. F. Wells, and D. Purdie, *J.C.S.* 1937, 1828.

[759] L. Lindet, *C.R.* 1884, 98, 1382.

[760] M. Levi-Malvano, *Atti R.* 1908, 17, 857 (C. 08. ii. 932).

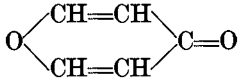
The aurous compounds were prepared by adding the phosphine or arsine to an aqueous-alcoholic solution of chloroauric acid $HAuCl_4$; if the latter is treated beforehand with excess of potassium iodide or thiocyanate the aurous iodide or thiocyanate complex is formed. The phosphine compounds are very stable and can be distilled under reduced pressure; the arsine compounds are relatively unstable and decompose slowly in light, with separation of gold.

The difference between the cuprous and argentous complexes with a covalency of 4, and the aurous with the simple monomeric formula and a covalency of 2, is striking and significant. It is characteristic of aurous gold to be satisfied with a covalency of 2: this is a further example of the stability of the valency quartet which seems to be a peculiarity of this part of the Periodic Table, since it is found in the two succeeding elements mercury (as in Cl—Hg—Cl) and thallium (as in $[CH_3—Tl—CH_3]I$), and there are signs of it in bismuth.

4. *Oxygen Complexes*

As we should expect from the slight affinity which these elements have for oxygen, the number of compounds they form with co-ordinated oxygen is very small. Among the cuprous compounds no open-chain complexes joined through oxygen seem to be known, although there are certain chelate compounds (see below, p. 145) in which one or both links are formed through oxygen. Much the same holds with the argentous compounds. The small affinity of silver for oxygen is shown by the fact that silver salts scarcely ever form hydrates. This does not of course prove that the silver ion is not hydrated in solution; the link to oxygen may be too weak to resist the electrostriction in the crystal. Indeed Bathe[761] has measured the mobility of complex silver cations containing ammonia, alkylamines, and pyridine, and from his results, and the observed mobility of the silver ion itself, he concludes that the latter is $[Ag(OH_2)_2]^+$.

Willstätter and Pummerer[762] obtained definite evidence that pyrone



forms complex salts with silver nitrate, although their analyses suggest that the product was not pure.

The solubility of argentous acetate in water is found to increase on addition of alkaline or alkaline earth acetates, or of silver nitrate or perchlorate[763]; this is a sign of the formation of a double acetate, presumably $M[Ag(O \cdot CO \cdot CH_3)_2]$ in solution, though no salt of this type has been isolated.

No oxygen complexes of aurous gold seem to be known.

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[761] A. Bathe, *Z. physikal. Chem.* 1931, **155**, 267.

[762] R. Willstätter and R. Pummerer, *Ber.* 1904, **37**, 3747.

[763] F. H. MacDougall and M. Allen, *J. physikal. Chem.* 1942, **46**, 730; F. H. MacDougall, ib. 738.

5. *Sulphur Complexes*

The affinity of these metals for sulphur is much greater than for oxygen, and they form a considerable number of complexes co-ordinated through sulphur. These are essentially of three kinds: (1) addition compounds of the thioethers R—S—R; (2) addition compounds of thiourea and other compounds with the C=S group; and (3) polysulphides such as $M(CuS_4)$.

Thioether Complexes

Not many of these have been made. The simplest is the aurous compound $Et_2S\rightarrow AuCl$, which was prepared by Mann, Wells, and Purdie[758] by the action of diethyl sulphide on a solution of auric chloride in hydrochloric acid. It forms colourless crystals melting at 38-40°; the association factor determined ebullioscopically in acetone is 1·01, and cryoscopically in ethylene dibromide 1·09 and in bromoform 1·10; so that the aurous atom, as in the phosphine and arsine compounds, is 2-covalent. It is soluble in most organic liquids, but like so many gold compounds it decomposes on exposure to light. The corresponding benzyl compound $(\Phi\cdot CH_2)_2S\rightarrow AuCl$ was prepared by Herrmann[749] by the action of excess of dibenzyl sulphide on auric chloride. The aurous halide cannot be made to take up more than one sulphide molecule because the co-ordination is not strong enough to break the Au-hal link. The compound is dimorphic (probably monotropic), one form being tetragonal and the other monoclinic. It is only slightly soluble in ether or carbon tetrachloride, but readily in chloroform. It is not very stable, and can scarcely be recrystallized without some separation of gold.

Analogous silver compounds have been prepared.[764]

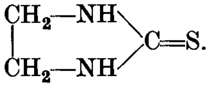
Thioacetamide Complexes

Four-covalent cuprous and argentous complexes $[M(SC(NH_2)CH_3)_4]X$ have been made, and the cuprous has been shown to be tetrahedral.[765] The aurous complex[766] is characteristically only 2-covalent,

$$[Au(SC(NH_2)CH_3)_2]Br.$$

Thiourea Complexes

These are formed by thiourea itself (Tu) and by the very similar ethylene-thiourea (etu)



The thiourea complexes of copper are numerous; Abegg's list[767] gives

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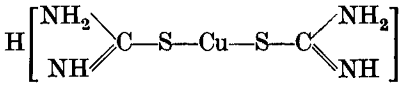
[764] F. W. Semmler, *Ann.* 1887, **241**, 139.

[765] E. G. Cox, W. Wardlaw, and K. C. Webster, *J.C.S.* 1936, 775.

[766] F. H. Brain and C. S. Gibson, *Ann. Rep. Brit. Assoc.* 1938, 37.

[767] *Handbuch*, ii. 1, p. 538 (1908).

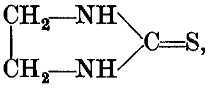
2 mono-, 2 di-, and 6 tri-compounds, so that the prevailing type is $[Cu(Tu)_3]X$. Kohlschütter[768] has examined these compounds in detail. The copper atom is almost invariably 3-covalent in these complexes; a complex with more than three thiourea molecules to one copper atom is never found. An acid presumably



can be prepared, and also a compound $Cu(Tu)_2Cl$ which is insoluble in water and is probably not a salt. These conclusions are confirmed by conductivity and transport data. There is, however, some reason to think that in solution the complex cation $[Cu(Tu)_3]^+$ can take up a fourth thiourea molecule.

Some of the thiourea compounds are highly complex, for example $[Cu_3(Tu)_7](NO_3)_3$, and it has been suggested[769] that the NH_2 group may take part in the formation of the complex, when it contains more than one metallic atom.

With the analogous ethylene thiourea (etu)



where this complication is less likely to occur,* Morgan and Burstall[769] prepared a series of complexes with 4, 3, 2, and 1 molecules of the urea; the relations are curious: the formulae are $[Cu(etu)_4]NO_3$: $[Cu(etu)_3]_2SO_4$: $[Cu(etu)_2]$hal (Cl, Br, I) : $[Cu(etu)]_2O$. (The last of these compounds may be covalent.) Conductivity measurements showed that the salts were strong electrolytes.

Argentous Thiourea Complexes

Morgan and Burstall[769] made a series of ethylene-thiourea complexes of silver similar to those of copper, with 1, 2, 3, and 4 molecules of the urea to one of silver.

Aurous Thiourea Complexes

Morgan and Burstall[769] have also prepared the gold complexes. They are remarkably stable, and are not reduced to metallic gold by formaldehyde. They are of two types, with one and with two thiourea molecules to each gold atom. The second class are soluble in water, and the first class practically not. They made of the type $[Au(etu)_2]X$, a nitrate, chloride, and bromide, all soluble in water and alcohol but not in organic solvents

* One Cu joined to Tu through S and N would involve a 4-ring.

[768] V. Kohlschütter, *Ber.* 1903, **36**, 1151: V. Kohlschütter and C. Brittlebank, *Ann.* 1906, **349**, 232.

[769] G. T. Morgan and F. H. Burstall, *J.C.S.* 1928, 143.

like ether and benzene; and of the other type an iodide Au(etu)I and an oxide $(Au \cdot etu)_2O$, both practically insoluble in water. Clearly the compounds of the first type are salts, and those of the second are not, the covalency of the gold being 2 in both.

Polysulphides

These form a very singular group of compounds. The alkaline polysulphides, in which the sulphur atoms are necessarily attached only to one another, can have any composition from M_2S_2 to M_2S_5. Of the elements of Group I B in the monovalent state only copper and gold are known to give complex polysulphides; with each of these only one type of complex is well established, and this is different for the two, being for copper $M(CuS_4)$ and for gold $M(AuS_3)$.

Cuprous Polysulphides

The ammonium salt $NH_4[CuS_4]$ has long been known, but its correct formula was first established by Hofmann and Höchtlen,[770] and it was more fully investigated by Biltz and Herms.[771] It is made by adding copper sulphate to a saturated solution of sulphur in ammonium sulphide, when fine red crystals of $NH_4[CuS_4]$ separate; the other salts can be prepared from this; the potassium salt can also be made by grinding cupric oxide with potassium pentasulphide solution and precipitating with alcohol. All the salts are anhydrous and deep red. The potassium, rubidium, and caesium salts were made; the solubility falls as the atomic weight of the alkali metal rises (the usual behaviour of the alkaline salts of strong acids), the caesium salt being almost insoluble in water. These compounds are fairly stable; concentrated hydrochloric, nitric, or sulphuric acid decomposes them very slowly in the cold, and quickly only on boiling.

The structure of this $[CuS_4]^-$ ion is unknown: it is presumably cuprous, and so should be diamagnetic, but this point has not been examined; the arrangement of the sulphur atoms can only be found by X-ray analysis of the crystal structure.

Potassium and rubidium will also give black salts of the approximate composition $M_2Cu_3S_{10}$.[771]

Aurous Polysulphides

The only known example was made by Hofmann and Höchtlen[770,772] from auric chloride and ammonium polysulphide; it has the formula $NH_4[AuS_3]$, yellow prisms, only slightly soluble in water.

Chelate Complexes

These are singularly few, and it is interesting to notice that none are formed through nitrogen; since all these ions will co-ordinate with

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[770] K. A. Hofmann and F. Höchtlen, *Ber.* 1903, **36**, 3090.

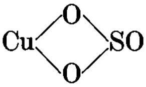
[771] H. Biltz and P. Herms, *Ber.* 1907, **40**, 974.

[772] K. A. Hofmann and F. Höchtlen, *Ber.* 1904, **37**, 245.

ammonia, we might have expected them to do so even more readily with diamines like ethylene diamine; but with central atoms of covalencies 2 and 3 stable ring complexes could not be formed. The rings that are actually formed in these chelate complexes are all co-ordinated through oxygen or sulphur or both, and it is clear that as in the open-chain complexes the affinity is much stronger for sulphur than for oxygen.

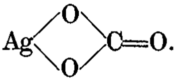
Oxygen-oxygen Rings

These are apparently confined to the sulphito- and carbonato-complexes.

Copper. Copper forms complex sulphites of the type of $K(CuSO_3)$, which presumably contain the ring  , with 2-covalent copper.[773]

Silver. Complex sulphites of silver do not seem to have been isolated though they occur in solution, but complex carbonate-compounds are known. Silver carbonate dissolves in concentrated potassium carbonate solution, and the colourless salt $K(AgCO_3)$ crystallizes out.

This has been shown[774] by X-ray analysis to contain the carbonato-ring



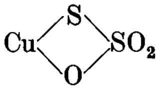
The Ag—O distance is 2·24 A (theory 2·19) (see above, p. 110).

Gold. A complex sulphite or the composition $Na_3[O_3S—Au—SO_3], 2H_2O$ has been described.[775]

Possible Oxygen-sulphur Rings

These comprise the complex thiosulphates, a remarkable group of compounds which are formed by all three metals. They can be formulated either as rings or as open-chain complexes of the type of

$$[O_3S\cdot S—Au—S\cdot SO_3]^{3-}.$$

Copper. The salts are made by adding alkaline thiosulphate to a cupric solution, the copper being reduced to the cuprous state. The composition of many of them is complicated, and it is possible that they form solid solutions with one another (see Rosenheim and Steinhäuser[773]); but simple salts of the type of $KCu(S_2O_3)$ are known. They may contain a 4-ring of the form  with a stability due to the affinity of the copper for the sulphur.

Silver. The complex thiosulphates of silver have been known for over a century,[776] and are familiar from their use in photography to dissolve out

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[773] A. Rosenheim and S. Steinhäuser, *Z. anorg. Chem.* 1900, **25**, 72.

[774] J. Donohue and L. Helmholz, *J.A.C.S.* 1944, **66**, 295.

[775] Haase, *Z. Chem.* 1869, 535.

[776] Discovered by Herschel, *Edinb. Phil. Journal*, 1819, **1**, 26; **2**, 154.

the unreduced silver halide after development, a reaction which shows how readily these complexes are formed. More recently the salts have been investigated by Rosenheim and Steinhäuser,[773] by Meyer and Eggeling,[777] and, lastly, by Rosenheim and Trewendt,[778] whose paper corrects the earlier observations. According to this work, the complexes are of three types:

1. $M[Ag(S_2O_3)]$: Li, $1/2\,H_2O$; Na, K, NH_4 anhydrous.
2. $M_3[Ag(S_2O_3)_2]$: K, H_2O.
3. $M_5[Ag_3(S_2O_3)_4]$: NH_4, Na, K, ? Rb, ? Cs.

Of the first type the lithium salt is easily soluble in water, but the rest are relatively insoluble.

These salts have a sweet taste, perceptible even in a dilution of 1 in 300,000 (Werner) (the complex mercuric thiosulphates are also said to have a sweet metallic taste). According to Bodländer[779] the equilibrium constant for these complexes is of the order 10^{13}, which means that in a decinormal solution of the sodium salt $Na_3[Ag(S_2O_3)_2]$ the concentration of silver cations is $\sqrt[3]{10^{-14}}$ or 2×10^{-5} normal. Such a solution gives a precipitate with potassium iodide or potassium sulphide, but not with potassium chloride; this agrees approximately with the known values of the normalities of the saturated solutions of these salts, which are at 25°: silver chloride $0{\cdot}88 \times 10^{-5}$; silver iodide $0{\cdot}98 \times 10^{-8}$; silver sulphide $1{\cdot}4 \times 10^{-6}$.

Gold. With this metal the 2-covalent salts $M[Au(S_2O_3)]$ are known,[780] but they appear to be less stable than the fourfold complex $M_3[Au(S_2O_3)_2]$[781]; this, if it is chelate, is very unusual for an aurous complex, and must be due to the extra stability caused by the chelation (compare the sulphite, p. 145). The sodium salt $Na_3Au(S_2O_3)_2, 2\,H_2O$ is quite stable if it is pure; it loses its water of crystallization at 150-60° without decomposition; the gold is precipitated by alkaline sulphides but not by ferrous sulphate or stannous chloride.[782] This substance has been used as a drug against tuberculosis under the name 'Sanochrysin'.[783]

Sulphur-sulphur Chelate Complexes

These are formed by copper and gold. Complexes of this type were prepared by Morgan and Ledbury[784] from dimethyldithiolethylene (thi), which gave the cuprous salt [Cu(thi)]Br, a pale blue compound melting at 162° and insoluble in water and organic solvents other than pyridine.

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[777] J. Meyer and H. Eggeling, *Ber.* 1907, **40**, 1351.

[778] A. Rosonheim and G. Trewendt, ib. 1928, **61**, 1731.

[779] G. Bodländer and R. Fittig, *Z. physikal. Chem.* 1902, **39**, 605; G. Bodländer, *Ber.* 1903, **36**, 3934.

[780] H. Brown, *J.A.C.S.* 1927, **49**, 958.

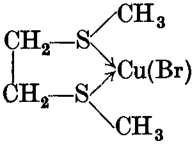
[781] K. L. McCluskey and L. Eichelberger, ib. 1926, **48**, 136.

[782] J. K. Gjaldbaek, *Dansk. Tidsskr. Farm.* 1927, **1**, 251.

[783] H. Möllgaard, *Chemotherapy of Tuberculosis*, Copenhagen, 1924.

[784] G. T. Morgan and W. Ledbury, *J.C.S.* 1922, **121**, 2882.

The corresponding gold compound [Au(thi)]Cl was obtained from a solution of auric chloride.



6. *Complex Halides*

Copper

Complex cuprous halides are formed by all the halogens except fluorine, and contain 2, 3, or 4 halogen atoms. Remy and Laves[785] find that of the complex chlorides described in the literature the numbers belonging to the various types $M[CuCl_2]$, $M_2[CuCl_3]$, $M_3[CuCl_4]$ are roughly in the ratio 10:5:1. No complexes with more than 4 halogen atoms are known. E.M.F. measurements indicate that in fairly strong (2 to 4 normal) potassium chloride solution the chief complex is $[CuCl_3]^{--}$, and that the amount of $[CuCl_4]^{---}$ present is negligible.[786]

Of the iodides the 2-covalent series $M[CuI_2]$ have been prepared from a series of organic bases (tetrapropyl ammonium, quinolinium, triethyl sulphonium).[787]

Silver

The formation of halide complexes is shown by the fact that silver chloride is about 100 times as soluble in normal hydrochloric acid as in water.[788-9] The most stable complexes are $M[Ag(hal)_2]$ and $M_2[Ag(hal)_3]$; a 4-covalent complex $K_3[AgI_4]$ has been described, but its existence is doubtful.

The bromide and iodide behave similarly.[790]

Gold

Complex halides of the type of $M[AuCl_2]$ are known, but here again the covalency of aurous gold seems to be limited to 2. These halides, which are formed by bromine and iodine as well, are unstable, the aqueous solution rapidly decomposing with separation of metallic gold.[791]

It has been shown by X-ray analysis[792] that the highly complex black salts $Cs_2AuAuCl_6$ and $Cs_2AgAuCl_6$ contain linear $AgCl_2^-$ and $AuCl_2^-$ ions as well as the planar ions of $AuCl^-$.

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[785] H. Remy and G. Laves, *Ber.* 1933, **66**, 571.

[786] S. v. Náray Szabó and Z. Szabó, *Z. physikal. Chem.* 1933, **166**, 228.

[787] R. L. Datta and J. N. Sen, *J.A.C.S.* 1917, **39**, 750.

[788] G. S. Forbes and H. I. Cole, ib. 1921, **43**, 2492.

[789] W. Erber and A. Schühly, *J. pr. Ch.* 1941, [ii] **158**, 176.

[790] W. Erber, *Z. anorg. Chem.* 1941, **248**, 32, 36.

[791] F. Lengfeld, *Amer. Chem. H.J.* 1901, **26**, 324.

[792] N. Elliott and L. Pauling, *J.A.C.S.* 1938, **60**, 1840.

Summary of the Co-ordination Numbers in these Complexes

The covalency limits for these elements are copper 6, silver and gold 8; but in their monovalent complexes none of them has a higher covalency than 4. A summary of the observed values is given below, the form with the most compounds being underlined; the extent of ionization (on which of course the covalency depends) is decided on grounds of general probability. The chelate compounds are essentially more stable; this is in accordance with general experience, and is obviously due to the fact that if the chelate group has one of its links broken it still remains attached by the other; also they must have an even covalency, so that if the naturally favoured covalency is 3 they must be either 2 or 4; hence the presence of covalencies of 4 in these chelate compounds is not surprising.

TABLE

Complex	*Cuprous*	*Argentous*	*Aurous*
CO	4	. .	2
Cyanides	2 3 $\underline{4}$	2 3	2
R-CN	2 4	2	. .
R-NC	2	2	. .
Amines	$\underline{2}$ 3	$\underline{2}$ $\underline{3}$	2 3
R_3P, R_3As compounds	4	4	2
Thioureas	2 $\underline{3}$ 4	2 3 4	2
Halides	2 3 4	2 3 ?4	2
	Chelate compounds		
O, O compounds	2	2	2
Thiosulphates, &c.	$\underline{2}$ 4	2 4	2 4

Otherwise we see that the covalency of 4 is seldom reached except with the sulphur compounds and the cyanides, and is never exceeded, the prevalent values being 2 and 3. Further, the usual covalencies are lower for silver than for copper, and still lower for gold, which in the monovalent state very rarely exceeds 2.

As regards the elements co-ordinated to the central atom, the preference is evidently for the cyanide group and for sulphur, and then for nitrogen and the halogens; while for oxygen it is very small.

POLYVALENT COPPER, SILVER, AND GOLD

THE behaviour of divalent copper and silver cannot be compared directly with that of trivalent gold, and at the same time the number of compounds of divalent silver is so small, on account of the instability of that valency, that they do not afford much opportunity for comparison with copper. The polyvalent compounds of these three elements will therefore be dealt with separately.

CUPRIC COMPOUNDS

THESE correspond primarily to the divalent compounds of the transitional elements preceding them in the Table, especially nickel, cobalt, and iron.

They should also be compared with those of the next following element, zinc, which is always divalent; this comparison may be expected to show some of the characteristics of transitional as contrasted with non-transitional elements.

The cupric ion Cu^{++} is a reasonably strong divalent ion. It is paramagnetic[793] and is strongly coloured, these being the natural results of the presence of the imperfect electronic group of 17. The cupric salts of strong acids in dilute aqueous solution all show the same absorption, which is obviously that of the (hydrated) cupric ion; but at higher concentrations, or in presence of excess of the alkaline salt of the same acid, the colour usually changes from blue to green or brown. This change is due to the formation of a differently coloured complex ion, as was first shown by Donnan, Bassett, and Fox,[794] who proved that in electrolysis the green cupric chloride in potassium chloride solution migrated towards the anode. The salts of weak acids such as acetic have a markedly stronger and rather different absorption even at considerable dilutions, which is perhaps due to incomplete ionization (see later under cupric acetate (p. 154)).

The solid cupric salts (where the anions are colourless) are in the hydrated state blue or green; but the anhydrous salts have the most varied colours, ranging from white in cupric fluoride to black in cupric bromide.

As is to be expected from their double charge, the cupric ions show a stronger tendency to form complexes than the cuprous, and give many co-ordination compounds, cationic, neutral, and anionic, in which the co-ordination number is usually 4 and sometimes 6.

Cupric Carbon Compounds

These are practically confined (apart from the complexes) to the cyanides; no cupric alkyls or aryls are known.

Cupric cyanide, $Cu(CN)_2$, is a very unstable substance formed as a brown precipitate when potassium cyanide is added to a cupric solution: it rapidly changes in the cold with evolution of cyanogen to a double compound $Cu(CN)_2, 2\,CuCN, 5\,H_2O$ (or $Cu[Cu(CN)_2]_2, 5\,H_2O$), and on heating is wholly converted into cuprous cyanide. Its instability is due, like that of cupric iodide, to the anion being oxidized by the cation: this gives the neutral CN radical, which then polymerizes.

The thiocyanate $Cu(CNS)_2$ is very similar. It is black and is rapidly converted by water into the cuprous compound. It is a strong oxidizing agent and will oxidize indigo. Like the cyanide, it forms stable complexes.

Cupric Nitrogen Compounds

It is remarkable that while divalent copper shows a very strong affinity for nitrogen in its co-ordination compounds, especially the ammines, it

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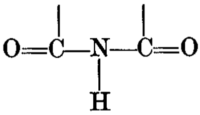
[793] For a discussion of the paramagnetism of transitional elements, see W. Klemm and W. Schüth, *Z. anorg. Chem.* 1931, **203**, 104; for cupric salts in particular, J. Reekie, *Proc. Roy. Soc.* 1939, **173**, 367.

[794] F. G. Donnan, H. Bassett, and C. J. J. Fox, *J.C.S.* 1902, **81**, 939.

forms scarcely any simple compounds with the Cu—N link. The Cu—N link must for some reason be much more stable when the covalency of the cupric atom is 4 or above than when it is only 2.

There is no cupric nitride except the black-violet explosive azide $Cu[N_3]_2$[795-6]; this substance (sol^y 0·0080/15°) is presumably ionized, but gives a series of complex azides (p. 159).

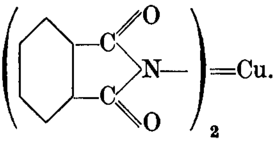
Among the few compounds in which divalent copper forms a normal covalent link with nitrogen are the derivatives of the imides,



$$O{=}\overset{|}{C}{-}\underset{\underset{H}{|}}{N}{-}\overset{|}{C}{=}O$$

in which of course the hydrogen has acquired activity through the neighbourhood of the two carbonyl groups.

Various cupric derivatives of the cyclic imides of dibasic acids—succinic, camphoric, dimethyl maleic, phthalic—have been prepared, in all of which a cupric atom replaces 2 imide hydrogens from two molecules of the imide. But almost all of these are known only as co-ordination products of ammonia, amines, or water, and as such are dealt with later among the cupric complexes (p. 158). The only one that is produced in the simple uncoordinated state is the phthalimide derivative.[797]



Cupric Oxygen Compounds

Cupric oxide, CuO, occurs in nature as the mineral tenorite. This has the lattice of a giant molecule in which each copper atom is surrounded by 4 oxygens, all lying in one plane with it, and with the valencies at right angles (the 'square planar' form); the Cu···O distance is 1·95 A as required for the covalent link[798] (calculated for the ionized Cu[O] link *ca.* 2·3, for Cu—O 2·01 A).

From the equilibrium between copper and steam the dissociation tension of cupric oxide at 450° has been calculated to be 2×10^{-25} atm.[799]

Cupric oxide can be precipitated from a solution of a cupric salt at 80° or above, and it has been shown that on heating it becomes coarser-grained with a proportionate loss of energy: after heating to 600° it has 1·45 k.cals. less energy per mole than when it is prepared at 80°[800]; this

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[795] A. Cirulis, *Naturwiss.* 1939, **27**, 583 (*B.C.A.* 39, i. 621, 1).

[796] M. Straumanis and A. Cirulis, *Z. anorg. Chem.* 1943, **251**, 315.

[797] H. Ley and F. Werner, *Ber.* 1907, **40**, 705.

[798] G. Tunell, E. Posnjak, and C. J. Ksanda, *Z. Krist.* 1935, **90**, 120.

[799] L. Wöhler and O. Balz, *Z. Elektrochem.* 1921, **27**, 406.

[800] R. Fricke, E. Gwinner, and C. Feichtner, *Ber.* 1938, **71**, 1744.

loss of energy is accompanied by a loss of catalytic power as is shown, for example, in the catalytic decomposition of nitrous oxide.[801]

Cupric hydroxide, $Cu(OH)_2$, as generally obtained, is a blue-green precipitate, which on heating in contact with the solution turns black, going over into the oxide CuO; measurements of the energy content through the heat of solution in hydrochloric acid have shown[800] that the hydroxide is more stable in water than the fine-grained oxide, but less so than the coarse-grained (like zinc and cadmium hydroxides). The precipitated hydroxide can be dried to the composition $Cu(OH)_2$ at 100°; thermal analysis of the dehydration of this hydroxide does not indicate the existence of any lower hydrate.[802-3] Cupric hydroxide can be obtained in blue crystals by leaving a solution of the oxide in ammonia to stand in a desiccator over sulphuric acid.[800]

The hydroxide is to some extent amphoteric; when freshly precipitated it is somewhat soluble in alkalies, forming a violet solution which contains the copper in the anion, no doubt as a 'cuprite' $M_2[CuO_2]$, or, according to Scholder,[804] $M_2[Cu(OH)_4]$. It has been shown[805] that while the saturated solution of copper oxide (or hydroxide) in water at 25° has 3×10^{-5} moles per litre, this rises to $1{\cdot}8 \times 10^{-3}$ in 4·2 normal potassium hydroxide; the relation of solubility to alkalinity shows that the acid $H_2[CuO_2]$ has a first dissociation constant of about 10^{-10}, and a second of 8×10^{-14}. Cupric oxide dissolves readily in aqueous ammonia to give a deep blue cuprammonium hydroxide

$$[Cu(NH_3)_4](OH)_2.$$

A peroxide CuO_2, H_2O is known, whose structure is established by its giving hydrogen peroxide with acids.

The existence of 'cupric acid', Cu_2O_3 (said to be formed by the action of chlorine on a suspension of cupric hydroxide in potassium hydroxide), is very doubtful.[806]

Cupric Compounds of Sulphur

Cupric sulphide, CuS, as precipitated by hydrogen sulphide from a solution of a cupric salt, is a black insoluble powder with a solubility product of $1{\cdot}2 \times 10^{-42}$ at 18°.[807-8] It can be obtained in the pure state by treating copper powder, prepared by heating the oxalate, with a solution of sulphur in carbon bisulphide; the sulphur reacts violently with the copper up to the point of forming cuprous sulphide Cu_2S, but after that very slowly. By

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[801] G. M. Schwab and H. Nakamura, *Ber.* 1938 **71**, 1755.

[802] O. Binder, *C.R.* 1939, **208**, 1995.

[803] H. B. Weiser, W. O. Milligan, and E. L. Cook [*J.A.C.S.* 1942, **64**, 503] agree: on the basis of X-ray and dehydration measurements they find that $Cu(OH)_2$ is the only compound of $CuO+H_2O$.

[804] R. Scholder, R. Felsenstein, and A. Apel, *Z. anorg. Chem.* 1933, **216**, 138.

[805] L. A. McDowell and H. L. Johnston, *J.A.C.S.* 1936, 58, 2009.

[806] E. Müller and I. Ernst, *Z. angew. Chem.* 1921, **34**, 371.

[807] I. M. Kolthoff, *J. Phys. Chem.* 1931, **35**, 2720.

[808] K. Jellinek and J. Czerwinski, *Z. physikal. Chem.* 1922, **102**, 476.

heating the cuprous sulphide formed with excess of sulphur in carbon bisulphide in a sealed tube to 100° for several hours, it is completely converted into cupric sulphide.[809] Cupric sulphide occurs in nature as the mineral 'Kupferindig' or covellite, in fairly soft blue-black masses, which can be ground to a blue powder.

Polysulphides of the compositions Cu_2S_5,[810] CuS_3, and Cu_2S_3[811] are said to occur.

Cupric Halides

Cupric Fluoride, CuF_2

In the anhydrous state this is a white crystalline substance which can be made by passing hydrogen fluoride over copper oxide at 400°. Ebert and Woitinek[812] found that it has a fluorite lattice, and that the $Cu \cdots F$ distance is 2·34 A. The calculated distances are for a covalent Cu—F link 1·99 A, and for an ionized link *ca.* 2·3 A. Hence cupric fluoride is ionized in the crystalline state. This is remarkable in view of Ebert and Woitinek's statement (loc. cit.) that the distance in cuprous fluoride is that of a covalent link; but as we have seen (p. 119), it is probable that their cuprous fluoride was a mixture.

Cupric fluoride melts at 950° to a red liquid, and then loses some of its fluorine, giving a mixture of cuprous and cupric fluorides[813] (see above, p. 120). It is volatile at a red heat; attempts to make it take up more fluorine to form a trivalent halide like an auric halide were not successful.[814]

Cupric fluoride gives a green mono- and a blue dihydrate. It is slightly soluble in cold water (0·075 g. in 100 g. at 25°). When it is warmed with water it hydrolyses, the basic fluoride $CuF \cdot OH$ being precipitated.[815–16] With excess of acid the compound CuF_2, 5 HF, 5 H_2O can be obtained, and this on dehydration loses water and hydrogen fluoride to form the basic salt CuF_2, CuO.[817]

Cupric Chloride, $CuCl_2$

The anhydrous salt forms dark brown crystals melting at 498°. The crystal lattice[817a] is exactly like that of $CuBr_2$ (below, p. 153). It gives a variety of hydrates with 4 (below 15°), 3 (below 26°), 2 (below 42°), and 1 (up to 117°) H_2O. The ordinary salt is the dihydrate; it has a bright blue colour, but when moist appears green, because the crystals are covered with a thin film of the saturated solution, which is brown. Examination of

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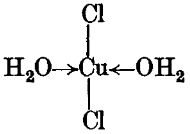
[809] K. Fischbeck and O. Dorner, *Z. anorg. Chem.* 1929, **182**, 228.
[810] F. Bodroux, *C.R.* 1900, **130**, 1397.
[811] A. Rössing, *Z. anorg. Chem.* 1900, **25**, 407.
[812] F. Ebert and H. Woitinek, ib. 1933, **210**, 269.
[813] H. v. Wartenberg, ib. 1939, **241**, 381.
[814] O. Ruff and M. Giese, ib. 1934, **219**, 148.
[815] A. Jaeger, ib. 1901, **27**, 29.
[816] E. Deussen, ib. 1905, **44**, 304.
[817] E. Böhm, ib. 1905, **43**, 329.
[817a] A. F. Wells, *J.C.S.* 1947, 1670.

the crystal structure of this dihydrate shows that it has a covalent structure with the four groups lying in a plane with the copper.[818]



$$\begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{H_2O}\rightarrow\mathrm{Cu}\leftarrow\mathrm{OH_2} \\ | \\ \mathrm{Cl} \end{array}$$

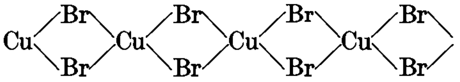
Cupric chloride is very soluble in water and in many organic solvents; the solubilities in moles $CuCl_2$ to 100 moles solvent at 25° (the values in g./100 g. solvent are added in brackets) are: water 10·1[819] (75·5; about 5-molar normal); methyl alcohol 13·8 (58·0); ethyl alcohol 19·1 (55·9); butyl alcohol 10·4 (21·2); ethyl formate 10·4 (18·9); acetone 10·3 (23·9). The saturated aqueous solution is dark brown; on dilution it turns first green and then blue; the addition of an alkaline chloride or a rise of temperature has the same effect as an increase of concentration. The dark colour is that of a complex ion $CuCl_3^-$ or $CuCl_4^{--}$ (Donnan, Bassett, and Fox[794]).[820] It forms numerous complex salts with other chlorides, and ammines with ammonia. At high temperatures it is converted into cuprous chloride and chlorine.

Cupric Bromide, $CuBr_2$

This consists of black crystals, very soluble in water. It forms an olive-green tetrahydrate (transition point 18°), but no other hydrates.[821]

It gives a brownish-green solution in water, which on addition of excess of potassium bromide turns purple-red. It forms numerous complexes. At a red heat it breaks up into cuprous bromide and bromine.

Its crystal structure has been determined[822]; it has flat chains



(individually, though not in their packing, like those of palladous chloride); the 4 Brs nearest to each Cu are 2·40 A away; each Cu also has 2 Brs of the next 2 chains 3·18 A away.

Cupric Iodide, CuI_2

This salt, like the cyanide, is exceedingly unstable, and breaks up almost as soon as it is formed into cuprous iodide and iodine, the anion being oxidized by the cation.

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[818] D. Harker, *Z. Krist.* 1936, **93**, 136.

[819] E. Boye, *Z. anorg. Chem.* 1933, **215**, 75.

[820] N. A. Yajnik, R. Chand, A. N. Kapur, and D. C. Jain (*J. Ind. Chem. Soc.* 1942, **19**, 357) confirm this by magnetic measurements; the slope of the magnetism/concentration curve (in H_2O, Me—Et—Pr—Bu—OH) changes at the same point as the colour.

[821] S. R. Carter and N. J. L. Megson, *J.C.S.* 1928, 2954.

[822] L. Helmholz, *J.A.C.S.* 1947, **69**, 886.

Cupric Salts of Oxy-acids

(*a*) *Oxy-acids of Carbon*

Copper carbonate, $CuCO_3$, has not been isolated, although two basic carbonates occur in nature, malachite $CuCO_3$, $Cu(OH)_2$, and azurite $CuCO_3$, $2\,Cu(OH)_2$; and double carbonates, such as $K_2[Cu(CO_3)_2]$ are known (see p. 168).

Cupric Salts of Carboxylic Acids

The cupric salts of the fatty acids show a remarkable graduation in properties as we ascend the series. Cupric formate is pale blue and fairly soluble in water; as the molecular weight of the acid increases, the salts become green (the acetate is green) and then dark green; their solubility in water tends to diminish, and that in organic solvents rises in a marked degree. The solubilities in water, in g. per 100 c.c. of solution at the ordinary temperature, were found by Pickering[823] to be:

Formate	1·73	Isobutyrate . . .	0·30
Acetate	2·30	Valerate . . .	0·012
Propionate . . .	3·81	Isovalerate . . .	0·047
Butyrate . . .	1·8		

By the time we have reached the butyrate we find that though it is still quite soluble in water, it can be extracted from its aqueous solution with ethyl acetate, chloroform, ethyl ether, or amyl alcohol.[824] This suggests that with increase in the length of the carbon chain the ionization diminishes and the compound tends to become covalent. The position of the absorption bands in solvents such as chloroform supports this view[825]; with the higher acids it approaches more nearly to that of undoubtedly covalent cupric compounds, such as the β-diketone derivatives. Further evidence is the change in the depth of colour of the blue (less than $N/_5$) solutions of these salts in water.[826] The copper salts of weak acids like acetic and propionic are much more intensely coloured in these solutions (where they all have the same blue tint) than those of strong acids like sulphuric or nitric; on further dilution the molecular colour diminishes, but it approaches asymptotically a limit which is different for each acid, and always greater than the colour of the strong acid salt, which presumably is that of the simple hydrated cupric ion. The molecular depth of colour (in arbitrary units) of some of these salts is:

	Sulphate	*Formate*	*Acetate*	*Propionate*
$V = 5$ . . .	1	3·55	6·16	8·40
$V = 15$ . . .	1·1	3·00	4·52	5·01

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[823] S. U. Pickering, *J.C.S.* 1912, **101**, 184.

[824] H. Agulhon, *Bull. Soc. Chim.* 1913, [4] **13**, 405.

[825] T. M. Lowry and H. S. French, *Proc. Roy. Soc.* 1924, **106**, 489.

[826] N. V. Sidgwick and H. T. Tizard, *J.C.S.* 1908, **93**, 187; 1910, **97**, 957.

This suggests that the organic salts dissociate mainly to the first stage, as [Cu—O—CO—R](O—CO—R) and that the limit of colour, which is nearly reached in N/15 solution, is that of the [CuA]$^+$ ion, and therefore different in each case. The formate (and the monochloracetate is very similar) is intermediate between the strong and the weak salts.

Cupric oxalate forms a monohydrate CuC_2O_4, H_2O, which is pale blue, and insoluble in water. It gives various double oxalates, mainly of the type $M_2[Cu(C_2O_4)_2], 2\,H_2O$.

(*b*) *Oxy-acids of Nitrogen*

Cupric nitrite can be made as a blue-green apparently insoluble precipitate, but it cannot be isolated as it soon decomposes (obviously through hydrolysis) into cupric nitrate and nitric oxide. Complex nitrites are known.

Cupric nitrate, $Cu(NO_3)_2$, forms hydrates with 9, 6, and $3\,H_2O$; the anhydrous salt is unknown. It is extremely soluble in water[827] (60/25°).

(*c*) *Oxy-acids of Sulphur*

Cupric sulphate, $CuSO_4$, is white in the anhydrous state and forms hydrates with 1, 3, 5, and probably[829] 2 and 4 H_2O; the ordinary salt is the pentahydrate; sol^y 22·7/25° (about 1·4 molecular-normal). The odd numbers of water molecules in most of the hydrates suggest that one of them is attached to the anion. Recently the crystal structure of the pentahydrate has been found[830] not to be quite so simple as this. The lattice is much distorted and there are two kinds of copper atoms. Each has six oxygen neighbours, four of them (no doubt the oxygens of the water molecules) in a plane with it at 2·0 A; the other two belonging to the SO_4 groups are at the poles of an irregular octahedron, and at distances from the copper of 2·3 and 2·45 A respectively: the normal distances are for the covalent Cu—O 2·01 and for the ionized Cu[O] 2·3 A.U.

(*d*) *Oxy-salts of Halogens*

Cupric chlorate, $Cu(ClO_3)_2, 4\,H_2O$, is a very soluble salt, sol^y 164/18°.[831]

Cupric perchlorate, $Cu(ClO_4)_2, 6\,H_2O$, is one of the very soluble perchlorates, and retains its water of crystallization very firmly. It melts at 60°; it will lose 2 molecules of water over sulphuric acid in the cold, but no more without decomposition even over phosphorus pentoxide in the cold.

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[827] A. Seidell, *Solubilities*, 1928, p. 1183. The molecular colour of the solution does not visibly change up to the highest concentrations, but its intensity increases markedly above 1-normal, where most cupric solutions turn green: the increase is about 10 per cent. between 1-normal and 2-normal. Hence probably the nitrate forms complexes at high concentrations like the other salts, but their tint does not differ sensibly from that of the simple cupric ion.[826]

[829] T. I. Taylor and H. P. Klug, *J. Chem. Phys.* 1936, 4, 601.

[830] C. A. Beevers and H. Lipson, *Proc. Roy. Soc.* 1934, 146, 570.

[831] A. Meusser, *Ber.* 1902, 35, 1414.

The solubility of the hexahydrate is 128·3/20°; the salt is also easily soluble in methyl and ethyl alcohol, in acetic acid, in acetic anhydride, and in acetone, and slightly in ether and ethyl acetate.[832]

Cupric iodate, $Cu(IO_3)_2$, unlike the chlorate, has the relatively small sol^y of 0·136/25°.

Cupric periodate. A derivative of the 6-covalent form of this acid is known, $Cu_5(IO_6)_2$, $7 H_2O$, which loses water *in vacuo* at 74° to give the corresponding pentahydrate.[833]

COMPLEX CUPRIC COMPOUNDS

The cupric ion, as might be expected from its double charge, forms complexes more readily than the cuprous. The co-ordination number is variable; 4 is by far the commonest, but 2 is not infrequent, and 6 (the covalency limit) is found in a few compounds.

A. *Open-chain Complexes*

1. Cu—C *compounds*

These are extremely few; they are confined to the small number of complex cyanides. Cupric cyanide though itself very unstable can form stable complexes, such as $K_2[Cu(CN)_4]$, which is white and very soluble in water. A hexacyanide $Cd_2[Cu(CN)_6]$ has been described but not confirmed. The complex cupric cyanides are little known.

2. Cu—N *Complexes*

Ammines. The tendency to co-ordinate with amine nitrogen is a marked characteristic of the cupric ion, which forms complexes with ammonia, alkyl and aryl amines, pyridine, and the like, and also chelate complexes with various diamines.

The simple ammines are all salts of the type $[Cu(NH_3)_n]X_2$. The complex ion forms a much stronger base than cupric hydroxide; these bases ($X = OH$) are easily soluble in water and are highly dissociated. The ions have a deep indigo blue (at any rate the tetrammines), quite distinct from the blue of the simple cupric salt and far more intense; these bases also have the valuable property of dissolving cellulose, which they oxidize to oxycellulose.

In the solid compounds n is usually 4 or 2; examples are known in which it is 5, or (especially in the chelate complexes) 6; no values higher than 6 have been found.

The co-ordination with ammonia is very strong. The freezing-point of a copper sulphate solution is scarcely lowered by the addition of 4 equivalents of ammonia[834]; it was found from E.M.F. measurements that in an N/200 cupric solution containing 0·4 normal ammonia (and so 140 times as many H_2O molecules as NH_3 molecules) the concentration of the simple

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[832] E. Heinerth, *Z. Elektrochem.* 1931, **37**, 64.

[833] R. K. Bahl and S. Singh, *J. Ind. Chem. Soc.* 1939, **16**, 269.

[834] A. Reychler, *Ber.* 1895, **28**, 555.

cupric ion at 25° is 10^{-14} molar (i.e. of the cupric ions present, only 1 in 10^{11} is not combined with ammonia).[835]

6-covalent ammines are known, though they are relatively unstable; in $[Cu(NH_3)_6]Br_2$ and $[Cu(NH_3)_6]I_2$ it has been shown from the crystal structure[836] that the cations are octahedral. Other compounds of this type are $[Cu(py)_6]Br_2$ and $[Cu(py)_6](NO_3)_2$[837] which easily lose pyridine.

Dawson and McCrae[838] determined the partition of ammonia between chloroform and an aqueous solution of cupric sulphate or chloride, and thus found for decinormal copper sulphate and 0·6–1 molar ammonia almost exactly the ratio 1:4 of copper to bound ammonia. Measurements of the solubility of cupric oxide in ammonia solution supported this conclusion. Dry copper sulphate absorbs ammonia gas at 1 atmosphere pressure up to the composition $CuSO_4, 5\,NH_3$; on warming, this is converted into the tetrammine $[Cu(NH_3)_4]SO_4$, which has an ammonia tension of 1 atmosphere at 90°.

Thus we have good evidence for the existence of a very stable tetrammine complex. The diammine complex is also stable. Thus cupric thiocyanate is found to give a stable pale blue diammine $[Cu(NH_3)_2](CNS)_2$ or perhaps $[Cu(NH_3)_2(CNS)_2]$ as well as the usual dark blue tetrammine $[Cu(NH_3)_4](CNS)_2$; the same is true of the sulphate and the fluorosulphonate. The behaviour of the nitrites shows that these ammines, both the tetra and the di, are much stronger bases than cupric hydroxide. The simple nitrite $Cu(NO_2)_2$ cannot be isolated, as it breaks up into the nitrate and nitric oxide. But the blue tetrammine $[Cu(NH_3)_4](NO_2)_2$ is quite stable. When this is heated it loses 2 molecules of ammonia to form the purple diammine $[Cu(NH_3)_2](NO_2)_2$,[839] which is also quite stable; but if by further heating more ammonia is removed from the complex, the product decomposes.[840] Other examples of these diammines occur among the substituted amines.

The brilliant colour of these cupric ammines is familiar. Various attempts have been made to interpret their absorption spectra. Weigert found[841] that there was a continuous change in the position of the absorption bands as the concentration of the ammonia increased, and concluded that the effect was purely physical; but later work, especially that of Rosenblatt,[842] does not support this conclusion, and makes it clear that the change in colour is the result of a chemical change in the proportions of the various ammoniated ions present. This is to be expected from the differences in colour of the solid ammines: as a rule the diammimes are pale blue (rarely green), the tetrammines violet-blue, and the pentammines and hexammines

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[835] C. Immerwahr, *Z. anorg. Chem.* 1900, **24**, 269.

[836] G. Peyronel, *Gaz.* 1941, **71**, 363.

[837] P. Pfeiffer and V. Pimmer, *Z. anorg. Chem.* 1905, **48**, 98.

[838] H. M. Dawson and J. McCrae, *J.C.S.* 1900, **77**, 1239; 1901, **79**, 1072.

[839] H. Bassett and R. G. Durrant, ib. 1922, **121**, 2630.

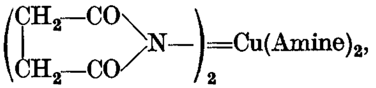
[840] H. J. S. King, ib. 1929, 2593.

[841] F. Weigert, *Z. physikal. Chem.* 1922, **101**, 414; **102**, 416.

[842] F. Rosenblatt, *Z. anorg. Chem.* 1932, **204**, 351.

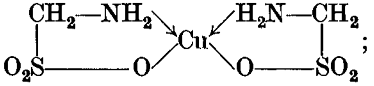
again pale blue. But with the derivatives of the simple monamines the equilibria in solution are numerous and difficult to interpret; see Bjerrum.[843] With the chelate derivatives the problem is simpler, and Rosenblatt's results will be discussed under these compounds (p. 164).

Substituted Ammines. These are formed by a variety of alkyl and aryl amines and similar substances; they have not been so fully investigated as the simple ammines. The introduction of alkyl and aryl radicals into the ammonia tends to reduce the co-ordinating power in this as in other cases. Thus Tschugaeff[844-5] examined the formation of the 4-covalent complex produced by adding two amine molecules to the cupric derivatives of succinimide



and found that while primary amines react quite readily, secondary do so with difficulty, and tertiary not at all; in this as in other reactions pyridine has the reactivity not of a tertiary but rather of a primary amine.

The behaviour of amino-acids is peculiar. If the relative positions in space of the amine and the acid group are suitable for the formation of chelate ring, then the ring is produced: e.g. the cupric derivative of aminomethane sulphonic acid is dark blue and insoluble in water[846]; it obviously contains two chelate rings



glycine behaves in the same way (these compounds are discussed under the chelate derivatives, p. 166). If the NH_2 and the acid group are too far apart in space to form a ring, as in meta or para aniline sulphonic acid, the product is greenish and reasonably soluble in water; it obviously cannot be a ring-compound for stereochemical reasons, but, on the other hand, the colour is not that of a simple cupric salt but rather of an ammine such as $[\Phi\cdot SO_3]_2[Cu(\Phi\cdot NH_2)_2]$. It is clear that in this compound the copper is ionized, and at the same time co-ordinated to the NH_2 group of its anion, giving the zwitter-ion[847]

$$\overset{-}{SO_3}\cdot C_6H_4—NH_2\rightarrow\overset{++}{Cu}\leftarrow NH_2—C_6H_4\cdot\overset{-}{SO_3}.$$

A third case arises with aminosulphonic acid $H_2N\cdot SO_3H$ itself.[846] This gives a copper derivative of the colour and solubility to be expected of a normal cupric salt. It obviously cannot be chelate, as this would imply a 4-ring; on the other hand, the colour makes it likely that the copper ion

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[843] N. Bjerrum, *Complex Ammine Formation in Solution*, Copenhagen, 1941.

[844] L. Tschugaeff, *Ber.* 1905, 38, 2899.

[845] See also H. Ley and F. Werner, ib. 1906, 39, 2177; 1907, 40, 705.

[846] J. Meyer and W. Taube, *Z. anorg. Chem.* 1936, **227**, 425.

[847] P. Pfeiffer, ib. 1936, **230**, 97.

is not co-ordinated to the NH_2, presumably owing to the effect of the immediately adjacent sulphonic group in weakening the co-ordinating power of the NH_2.

One result of the diminished co-ordinating power produced by substitution in the amine is to give complexes of a lower co-ordination number. King[840] found that the complex ammine nitrites formed with aniline, *p*-toluidine, β-naphthylamine, and pyridine contained not 4 molecules of base (as did the simple ammonia compounds) but 2. Auméras and Tamisier examined[848] by means of the colour the degree of co-ordination in solution (which is often higher than in the solid) of the tetrammines produced by cupric salts with the bases methylamine, pyridine, and piperidylpiperidine $C_5H_4N \cdot C_5H_{10}H$; they found the dissociation constants to be $1{\cdot}6 \times 10^{-8}$, $3{\cdot}1 \times 10^{-4}$, and $2{\cdot}2 \times 10^{-3}$ respectively, the stability thus diminishing as the molecular weight of the base increases.

Complex Cupric Azides[849, 851-2]

Cupric azide (p. 150) dissolves in solutions of the azides of the alkalies and substituted ammoniums to give a series of red-brown or blue complexes of the types $M[Cu(N_3)_3]$, $M_2[Cu(N_3)_4]$, and $M[Cu_2(N_3)_5]$, the last type the commonest, all of which are capable of hydration; the non-salt types $R \cdot NH_2Cu(N_3)_2$ and $(R \cdot NH_2)_2Cu(N_3)_2$ have also been obtained.[850] They are usually explosive; they are always decomposed by much water, but will sometimes dissolve in a small quantity without change. Among the alkaline salts it is found that as the atomic weight of the alkali increases, the number of azide groups per copper atom falls, the ease of crystallization and the stability to water increase, while the solubility in water diminishes (this last is characteristic of the alkaline salts of strong acids).

Nitro-complexes

Double nitrites (i.e. nitro-complexes) of divalent copper exist, but are little known. Soluble potassium and rubidium salts of the unusual but not impossible type $M_3[Cu(NO_2)_5]$ have been prepared[853-4]; they give yellow solutions in water. The thallous salt $Tl_3[Cu(NO_2)_5]$[855] is black, and its aqueous solution green. All these salts and their solutions are stable in the cold.[856]

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[848] M. Auméras and A. Tamisier, *Bull. Soc. Chim.* 1933, [4] **53**, 97.

[849] A. Cirulis and M. Straumanis, *Ber.* 1943, **76**, 825.

[850] Id., *Z. anorg. Chem.* 1943, **251**, 341.

[851] M. Straumanis and A. Cirulis, ib. 1943, **252**, 9.

[852] Id., ib. 121. [853] A. Fock, *Z. Krist.* 1890, **17**, 177.

[854] A. Kurtenacker, *Z. anorg. Chem.* 1913, **82**, 204.

[855] V. Cuttica and A. Paciello, *Gaz.* 1922, **52**, [i] 141.

[856] For measurements of the light absorption and equilibrium of these ions in solution see A. Kossiakoff and D. V. Sickman, *J.A.C.S.* 1946, **68**, 442.

A series of hexanitrito-salts $M'_2M''[Cu(NO_2)_6]$ (where $M' = NH_4$ or $K : M''$ = calcium of lead) were described by Przibylla.[857] It is remarkable that an exactly corresponding series of argentous salts (allowing for the difference of valency) $M'_3M''[Ag(NO_2)_6]$ is said to occur (p. 138), and another of hexanitrato- (not nitrito) auric salts (p. 189); these if they are real are the only known examples of argentous or auric complexes with a covalency higher than 4.

Nitric Oxide Complexes

The last series of open-chain complexes with the Cu—N link consists of those formed by nitric oxide.

Complexes with carbon monoxide, corresponding to those formed by cuprous compounds (p. 131), do not seem to be formed by cupric salts. But an analogous complex with nitric oxide has been prepared by Kohlschütter and Kutscheroff.[858] They found that blue solutions of cupric salts absorb no nitric oxide, but if the solution is turned green—i.e. if a complex anion is formed—either by increasing the concentration, or by adding a soluble alkaline chloride, or by dissolving the cupric salt in an organic solvent, especially acetone, a rapid absorption of nitric oxide occurs. With cupric chloride dissolved (at $V = 1{,}166$ litres) in acetone or in glacial acetic acid, the absorption rises to 81 litres of NO per g. atom of copper, giving the ratio NO : Cu of 3·6 : 1 (the CO : Cu′ ratio does not exceed 1). The reactions of formation in the two cases are obviously similar; in both it is only a copper complex that will absorb the gas: solid cuprous chloride is not acted on. Now there is reason to think (see below, Gp. V. 685) that both carbon monoxide and nitric oxide in their metallic compounds are attached by a pair of electrons, but that the nitric oxide molecule in addition to providing the electrons for the link transfers its 'odd' electron to the metal: thus we have

$$\overset{-}{M}—C\equiv\overset{+}{O} \quad \text{and} \quad \overset{=}{M}—\overset{+}{N}\equiv\overset{+}{O}.$$

If this view is correct, the result of attaching a CO to a cuprous atom and an NO to a cupric atom will be to give the copper precisely the same effective atomic number and the same number of shared electrons.

Oxygen Complexes

The cupric atom has a much stronger tendency to form complexes through oxygen than any of the three metals in the monovalent state.

The first indication of this is the prevalence of hydration among the cupric salts, which is in sharp contrast to their absence among the argentous. Most of the soluble cupric salts form hydrates, e.g. the fluoride, chloride, bromide, chlorate, perchlorate, nitrate, sulphate, formate, acetate, propionate, and butyrate. Werner[859] has pointed out that

[857] C. Przibylla, *Z. anorg. Chem.* 1897, 15, 419.
[858] V. Kohlschütter and M. Kutscheroff, *Ber.* 1904, 37, 3044.
[859] *N.A.* ed. 5 [1923], p. 199.

a very large number of the salts have 4 molecules of water of crystallization, and must be supposed to contain the complex ion $[Cu(OH_2)_4]^{++}$. He draws attention to the series of the general type $[Cu(OH_2)_4]X''$, where $X'' = SiF_6$, SnF_6, $NbOF_5$, $MoOF_5$, MoO_2F_4, WO_2F_4, all of which are isomorphous. There is an obvious analogy to these salts in the very stable tetrammines.

We have examples of oxygen complexes in the double formates, such as $Ba_2[Cu(O \cdot CHO)_6]$, 4 H_2O[860-1]: an analogous strontium salt is known; and in the double acetates, such as $K_4[Cu(O \cdot CO \cdot CH_3)_6]$, 12 H_2O and

$Ca[Cu(O \cdot CO \cdot CH_3)_4]$, 6 H_2O.[862]

The occurrence of the co-ordination number of 6 in these compounds will be noticed, but X-ray data are unfortunately lacking.

It is, of course, by the formation of oxygen complexes that sugar, glycerol, and other hydroxylic compounds prevent the precipitation of copper by alkalies; they lower the Cu^{++} concentration so that the solubility product of cupric hydroxide (3×10^{-5} at 25°) is not reached.

The majority of the oxygen complexes of divalent copper are chelate compounds, and will be described later (N, O, p. 165; O, O, p. 168).

Sulphur Complexes

Cupric copper, unlike cuprous, forms far fewer complexes through sulphur than through oxygen, and the majority of these (as with oxygen) are chelate compounds (p. 173). A few open-chain derivatives are known. Thiourea $S{=}C(NH_2)_2$ forms complex salts with copper sulphate containing 1, 2, and 3 molecules of thiourea,[863-6] but no other complexes with a cupric atom co-ordinated to sulphur seem to have been prepared.

Halide Complexes

The readiness with which the cupric ion co-ordinates with halogen ions is shown by the change of colour occurring in the solutions of the simple halides at high concentrations. To judge by the colour the formation of the complex anions is promoted by a rise of temperature, so that they must be formed with absorption of heat.

All the four halogens behave in this way. Remy and Laves in 1933[867] classified all the then known complex cupric chlorides (33 in all) and showed that the number of each kind was:

$CuCl_3^-$	$CuCl_4^{--}$	$CuCl_5^{---}$	$CuCl_6^{----}$
9	22	2	0*

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* A few salts of this type have recently been discovered: see later.

[860] P. Friedländer, *Z. Krist.* 1879, **3**, 180.

[861] See also A. W. Davidson and V. Holm, *J.A.C.S.* 1931, **53**, 1350.

[862] F. Rüdorff, *Ber.* 1888, **21**, 279.

[863] A. Rosenheim and W. Loewenstamm, *Z. anorg. Chem.* 1903, **34**, 62.

[864] A. Rosenheim and W. Stadler, ib. 1906, **49**, 1.

[865] V. Kohlschütter, *Ber.* 1903, **36**, 1151.

[866] V. Kohlschütter and C. Brittlebank, *Ann.* 1906, **349**, 232.

[867] H. Remy and G. Laves, *Ber.* 1933, **66**, 401.

With the chlorides, the hydrogen compounds themselves are known; they separate from a solution of cupric chloride in concentrated hydrochloric acid, and are reddish-blue or garnet-red (for compositions see below).

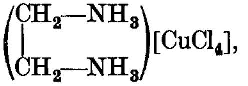
These complex halides are remarkable, even among the complex cupric compounds, for the diversity of their colours. The following are examples, largely taken from Abegg.[868]

Fluorides: $K[CuF_3]$, $Rb[CuF_3]$, almost white, slightly soluble in water; $(NH_4)_2[CuF_4]$, 2 H_2O, pale blue, almost insoluble.[869,870] It has not been found possible to prepare mixed halides, containing both fluorine and chlorine.

Chlorides. (1) Acids: $H[CuCl_3]$, 3 H_2O, and $H_2[CuCl_4]$, 5 H_2O; these are garnet red;[871-3] $H_3[CuCl_5]$, brown, precipitated from ethyl acetate solution (no analyses given).[874]

(2) Alkaline salts: $M[CuCl_3]$; Li, 2 H_2O, garnet red; NH_4, anhydrous, red; 2 H_2O, blue; K, brown-red; Cs, garnet red; the crystals of $CsCuCl_3$ have been shown[874a] to consist of continuous chains of $CuCl_4$ groups, each attached to the next by a common Cl atom, the chains being held together by the Cs cations. $M_2[CuCl_4]$; $(NH_4)_2$ 2 H_2O, greenish-blue; K_2, 2 H_2O, blue; Cs_2, anhydrous, bright yellow; 2 H_2O, blue-green.

(3)



$$\begin{pmatrix} CH_2-NH_3 \\ | \\ CH_2-NH_3 \end{pmatrix}[CuCl_4],$$

anhydrous, brownish-yellow. Two salts, solvated with other molecules than water, are $Li[CuCl_3]$, $H\cdot COOH$ (crystallized from formic acid), dark red, and $Li[CuCl_3]$, CH_3CN, from acetonitrile, yellow-red.

Various attempts have been made[875] to relate the colours of these salts to their constitution, but the conclusions are vitiated by the absence of X-ray data for many salts; as the example of the potassium double chloride (below, p. 163) shows, the true structures may be very different from the apparent.

Other more recent investigations of these chlorides, and of the conditions of their existence, have been made by Lopatkin,[876] Chretien,[877] and Amiel.[878] Lopatkin was able from the investigation of the system $LiCl-CuCl_2-H_2O$ to isolate the 6-covalent salt

$$Li_4[CuCl_6], 10\ H_2O;$$

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[868] *Handbuch*, 1908, ii. 1. 544.

[869] J. Kaas, *Chem. Ztg.* 1908, **32**, 8.

[870] H. v. Helmolt, *Z. anorg. Chem.* 1893, **3**, 138.

[871] A. Ditte, *Ann. Chim. Phys.* 1881, [5] **22**, 561.

[872] R. Engel, *C.R.* 1888, **106**, 273.

[873] P. Sabatier, ib. 1724; **107**, 40.

[874] A. Naumann, *Ber.* 1899, **32**, 1002.

[874a] A. F. Wells, *J.C.S.* 1947, 1662.

[875] A. Werner, *N.A.*, ed. 5 (1923), p. 104.

[876] J. M. Lopatkin, *Trans. Butlerov Inst. Kazan*, 1934, **1**, 13.

[877] A. Chretien and R. Weil, *Bull. Soc. Chim.* 1935, [v] **2**, 1577.

[878] J. Amiel, *C.R.* 1935, **201**, 1383.

it is, however, unstable; it is very hygroscopic, and is decomposed by water to give the 3-covalent salt $Li[CuCl_3]$, $2 H_2O$.

A warning against too great a reliance on composition in the absence of X-ray data is afforded by the salt $2 KCl$, $CuCl_2$, $2 H_2O$, usually written $K_2[CuCl_4]$, $2 H_2O$; Hendricks and Dickinson[879] and Chrobak[880] have shown by X-ray analysis that each copper atom has 2 chlorine atoms 2·32 A, and 2 oxygens 1·97 A away, all in the same plane with it: and further 2 Cl atoms above and below the plane at a distance of 2·95 A; 'in fact the crystal is a closely packed aggregate of $CuCl_2(OH_2)_2$ molecules, chlorine ions, and potassium ions'.[882] A similar arrangement has been found in $2 NH_4Br$, $CuBr_2$, $2 H_2O$.[881]

The bromides are analogous to the chlorides, but are much more deeply coloured. They are of two types, $M[CuBr_3]$ and $M[CuBr_4]$. Examples (with probable distribution of the water molecules) are: $M[CuBr_3]$; (H, $2 H_2O$) dark red-brown; K, Cs, anhydrous, black; $M_2[CuBr_4]$: (Li, $3 H_2O)_2$, Cs_2, black. Complex tetrabromides of organic bases like pyridine, quinoline, and ethylene diamine are known.[883]

Complex iodides are little known, owing to the instability of the simple iodide; but salts of the type $M_2[CuI_4]$ have been prepared.

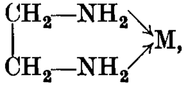
Chelate Cupric Complexes

Chelate groups, being attached by two atoms, always tend to be more stable than open-chain groups, and this is particularly true with the cupric compounds: the chelate derivatives are remarkable for their number and their stability. The atoms directly attached to the copper may be 2 nitrogens, a nitrogen and an oxygen, 2 oxygens, or 2 sulphurs.

Nitrogen-nitrogen Complexes

These form an important class of cupric complexes. Most of them are diamine derivatives, in which a molecule with 2 NH_2 groups plays the part of two amine molecules; other basic nitrogen atoms can replace those of the NH_2 groups, for example, the nitrogens in dipyridyl.

The ethylene diamine (*en*) molecule $H_2N—CH_2—CH_2—NH_2$ is remarkable for its power of forming a stable 5-ring of the type



though the stability of this ring is less with copper than with cobalt and much less than with platinum. With trivalent transitional atoms such as those of chromium and cobalt Werner has prepared a large series of stable salts of the type $[M(en)_3]X_3$. With the divalent cupric atom 6-covalent complexes of this kind can be made, such as $[Cu(en)_3]Br_2$, and the corre-

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[879] S. B. Hendricks and R. G. Dickinson, *J.A.C.S.* 1927, **49**, 2149.

[880] L. Chrobak, *Z. Krist.* 1934, **88**, 35.

[881] A. Silberstein, *Bull. Soc. franç. Min.* 1936, **59**, 329.

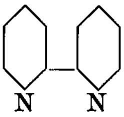
[882] L. Pauling, *Chemical Bond*, p. 101.

[883] See, for example, P. Pfeiffer and V. Pimmer, *Z. anorg. Chem.* 1906, **48**, 98.

sponding sulphate (5 H_2O), nitrate (2 H_2O), acetate (2 H_2O), and recently the aryl-sulphonates.[884] But a more usual and an exceptionally stable[885] type is the 4-covalent dichelate form $[Cu(en)_2]X_2$ which is not reduced even by hypophosphite. Morgan and Burstall[886] have made a whole series of salts of this type (especially with dibasic anions), practically none of which form hydrates. It is, therefore, probable that even with these powerful chelate groups the 4-covalent state is more stable for the cupric ion than the 6. This is supported by the work of Amiel,[887] who found that his tri-*en* salts, such as $[Cu(en)_3](ClO_4)$, H_2O lose one diamine group to go over into the more stable $[Cu(en)_2]$ compounds. Conversely, Rosenblatt has concluded[888] from an examination of the absorption spectra of the di-*en* compounds that in solution a 6-covalent $[Cu(en)_2(OH_2)_2]$ complex is formed, and further, that if ammonia is added to the solution this gradually replaces the water in the complex. Wahl[889] claimed to have resolved the salt $[Cu(en)_2(OH_2)_2]X_2$ through the tartrate; this would imply that the 6-covalent form (which alone can be optically active) persisted unchanged throughout the manipulation. But later workers, especially Johnson and Bryant,[890] failed to repeat the work, and it is probably incorrect.

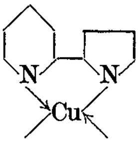
Complexes with only one ethylene diamine attached to the copper have been described, such as $Cu(en)Cl_2$; this might be a 4-covalent non-ionized amine, or a 2-covalent salt $[Cu(en)]Cl_2$. Investigation has, however, shown[891] that it is really the salt $[Cu(en)_2]\cdot[CuCl_4]$, since the cation can be precipitated as the chloroplatinate $[Cu(en)_2]\cdot[PtCl_6]$.

Other diamino-compounds will form chelate complexes in the same way as ethylene diamine if they have their nitrogen atoms in stereochemically suitable positions. A series of dichelate derivatives have been obtained from propylene diamine.[892] With α-pyridyl-pyridine



Jaeger and van Dijk[894] have made a series of cupric complexes, containing 1, 2, and 3 of these chelate (dipy) rings in the molecule.

The rather similar α-pyridyl pyrrol[893]



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[884] J. V. Dubsky and J. Trtilek, *J. prakt. Chem.* 1934, [ii] **140**, 47.

[885] See P. Job, *C.R.* 1927, **184**, 1066.

[886] G. T. Morgan and F. H. Burstall, *J.C.S.* 1927, 1259.

[887] J. Amiel, *C.R.* 1934, **199**, 201.

[888] *Z. anorg. Chem.* 1932, **204**, 351.

[889] W. Wahl, *Soc. Sci. Fennica*, 1927, 4, (14) 1.

[890] C. H. Johnson and S. A. Bryant, *J.C.S.* 1934, 1783.

[891] F. W. Chattaway and H. D. K. Drew, ib. 1937, 947.

[892] G. Spacu and P. Spacu, *Bul. Soc. Stiinte Cluj*, 1932, 7, 95.

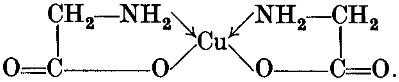
[893] B. Emmert and F. Brandl, *Ber.* 1927, 60, 2211.

forms a series of dichelate cupric (and zinc) complexes; those of trivalent iron and cobalt are trichelate.

Another class of N,N chelate cupric complexes is formed by the *o*-amino-azo-compounds.[895]

Chelate Nitrogen-oxygen Complexes

The simplest compounds of this kind are the glycocoll (amino-acetic acid) derivatives.[896–7] The cupric 'salt' of this acid has few of the properties of a salt. It is very slightly soluble in water; it has a deep blue-violet colour more like that of a cuprammonium compound[898]; the solution has a very small conductivity, and it shows a minute concentration of cupric ions, so that the copper is not precipitated by alkali, and indeed only imperfectly by alkaline sulphide. There can be no doubt that it is a non-ionized compound of the dichelate structure



Cupric derivatives of precisely the same properties and evidently the same type are formed by a number of naturally occurring α-amino-acids such as alanine (α-amino-propionic acid) and leucine (α-amino-isocaproic acid); the electrical conductivity of these compounds in solution is not more than a tenth of that of the corresponding derivatives of dibasic amino-acids, which must have one carboxyl group free.[899]

The ease of formation of the ring must obviously depend on the relative positions of the carboxyl and the amino-group. Tschugaeff and Serbin[900] have compared the cupric derivatives of α-, β-, γ-, and δ-amino acids (which would give rings of 5, 6, 7. and 8 atoms respectively), and they find that while the tendency to complex formation is very strong with the α- (giving 5-rings) it is weaker with the β-, and entirely absent from the γ- and δ-. (It will be remembered that for plane isocyclic rings the least strain is in the 5-ring.)

If ammonia is added to a solution of copper glycinate, the colour and the conductivity change in such a way as to indicate that the NH_2 of the chelate group is gradually replaced by ammonia, with the conversion of the complex into a normal cuprammonium salt.[901] On the other hand, in the presence of aminoacetate ions (an alkaline salt of glycine) a complex

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[894] F. M. Jaeger and J. A. van Dijk, *Proc. K. Akad. Amst.* 1934, **37**, 395 (*B.C.A.* 1934, 1317).

[895] See, for example, G. Charrier and A. Beretta, *Gaz.* 1927, **56**, 865.

[896] For the crystal structures see A. A. Grinberg and Z. E. Goldbreich, *J. Gen. Chem. Russ.* 1941, **11**, 1039.

[897] For the crystal structure of α-amino-isobutyrate see A. J. Stosick, *J.A.C.S.* 1945, **67**, 362.

[898] The stability of the complex is shown by the fact that in solution it obeys Beer's law [H. Ley, *Z. anorg. Chem.* 1927, **164**, 377].

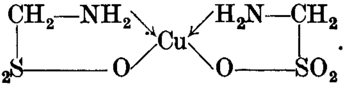
[899] E. Abderhalden and H. Schnitzler, *Z. physikal. Chem.* 1926, **163**, 94.

[900] L. A. Tschugaeff and E. Serbin, *C.R.* 1910, **151**, 1361.

[901] H. Ley and F. Vanheiden, *Z. anorg. Chem.* 1930, **188**, 240.

cupric anion is formed. The E.M.F. measurements of Riley and Gallafent[902] indicate that this is the trichelate complex $[Cu(gl)_3]^-$ (glycine = Hgl). The formation of a complex of this type with glycine, while it is not formed with glycollic acid (hydroxyacetic acid), seems to show that the co-ordination of the copper atom is stronger to nitrogen than to oxygen, as we have seen elsewhere. At lower concentrations it has been found[903] that dichelate complexes are formed.

A very similar complex is formed by aminomethane sulphonic acid $H_2N \cdot CH_2 \cdot SO_3H$, the cupric derivative of which is quite insoluble in water, and is dark blue: it obviously has the dichelate structure[904]



It is probable that we should include among the N,O-chelate complexes the red cupric compounds formed in the biuret reaction. Biuret can be made by heating urea, and has the formula $NH_2 \cdot CO \cdot NH \cdot CO \cdot NH_2$. With copper sulphate alone biuret gives a normal blue cupric derivative, but in presence of alkali a reddish-purple colour is produced, which is an indication of complex formation. This was discovered by Wiedemann in 1847,[905] and investigated by Schiff[906] and Emil Fischer.[907] Later work, especially by W. Traube,[908-9] has made it clear that the red compound is the alkaline salt $K_2[Cu(C_2O_2N_3H_3)_2]$ (biuret = $C_2O_2N_3H_5$)—the salt of a complex cupric anion, in which two hydrogen atoms of each biuret molecule are replaced. Schiff has shown that the potassium atoms can be replaced by two monovalent cations of any strong base, tetramethyl ammonium, tetraethyl phosphonium, triethyl sulphonium, cuprammonium $Cu(NH_3)_4''$, or the diammine of monovalent silver $Ag(NH_3)_2'$.

The structure of the product is still very obscure; the reaction presumably depends on the formation of a chelate ring, but it is not even clear whether this is a 5- or a 6-ring, or whether it is attached to the copper through two nitrogens, a nitrogen and an oxygen, or two oxygens. It does not seem possible to find any single type of ring that could be formed by all the compounds including biuret, oxamide, and malonamide[907,910] that will give the red colour under these conditions.

Another compound which gives chelate O,N-complexes of divalent copper, with a 6-ring containing two double links, is salicylaldoxime. This particular type of compound seems to give peculiarly insoluble cupric derivatives. Salicylaldoxime can be used to determine copper quantita-

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[902] H. L. Riley and V. Gallafent, *J.C.S.* 1931, 2029.

[903] R. M. Keefer, *J.A.C.S.* 1946, **68**, 2329.

[904] J. Meyer and W. Taube, *Z. anorg. Chem.* 1936, **227**, 425.

[905] G. Wiedemann, *J. prakt. Chem.* 1847, **42**, 255.

[906] H. Schiff, *Ann.* 1897, **299**, 236.

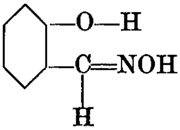
[907] E. Fischer, *Ber.* 1902, **35**, 1105.

[908] W. Traube, *Ber.* 1923, **56**, 1653.

[909] W. Traube and W. Wolff, ib. 1927, **60**, 43.

[910] H. Schiff, *Ann.* 1907, **352**, 73.

tively by precipitation in presence of any other metals whatever. Nickel and cobalt come nearest, but the complexes they yield, though insoluble in water, will dissolve in dilute acetic acid, in which the copper complex is quite insoluble.[911-12] In a later paper Ephraim shows[913] that this peculiar

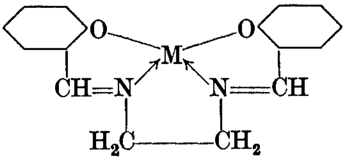


insolubility of the cupric compound extends to a whole series of *o*-hydroxybenzaldoxime derivatives: to the oximes of 6-methoxybenzaldehyde, of α-hydroxy-β-aldehydonaphthalene, of β-hydroxy-α-acetyl naphthalene, and of 1-hydroxy-acetophenone and the following of its substitution products: 3-OH, 4-OH, 3-OMe, 4-OMe, 3, 4 dihydroxy. The relative solubilities for different metals, either in water or in dilute acetic acid, are nearly always in the same order,

$$\mathrm{Cu} < \mathrm{Ni} < \mathrm{Co} < \mathrm{Zn} < \mathrm{Cd},$$

all other metals giving much more soluble derivatives; silver, lead, and mercury come nearest to those already mentioned; then the alkaline earth metals, magnesium, calcium, strontium, and barium; and finally the alkaline derivatives, which are presumably true salts, and are the most soluble of all. Chromic and aluminium salts give no precipitates with these oximes; ferric salts give deeply coloured solutions (i.e. complexes are formed) and sometimes a precipitate, but this is always soluble in dilute acids. For other α-keto-oxime derivatives see Tschugaeff's papers.[914-16]

Pfeiffer prepared[917] a series of aldimine complexes with the ethylene diimine compound I below and compared the stability of various metals at M by boiling the complex of one with the acetate of another; he found divalent copper the most stable; it replaces nickel, vanadyl, ferrous iron, and zinc, and cannot be replaced by them.



I.

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[911] F. Ephraim, *Ber.* 1930, **63**, 1928.

[912] See also L. P. Biefeld and D. E. Howe, *J. Ind. Eng. Chem.* 1939 [Anal.], **11**, 251.

[913] F. Ephraim, *Ber.* 1931, **64**, 1210.

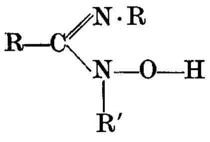
[914] L. Tschugaeff, *Z. anorg. Chem.* 1905, **46**, 144.

[915] Id., *Ber.* 1908, **41**, 1678, 2226.

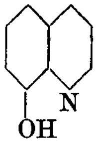
[916] L. Tschugaeff and L. Spiro, ib. **41**, 2219.

[917] P. Pfeiffer, H. Thielert, and H. Glaser, *J. prakt. Chem.* 1939, [ii] **152**, 145.

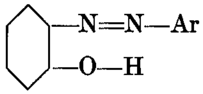
Similar complexes are formed by oxy-amidines[918] (formula II) by 8-oxyquinoline (formula III)[919,920] and by *o*-oxy-azo-dyes (formula IV)[921]:



II.



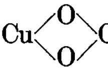
III.



IV.

The magnetic properties of these chelate complexes have been examined by G. N. Tyson and S. C. Adams,[922] who found that cupric disalicylaldehyde (O, O) and cupric disalicylaldimine (O, N) are both paramagnetic, with a susceptibility of 1·9 Bohr magnetons (theory requires 1·73). Hence both are probably (as we should expect) planar.

Oxygen-oxygen Complexes

These are very numerous, and can be divided into three classes: (*a*) the 'ato' complexes in which the chelate group is the anion of an oxy-acid, which links up with the copper through two of its oxygen atoms; (*b*) those in which the chelate group is a neutral molecule with two oxygens in suitable positions to form a stable ring with the copper, usually with the replacement of a hydroxylic hydrogen; (*c*) the peculiar 'hexol' compounds of Werner, in which one copper atom is linked through two oxygens to another copper atom, giving the 4-ring  The 'ato' compounds are practically always complex anions: compounds of class (*b*) are usually neutral molecules, while those of class (*c*) are either neutral or cationic.

(*a*) '*Ato*' *complexes*

Carbonato. Cupric hydroxide dissolves in potassium carbonate solution, the resulting solution having a very intense blue colour for the rather small amount of copper it contains. Reynolds[923] obtained from potassium carbonate and cupric acetate a complex salt $K_2[Cu(CO_3)_2]$, forming a dark blue anhydrous salt, a light blue monohydrate, and a greenish-blue tetrahydrate. It is readily soluble in water, and the solution begins to decompose at 65°. Luther and Krsnjavi showed[924] by transport experiments that the solution contained a deep blue cupric anion. Applebey and Lane[925] worked out the phase-rule relations for the system, and prepared two of the potassium salts and also a sodium salt $Na_2[Cu(CO_3)_2]$, 3 H_2O, which likewise had an intense blue colour.

[918] R. Kuhn and H. Machemer, *Ber.* 1928, **61**, 118.

[919] R. Berg, *Z. anorg. Chem.* 1932, **204**, 208.

[920] R. Berg and H. Kustenmacher, ib. 215.

[921] H. D. K. Drew and J. K. Landquist, *J.C.S.* 1938, 292.

[922] *J.A.C.S.* 1940, **62**, 1228.

[923] W. C. Reynolds, *J.C.S.* 1898, **73**, 262.

[924] R. Luther and B. Krsnjavi, *Z. anorg. Chem.* 1905, **46**, 170.

[925] M. P. Applebey and K. W. Lane, *J.C.S.* 1918, **113**, 609.

Oxalato. A lithium salt $Li_2[Cu(C_2O_4)_2]$, $2\,H_2O$ was obtained by Troost[926] and the corresponding sodium salt (also with $2\,H_2O$) by Riley.[927] Both are sky-blue and fairly soluble in water; the solution decomposes only on long boiling.

Dicarboxylato. H. L. Riley[927-8] has made an interesting study of the cupric complexes in the series carbonato-oxalato-malonato-succinato and some of their derivatives. The carbonato and succinato complexes are very unstable, and only exist in solution in presence of excess of carbonate or succinate ions: they contain, of course, a 4-ring and a 7-ring respectively; the oxalato- (5-ring), malonato- (6-ring), and also the *o*-phthalato (7-ring) complexes are more stable. They all form salts of the type of $Na_2[CuA_2]$, 2 aq. which do not lose their water of crystallization in a vacuum. The stability of the complexes was determined by means of the E.M.F. The values for the dissociation constant

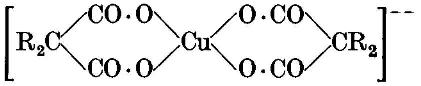
$$K = \frac{[Cu^{++}]\cdot[A^{--}]^2}{[CuA_2^{--}]}$$

were: oxalato $0{\cdot}33 \times 10^{-8}$; malonato $0{\cdot}54 \times 10^{-7}$; phthalato $0{\cdot}31 \times 10^{-4}$; the phthalato is the only one of these three salts that is hydrolysed by water, so that the effect of the 7-ring, though it is weakened by that of the aromatic nucleus, is still apparent.

In his second paper[928] Riley determines the effect on the stability of the malonato-complex of replacing the hydrogens in the CH_2 group by alkyls. The method used is electrometric titration. The general conclusions are shown by the dissociation constants for the complex given in the following table, which also indicates the curious way in which the colour varies:

$$K = [Cu^{++}]\cdot[A^{--}]/[CuA_2^{--}]^2$$

for



R_2	Et_2 Pr_2	Me_2	H_2 MeH EtH PrH	IsoPrH
K. *ca.*	1×10^{-5}	$0{\cdot}4 \times 10^{-8}$	1×10^{-8}	1×10^{-9}
1 N-soln.	Deep blue		Pale blue	Deep blue

The dialkyl derivatives (Me_2, Et_2, Pr_2) were all hydrolysed by water, but the others were stable.

Tartrato. These complexes are contained in Fehling's solution. It was shown by Masson and Steele[929] that the coloured cupric complex in this solution moves in electrolysis towards the anode, and Kahlenberg[930] found by E.M.F. measurements that in a N/264 solution the concentration of free copper ions was only 10^{-10}. The structure of tartaric acid allows of the

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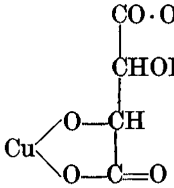
[926] *Ann. Chim. Phys.* 1857, **51**, 143.

[927] H. L. Riley, *J.C.S.* 1929, 1307.

[928] Ib. 1930, 1642.

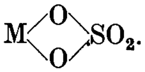
[929] O. Masson and B. D. Steele, ib. 1899, **75**, 725.

formation of an ato ring of 5, 6, or 7 atoms; it is probable that a 5-ring is formed, especially as Wark has shown (see below) that other α-oxy-acids



form similar complexes. If so, these compounds may be regarded as intermediate between the 'ato' complexes and such compounds as the catechol derivatives of Weinland (see below). This view is confirmed by the investigations of Wark,[931-4] who showed that other α-oxy-acids, such as malic and mandelic, behave in the same way.

Similar *phosphito*,[935-6] *phosphato*, and *arsenito* complexes have been shown to be formed.

Sulphato.  $\mathrm{M}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{SO_2}$. Double sulphates of copper are known, such as $Na_2[Cu(SO_4)_2]$, 2 and 6 H_2O. We have to be cautious in inferring the existence of a complex merely from that of a double salt in the solid phase, especially since so extensive and so well marked a group of double sulphates as the alums is not really complex. But there is more evidence that copper forms a sulphato-complex. A. A. Noyes[937] showed that the solubility of sodium sulphate decahydrate in water is increased by the addition of copper sulphate, and Rieger[938] found that the transport number of copper sulphate is changed by 25 per cent. on adding potassium sulphate.

(*b*) *Neutral Chelate Oxygen Complexes*

The number of these complexes that is known is very large, and is evidence that the cupric atom, unlike the cuprous, has a strong affinity for oxygen.

Alcohols will take the place of water in some cupric salts,[939] and so di-hydroxy-compounds should do the same more easily. This certainly happens. Glycol and glycerol prevent the precipitation of copper from a cupric solution by alkalies, obviously by depressing the concentration of the free cupric ion below that corresponding to the solubility product of copper hydroxide. A compound of glycol and copper sulphate of the

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[930] L. Kahlenberg, *Z. physikal. Chem.* 1895, **17**, 577.

[931] J. Packer and I. W. Wark, *J.C.S.* 1921, **119**, 1348.

[932] I. W. Wark, ib. 1923, **123**, 1816.

[933] Id., ib. 1927, 1753.

[934] E. E. Wark and I. W. Wark, ib. 1930, 2474.

[935] L. Vanino, *Pharm. Centr.-H.* 1899, **40**, 637 (C. 99. ii. 930).

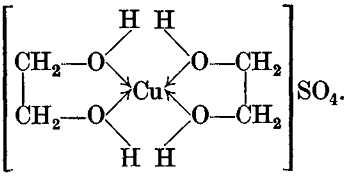
[936] R. Kremann, *Z. anorg. Chem.* 1903, **33**, 93.

[937] *Z. physikal. Chem.* 1890, **6**, 257.

[938] E. Rieger, *Z. Elektrochem.* 1901, **7**, 863.

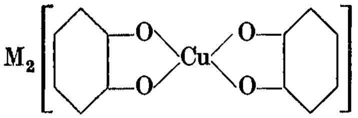
[939] For example, in $CuSO_4$, CH_3OH: R. de Forcrand, *C.R.* 1886, **102**, 551.

composition $CuSO_4$, 2 glycol, 2 H_2O, which no doubt contains the dichelate structure, has been isolated.[940]



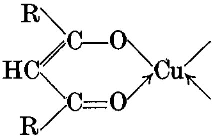
These are addition products; but many more compounds are known in which the hydrogen of the hydroxyl is replaced in the formation of the complex; we should expect this to occur when the hydroxylic compound used is more or less acidic.

Examples of this kind are the catechol derivatives prepared by Weinland[941]; these might be classed as 'ato' compounds if we can regard catechol as a dibasic acid. They are all derived from the complex anion $[Cu(O \cdot C_6H_4 \cdot O)_2]^{--}$, that is



($[Cu(cat)_2]$). For example, we have $(NH_4)_2[Cu(cat)_2]$, 2 and 0 H_2O; Li_2, 9 H_2O; K_2, 2 H_2O; Mn″, 4 H_2O; Ba, anhydrous. They are all olive-green, whether they are hydrated or not.

By far the greater number, however, of these chelate oxygen-oxygen complexes are formed from enols (compounds containing the group C=C—OH), with a CO group in the position to form a ring, as in CO—CH=C—OH, the mono-enolic forms of β-diketones and β-keto-esters; these are weakly acidic,[942] and by replacement of the hydroxylic hydrogen and co-ordination of the second oxygen give the ring



The remarkable stability of this ring is partly due to the absence of strain in the stereochemical sense, and partly no doubt to the possibility of resonance by migration of the double links.

A great many compounds of this type have been prepared: they are formed by α-dicarboxylic esters, as malonic; by β-keto-esters, as aceto-acetic and benzoylacetic; by β-diketones, as acetyl acetone; by salicylic

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[940] Werner, *N.A.* 1923, p. 202.

[941] R. Weinland and E. Walter, *Z. anorg. Chem.* 1923, **126**, 145.

[942] The classical dissociation constants at 25° are of acetyl acetone $1{\cdot}17 \times 10^{-9}$ and of ethyl acetoacetate $2{\cdot}09 \times 10^{-11}$ (M. L. Eidinoff, *J.A.C.S.* 1945, **67**, 2072).

aldehyde acid and ester; and by many other substances. The complexes are all of the dichelate (4-co-ordinated) type, and they display the usual intensity and variation of colour. They have the characteristic properties of non-ionized organic derivatives; they are as a rule fairly low melting; they can often be volatilized unchanged; they are relatively insoluble in water, but easily soluble in organic solvents including hydrocarbons; their molecular weights when determined cryoscopically in benzene have always been found to be normal.[943]

They are usually made by the action of cupric acetate on a solution of the diketone or ketoester, sometimes assisted by the addition of ammonia. For example, copper acetylacetonate CuA_2 (HA may be used as a general symbol for these chelating enols) forms dark blue crystals; it does not melt below 230°, but on heating it sublimes in pale blue needles[944]; it is slightly soluble in water, and easily in chloroform and benzene, especially when hot (0·89 g. dissolves in 1 litre of benzene at 25°).[943] The acetoacetic derivative[945] forms crystals of a peculiar green colour, which melt at 192° and sublime on heating with only partial decomposition; it is insoluble in water but easily soluble in ether, carbon disulphide, and alcohol; it can be recrystallized from benzene, a litre of which dissolves 9·02 g. of it at 25°.[943]

Moore and Young[943] have examined the extent to which one diketone or keto-ester will expel another from its cupric compound in solution. When the two cupric compounds have different colours, the replacement is often obvious to the eye, and it is remarkable that in all cases the change is apparently instantaneous, and involves no measurable heat of activation. The extent of the replacement and the equilibrium in the system can be determined

$$\mathrm{CuA_2 + HB \rightleftharpoons CuAB + HA}$$

by estimating the total copper concentration in a solution saturated with respect to one cupric compound, and containing known amounts of the organic reactant. It is found that the co-ordinating affinity decreases in the order dibenzoyl methane > acetyl acetone > benzoyl acetone $\gg$ acetone dicarboxylic ester > acetoacetic ester.

Moore and Young point out that this order of strengths is very nearly that of the percentage of enol found in the pure liquids by Kurt Meyer, whose values were[947]: dibenzoyl methane 100; benzoyl acetone 97; acetyl acetone 80·4; acetone dicarboxylic ester 16·8; acetoacetic ester 7·4. This would seem to suggest that the tendency of all the enolic forms to react with the copper was much the same. On the stability of chelate cupric complexes see further references.[948–50]

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[943] T. S. Moore and M. W. Young, *J.C.S.* 1932, 2694.

[944] L. Claisen and E. F. Ehrhardt, *Ber.* 1889, **22**, 1010.

[945] W. Wislicenus, ib. 1898, **31**, 3158. [947] K. H. Meyer, ib. 1911, **380**, 242.

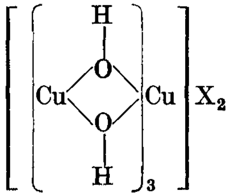
[948] M. Calvin and K. W. Wilson, *J.A.C.S.* 1945, **67**, 2003.

[949] R. B. Duffield and M. Calvin, ib. 1946, **68**, 557.

[950] M. Calvin and R. H. Bailes, ib. 949.

(*c*) *Hexol Complexes*

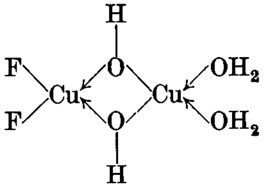
An entirely different group of oxygen co-ordinated rings is assumed with some probability by Werner in his 'hexol' compounds.[951] He points out the frequent occurrence of basic compounds of the type of CuX_2, 3 $Cu(OH)_2$, as in the minerals brochantite ($X_2 = SO_4$), atacamite ($X_2 = Cl_2$), and gerhardtite ($X_2 = (NO_3)_2$); numerous compounds of the same kind have been prepared artificially, such as the nitrite, chlorate, periodate, and dithionate. Werner writes these structures thus:



The same type of ring may occur in the basic fluoride

$$CuF(OH), H_2O \text{ or } CuF_2, Cu(OH)_2, 2\,H_2O,$$

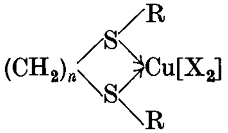
which separates by hydrolysis on warming a cupric fluoride solution, and may be written thus:



An observation which may be of interest here, though it is difficult to interpret it without further X-ray data, was made by Brasseur; he measured[952] by X-ray methods the Cu···O distances in the rather similar compound 2 $CuCO_3$, $Cu(OH)_2$, and found them to be of two kinds, with the lengths 2·05 and 2·4 A.U. respectively. These are very nearly the calculated distances for the covalent (2·01) and the electrovalent (2·3) links of copper to oxygen.

Chelate Sulphur-sulphur Complexes

These are remarkably more stable than the open-chain sulphur complexes, which are scarcely known (see p. 161); they have not, however, received much attention. So far as they are known, they only contain one chelate ring. Tschugaeff[953] found that with the disulphides $R \cdot S \cdot (CH_2)_n S \cdot R$ divalent copper and nickel form monochelate compounds of the type



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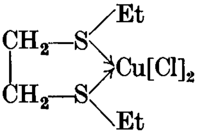
[951] *N.A.* 1923, p. 207.

[952] H. Brasseur, *Z. Krist.* 1932, **82**, 195.

[953] L. Tschugaeff, *Ber.* 1908, **41**, 2222.

when $n = 2$ (5-ring), and R = Me, Et, Pr, isoBu, amyl, or benzyl: but not if $n = 0$, 1, 3, or 5; i.e. not when the ring would contain 3, 4, 6, or 8 atoms. The ethyl compound



was made by shaking a solution of cupric chloride in hydrochloric acid with the sulphur compound. It forms very dark green crystals, m.pt. 113°, is insoluble in and rapidly decomposed by water. The isobutyl compound is quite similar and melts at 115°. The corresponding methyl compound[954] is similar and melts at 130°.

ARGENTIC COMPOUNDS

Silver in the divalent state is very unstable, and very ready to oxidize its surroundings and revert to the lower valency. The number of its divalent compounds is correspondingly limited.

Argentic Oxide

It is not certain whether a true argentic oxide exists. There seems to be no doubt that an oxide of the composition AgO can be obtained either (in the impure state) by the action of potassium persulphate on silver nitrate solution,[955] or by the anodic oxidation of silver.[956-7] This last process appears to give first Ag_2O, then AgO, and finally a solid with a composition between AgO and Ag_2O_3. The sesquioxide Ag_2O_3 cannot be got in the pure state; the E.M.F. measurements indicate that the most highly oxidized product is a solid solution of Ag_2O_3 in AgO. If this product is heated not above 100°, it evolves oxygen and yields pure AgO.

There are, however, two possible formulae for a compound of the composition AgO: it may be a true argentic oxide, or it may be argentous peroxide Ag_2O_2: it should be possible to decide from the magnetic properties. Sugden[958] has examined the AgO produced by Austin's method (from potassium persulphate) and finds it to be diamagnetic; on the other hand, Klemm[959] finds that his AgO is weakly paramagnetic, but he does not say how he obtained it. Noyes's work (next section) seems to make it clear that the product of anodic oxidation is argentic, and it is difficult to see how a compound of the composition Ag_2O_3 can be formulated, except as containing both an argentic atom and a peroxide group.

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[954] G. T. Morgan and W. Ledbury, *J.C.S.* 1922, **121**, 2882.
[955] P. C. Austin, ib. 1911, **99**, 262.
[956] F. Jirsa, *Z. anorg. Chem.* 1925, **148**, 130.
[957] F. Jirsa, J. Jelinek, and J. Srbek, ib. 1926, **158**, 33, 61.
[958] S. Sugden, *J.C.S.* 1932, 161.
[959] W. Klemm, *Z. anorg. Chem.* 1931, **201**, 32.

Argentic Ions in Solution

There is no doubt that an argentic ion can be produced in solution. A. A. Noyes and his colleagues[960] showed that the black anodic deposit from the electrolysis of an aqueous solution of silver nitrate can be dissolved in nitric acid, and this solution has properties which are not those of a peroxide; it contains no hydrogen peroxide, and it is not reduced by potassium permanganate or lead dioxide.* Noyes and his collaborators examined in particular the reaction of ozone on a solution of silver nitrate in strong nitric acid. They showed that a black solution is produced which must contain a salt of the argentic ion Ag^{++}, both from its chemical properties and from its paramagnetism. In concentrated nitric acid at 0° the oxidation of the silver is nearly complete, but in dilute acid it is imperfect, because the argentic ion reacts with the water to form the argentous ion and oxygen. Measurements of the E.M.F. showed that the polyvalent ion must be Ag^{++} and not Ag^{+++}; they gave for the oxidation potential E° of the reaction

$$Ag^{++} + e^- = Ag^+$$

the value of 1·914 volts.

Though it is clear that these solutions must have contained the ions of argentic nitrate $Ag(NO_3)_2$, no solid was isolated from them, and, in fact, the only argentic salts so far obtained have been the fluoride and a series of salts of complex argentic cations.

Argentic Fluoride, AgF_2

If fluorine acts on silver at 300° an unstable black substance is formed, which contains more than 75 per cent. of argentic fluoride.[961] With dilute acids or water it liberates ozone. With concentrated potassium hydroxide it gives a solid of high oxidizing power. Ruff and Giese[962] find that fluorine will act on argentous halide, or molecular silver, or silver gauze at 150-200° to give the difluoride AgF_2. It is dark brown and strongly paramagnetic, and is very reactive. Ruff and Giese find its dissociation pressure to be 1 atmosphere at 435-450°. The compound has recently been re-examined by v. Wartenberg,[963] who finds that it melts at 690°, and that its heat of formation from the elements in their usual states is 84·5 ± 1·2 k.cals. per mole. This implies a much smaller dissociation by heat than is given by Ruff and Giese, and, in fact, v. Wartenberg found that the compound is stable at 700° under one-tenth of an atmosphere of

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* A full and careful survey of the literature on this point is given in Noyes's first paper.

[960] (i) A. A. Noyes, J. L. Hoard, and K. S. Pitzer, *J.A.C.S.* 1935, **57**, 1221; (ii) A. A. Noyes, K. S. Pitzer, and C. L. Dunn, ib. 1229; (iii) A. A. Noyes and A. Kossiakoff, ib. 1238; (iv) A. A. Noyes, C. D. Coryell, F. Stitt, and A. Kossiakoff, ib. 1937, **59**, 1316; (v) A. A. Noyes, D. DeVault, C. D. Coryell, and T. J. Deake, ib. 1326.

[961] M. S. Ebert, E. L. Radkowskas and J. C. W. Frazer, ib. 1933, **55**, 3056.

[962] O. Ruff and M. Giese, *Z. anorg. Chem.* 1934, **219**, 143.

[963] H. v. Wartenberg, ib. 1939, **242**, 406.

fluorine. The paramagnetic susceptibility found by Ruff has been confirmed by Klemm.[964] (The silver difluoride AgF_2 obtained as a yellow solid from silver and fluorine by Jockusch[965] has quite different properties, and must be some other substance.)

Complex Argentic Compounds

All the other known argentic compounds are complexes formed with nitrogenous bases, mostly of the type $[AgB_4]X_2$ (where B stands for a molecule of a monamine, or half a molecule of a di-nitrogen base), but a few are of the tri-chelate 6-covalent form. Barbieri in 1912,[966] by the action of potassium persulphate $K_2S_2O_8$ on a solution of silver nitrate in pyridine, got the compound $[Ag(py)_4]S_2O_8$: orange prisms, forming mixed crystals with the corresponding cupric compound. In 1927,[967] by the electrolytic oxidation of silver nitrate in a solution containing pyridine, he obtained the nitrate of this complex. In 1928 Hieber,[968] using phenanthroline (phn) as his co-ordinating base, prepared from silver nitrate and potassium persulphate the salt $[Ag(phn)_2]S_2O_8$, and hence by double decomposition a series of salts of this cation with the anions ClO_4, ClO_3, NO_3, SO_4H. This cation is a remarkably stable complex; the phenanthroline is not split off from it even by 66 per cent. acid. These substances are all coloured (mostly brown), and form mixed crystals with the analogous cupric and cadmium salts.[969]

Morgan and Burstall, using the same oxidizing agent, but with α, α-dipyridyl (dipy) as the co-ordinating base,[970] prepared a series of salts, mostly of the dichelate cation $[Ag(dipy)_2]^{++}$, but others of the trichelate 6-covalent cation $[Ag(dipy)_3]^{++}$.

The final proof of the presence of an argentic atom in these substances is their paramagnetism, established by Sugden[971] with Morgan's compounds, and by Klemm[972] with those of Hieber. Klemm also measured for comparison the corresponding cupric compounds. The values of the susceptibility $\times 10^6$ are given in the following table (1 Bohr magneton corresponds to a susceptibility of about $1{,}300 \times 10^{-6}$).

Paramagnetic Susceptibility $\times 10^6$

$[Ag(py)_4]S_2O_8$ Sugden	1,303	$[Cu(py)_4]S_2O_8$	1,200
,, Klemm	1,260		
$[Ag(dipy)_2]S_2O_8$	1,367		
$[Ag(phn)_2]S_2O_8$	1,400	$[Cu(phn)_2]S_2O_8$	1,100
$[Ag(dipy)_3](NO_3)_2$	1,851		
,, $(ClO_3)_2$	1,789		
,, $(ClO_4)_2$	2,155		
$[Ag_2(dipy)_5](S_2O_8)_2$	1,720		
AgO Sugden	0		
,, Klemm	40	CuO Klemm	240

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[964] E. Gruner and W. Klemm, *Naturwiss.* 1937, **25**, 59.

[965] H. Jockusch, ib. 1934, **22**, 561.

[966] G. A. Barbieri, *Gaz.* 1912, **42**, ii. 7.

It will be observed that the values for the 6-covalent compounds are noticeably higher than those for the 4.

As has been mentioned above, Klemm does not say how he prepared his AgO.

AURIC COMPOUNDS

The polyvalent state of gold, like that of copper and unlike that of silver, is much more stable than the monovalent, and the majority of the compounds of gold are auric; the ratio Au^+/Au^{+++} is unknown, because owing to the strong tendency of the auric ion to form complexes, the concentration of the free ion cannot be determined. The trivalent atom, with an outer electronic group of 16, is obviously transitional in character (like the cupric) and should be comparable with the trivalent ions of other transitional elements such as iridium and osmium. The auric ion, however, scarcely exists at all; the auric compounds are covalent, and so far as they dissolve in water do so in the form of complexes; even in pure water auric chloride has been shown by transport experiments to be present wholly as a complex ion.[973] This is a common characteristic of the heaviest elements of the B subgroups, and in particular of the three elements which precede gold, osmium, iridium, and platinum.

The most remarkable peculiarity about trivalent gold is that not only does the ion Au^{+++} not occur but all its compounds are complex, and the gold always has a covalency of 4. No exceptions to this have been discovered although the structures of some of the compounds have not yet been made out. The majority of the reactions of the compounds of auric as of aurous gold consist in their reduction to the metallic state, which is brought about by all reducing agents including practically all the metals (mercury is peculiar in reducing the auric only to the aurous state, i.e. to aurous oxide Au_2O).

The most delicate test for auric gold is the formation of 'Purple of Cassius', an amorphous strongly coloured substance containing colloidal gold on reduction with stannous solutions.

Supposed Divalent Gold Compounds

Various substances have been described whose composition is that of derivatives of divalent gold. Julius Thomsen[974] claimed to have prepared a dichloride and a dibromide by the action of the halogens on the metal,

[967] G. A. Barbieri, *Ber.* 1927, **60**, 2424.

[968] W. Hieber and F. Mühlbauer, ib. 1928, **61**, 2149.

[969] G. A. Barbieri, *Atti R.* 1931, [vi] **13**, 882.

[970] G. T. Morgan and F. H. Burstall, *J.C.S.* 1930, 2594.

[971] G. T. Morgan and S. Sugden, *Nature*, 1931, **128**, 31; S. Sugden, *J.C.S.* 1932, 161.

[972] W. Klemm, *Z. anorg. Chem.* 1931, **201**, 32.

[973] W. Hittorf and S. Salkowski, *Z. physikal. Chem.* 1899, **28**, 546.

[974] *Thermochem. Untersuch.*, Leipzig, 1883, pp. 383, 386.

but Krüss[975] failed to find any evidence for an intermediate stage between the mono- and the trihalide.

Some compounds of these compositions, however, certainly exist. A sulphate $AuSO_4$ was obtained by Schottländer[976] by evaporating a solution of aurous oxide in sulphuric acid; it forms bright red prisms which are hydrolysed by water to give the hydroxide $3\,AuO, H_2O$. This work was confirmed by Krüss.[977]

The oxide AuO was found by Krüss[977] to be formed by heating this hydroxide to 150-165°. It is a dark brown powder which readily absorbs moisture, apparently reverting to the hydroxide $3\,AuO, H_2O$.

Gold monosulphide AuS was obtained by Hoffmann and Krüss[978] by precipitating neutral auric chloride solution with hydrogen sulphide and removing excess of sulphur from the precipitate with carbon bisulphide. It is a black insoluble powder.

All these compounds are insoluble solids, and while there seems to be no doubt of the existence of several of them as chemical individuals, their molecular weights and their structures are entirely unknown. It is obvious that they must have complex molecules containing an equal number of aurous and auric atoms. In the remarkable complex halides of the type $M[AuCl_3]$, which are black, this conclusion has been established by X-ray analysis (see below, p. 190). There is no evidence that gold can follow copper and silver in forming a divalent atom.

Auric Compounds of Carbon

These are practically limited to the cyanides and the very interesting alkyl and aryl derivatives which are better dealt with after the binary compounds such as the oxides and halides.

Auric Compounds of Nitrogen

'Explosive gold', obtained by the action of ammonia or ammonium salts on auric oxide or chloride, is a dark powder which explodes on heating or rubbing to give gold, nitrogen, and ammonia. Raschig[979] showed that this product contains chlorine, and apparently is a mixture of two substances. They are too explosive to be dried, so that the only elements that can be determined are gold, nitrogen, and chlorine. They have been elaborately re-examined by Weitz,[980] who suggests various possible formulae. It seems clear that they contain gold linked to nitrogen; but the only points really established about them appear to be (1) that the ratio of gold to nitrogen remains constant at 2:3 over a considerable range of chlorine concentration, and (2) that the more concentrated the ammonia solution used in their preparation the less chlorine they contain, possibly

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[975] G. Krüss and F. W. Schmidt, *Ber.* 1887, **20**, 2634; *J. prakt. Chem.* 1888, [2] **38**, 77; see also E. Petersen, ib. 1892, [2] **46**, 328.

[976] F. Schottländer, *Ann.* 1883, **217**, 337.

[977] G. Krüss, ib. 1887, **237**, 296.

[978] L. Hoffmann and G. Krüss, *Ber.* 1887, **20**, 2705.

[979] F. Raschig, *Ann.* 1886, **235**, 355.

[980] E. Weitz, ib. 1915, **410**, 117.

owing to the hydrolytic replacement of chlorine atoms by hydroxyl groups.

Kharasch and Isbell have shown[981] that imides R_2NH, such as succinimide, phthalimide, and saccharine (*o*-sulphobenzoic imide), will dissolve auric hydroxide and form acids of the type $H[Au(NR_2)_4]$ and their salts, which are often hydrated and are very soluble in water; they are fairly stable and seem to be stronger acids than acetic.

Auric Oxide and Hydroxide

If an auric solution is treated with magnesia, a precipitate of the aurate $Mg[AuO_2]_2$ is formed, which with nitric acid forms the hydroxide $AuO \cdot OH$. This can also be obtained by precipitation with alkali, and purified by solution in excess of the reagent, and reprecipitation.[982] When dried over phosphorous pentoxide it forms a brown powder with the composition $AuO \cdot OH$; after prolonged heating at 140-150° it loses its water to give the oxide Au_2O_3 (also brown), which a little above this loses oxygen and passes into aurous oxide Au_2O.

Auric hydroxide, $AuO \cdot OH$, is generally known as auric acid; its behaviour is that of a weak acid. Though it is practically insoluble in water it dissolves in potassium hydroxide (hence the precipitate produced by adding alkali to an auric chloride solution is soluble in excess), and on evaporation potassium aurate, $K[AuO_2]$, $3\,H_2O$, or, as it is more correctly written, $K[Au(OH)_4]$, H_2O, separates out. This salt is soluble in water, and as it is the salt of a weak acid the solution has a strong alkaline reaction; addition of hydrochloric acid precipitates auric hydroxide.

Johnson and Leland[983] have measured the remarkable changes (see original) which occur in the solubility of auric oxide in water as the alkalinity is increased from zero to 8 times normal. They show that the results can be accounted for by assuming that the trihydroxide $Au(OH)_3$ acts as a tribasic acid with the dissociation constants k_1 $1{\cdot}8 \times 10^{-12}$; k_2 $4{\cdot}4 \times 10^{-14}$; k_3 5×10^{-16}.

Auric Sulphide, Au_2S_3

This can be made by treating dry lithium aurichloride $Li[AuCl_4]$ with hydrogen sulphide at $-10°$. These substances react to form hydrogen chloride, lithium chloride, and auric sulphide Au_2S_3; the lithium chloride is then dissolved out by alcohol.

Auric sulphide, Au_2S_3, is a black powder, dissociating at 200° into its elements. It is at once decomposed by water to give sulphuric acid and metallic gold or aurous and auric compounds. The auric ion Au^{+++} and the sulphide ion S^{--} are among the weakest ions of their respective kinds and react with water at once.

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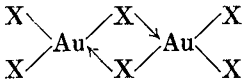
[981] M. S. Kharasch and H. S. Isbell, *J.A.C.S.* 1931, **53**, 3059.

[982] W. E. Roseveare and T. F. Buehrer, ib. 1927, **49**, 1221.

[983] H. L. Johnson and H. L. Leland, ib. 1938, **60**, 1439.

Auric Halides

The co-ordinating tendency of trivalent gold is so great that when the halides dissolve in water the gold is present entirely as a complex ion; these complexes are described later (p. 191). The same thing happens with the simple halides themselves: wherever the molecular weight can be determined it is always that of the dimeric molecule $Au_2(hal)_6$, and we have good reason to believe that this has the structure



like its alkyl derivatives (see below, p. 183).

Auric fluoride. No definite compound of gold and fluorine has been obtained.

Auric chloride, $AuCl_3$. This is a brown crystalline substance formed by the direct combination of its elements. It decomposes to aurous chloride and chlorine at 220-230°, but in chlorine under pressure it melts at 288°. From the extent of the dissociation at various temperatures Biltz and Fischer[984] have determined the heats of dissociation, and hence the heats of formation of the solid halides from metallic gold (or the solid monohalides) and gaseous chlorine or bromine. The values they get, which agree well with the direct thermochemical results, are:

$$2\,Au + Cl_2 = 2\,AuCl + 16{\cdot}5 \text{ k.cals.}$$

$$AuCl + Cl_2 = AuCl_3 + 18{\cdot}7 \text{ k.cals.}$$

$$2\,Au + Br_2 = 2\,AuBr + 15{\cdot}7 \text{ k.cals.}$$

$$AuBr + Br_2 = AuBr_3 + 16{\cdot}9 \text{ k.cals.}$$

Auric chloride is perceptibly volatile at all temperatures above 180°. Fischer[985] has measured the vapour pressure of auric chloride in excess of chlorine by a differential method, and finds it to be 3·5 mm. at 250° and 7·5 mm. at 263°. He also determined the molecular weight of the chloride in the vapour by combining these results with measurements of the rate of transportation in a current of chlorine. The results agree closely with the formula Au_2Cl_6.

Auric bromide, $AuBr_3$. This is a dark brown substance which is entirely converted into aurous bromide and bromine at 160°. Its molecular weight has been found by the elevation of the boiling-point in bromine to be that of Au_2Br_6.[986]

These dimeric formulae for the auric halides are entirely confirmed by the behaviour of their alkyl substitution products (see below, p. 183).

Auric iodide, AuI_3. The careful addition of aqueous auric chloride to potassium iodide solution gives the complex salt $K[AuI_4]$, and if more

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[984] W. Fischer and W. Biltz, *Z. anorg. Chem.* 1928, **176**, 81.

[985] W. Fischer, ib. 1929, **184**, 333.

[986] A. Burawoy and C. S. Gibson, *J.C.S.* 1935, 217.

auric chloride is added and the solution warmed, auric iodide separates according to the equation

$$3\,K[AuI_4] + AuCl_3 = 4\,AuI_3 + 3\,KCl.$$

Auric iodide is dark green and almost insoluble in water. It slowly loses iodine at the ordinary temperature to give aurous iodide.

Auric Cyanide $Au(CN)_3$

If a solution of potassium auricyanide $K[Au(CN)_4]$ is treated with fluosilicic acid (which cannot form complex ions with the gold), the hydrogen ion removes the free cyanide ions (present through a slight dissociation of the complex) so completely, owing to the weakness of hydrogen cyanide as an acid, that the complex is decomposed, and auric cyanide, of the composition $Au(CN)_3$, 3 or 1·5 H_2O, crystallizes out (Rammelsberg, 1837). This product is no doubt in fact a complex acid (for steric reasons $Au(CN)_3$ cannot polymerize in the same simple way as the trihalides).

Auric Alkyl and Aryl Compounds

The derivatives of gold were discovered by Pope and Gibson in 1907.[987] In recent years they have been investigated in more detail by Gibson and his co-workers[988–96] and by Kharasch and Isbell[997–8] who have also prepared certain aryl derivatives; and also by Gilman *et al.*[999–1000] who have obtained evidence of the existence of auric trialkyls.

Auric Alkyl Compounds

These are of three kinds: (*a*) the trialkyls R_3Au which only occur (no doubt as etherates) in ether below −35° or as certain ammines at the ordinary temperature, (*b*) the dialkyls $R_2Au \cdot X$, and (*c*) the mono-alkyls $R \cdot AuX_2$.

Various attempts[997] to prepare the trialkyls have failed. Gilman and Woods, however,[1000] succeeded by treating auric bromide with lithium methyl in ether at −65° in obtaining a solution of gold trimethyl $Au(CH_3)_3$ (no doubt really $(CH_3)_3Au \leftarrow OEt_2$) which began to decompose at −35° into

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[987] W. J. Pope and C. S. Gibson, *J.C.S.* 1907, **91**, 2061.

[988] C. S. Gibson and J. L. Simonsen, ib. 1930, 2531.

[989] C. S. Gibson and W. M. Colles, ib. 1931, 2407.

[990] A. Burawoy and C. S. Gibson, ib. 1934, 860. [991] Id., ib. 1935, 219.

[992] A. Burawoy, C. S. Gibson, and S. Holt, ib. 1935, 1024.

[993] A. Burawoy and C. S. Gibson, ib. 1936, 324.

[994] A. Burawoy, C. S. Gibson, G. C. Hampson, and H. M. Powell, ib. 1937, 1690.

[995] F. H. Brain and C. S. Gibson, ib. 1939, 762.

[996] R. F. Phillips and H. M. Powell, *Proc. Roy. Soc.* 1939, **173**, 147.

[997] M. S. Kharasch and H. S. Isbell, *J.A.C.S.* 1931, **53**, 2701.

[998] Id., ib. 3053.

[999] H. Gilman and L. A. Woods, *J. Iowa State College*, 1943.

[1000] Id., *J.A.C.S.* 1948, **70**, 550.

gold, ethane, and methane. Gold triethyl seems to be even less stable. In presence of benzylamine or of ethylene diamine the solution (containing presumably the monammine) is stable up to room temperature (the trialkyl thalliums show a rather similar instability). The gold trialkyl reacts with hydrogen chloride or with auric bromide to give the dimethyl halide. The dialkyl compounds are made by the action of the Grignard reagent on a solution of hydrated auric chloride or bromide (actually in all probability the acid $H[AuCl_3(OH)]$ or a hydrated form of this[998]) in ether or better[995] on auric chloride in pyridine (i.e. $py \rightarrow AuCl_3$). When they are treated with bromine they give the mono-alkyl derivatives and ethyl bromide. Both classes, the mono- and the dialkyls, are soluble in organic solvents, including hydrocarbons and their halogen substitution products, and are insoluble in water[988-90], showing that they are covalent compounds. The dialkyl compounds are colourless; the mono-alkyl are red and very like the auric halides themselves.

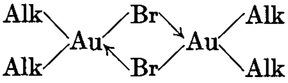
Dialkyl compounds $(Alk)_2AuX$. These are usually made as bromides, but the chlorides and iodides are known and are quite similar. The halides can be converted by treatment with silver cyanide into the cyanides[992, 997] which are more highly polymerized and have higher melting-points. The halides can also be converted by silver sulphate into the sulphates $(Alk_2Au)_2SO_4$, which are soluble in benzene and easily soluble in chloroform, and so must be covalent (see below, p. 184). The melting-points of some of these compounds are given in the table, which is taken mostly from the work of Kharasch and Isbell.[997]

Alkyl	*Chloride*	*Bromide*	*Cyanide*
Methyl[a]	..	68°	..
Ethyl	48°	58°	103-105° [b]
n-Propyl	Liquid	Liquid	94-95° [b]
isoPropyl	Decp.	Decp.	88-90°
n-Butyl	..	Liquid	Decp.
isoButyl	..	Liquid	Decp.
isoAmyl	..	Liquid	70°
Benzyl	100° Decp.	Decp.	Decp.
$C_8H_5.CH_2\ CH_2$	..	112·5°	..
$(CH_2)_5$[c]	..	Decp. 80°	..
$(CH_2)_{10}$[c]	.	Decp. 150°	..

a = [995]; *b* = [992]; *c* = [993].

They are sufficiently stable not to be reduced by hydroquinone or stannous chloride, and the benzyl and phenyl-ethyl compounds can even be sulphonated in fuming sulphuric acid at a low temperature without decomposition.[997]

The whole behaviour of these compounds is a remarkable proof of the strong tendency of auric gold to assume the 4-covalent state. The trialkyls are known only in ethereal solution, where they are no doubt solvated. The dialkyl halides form double molecules in solution (as determined cryoscopically in benzene[988] and in bromoform[990] and these must have the structure



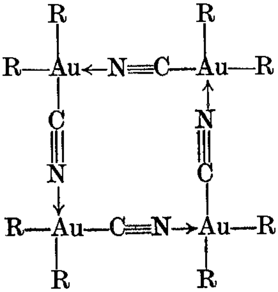
which has since been confirmed by X-ray analysis[994]; the dipole moment of 1·32 D observed for the diethyl bromide in benzene solution at 25° [994] may be due to atom polarization or to flexibility, but at least it shows that the molecule is not far from symmetrical.

The cyanides $\mathrm{Alk_2AuCN}$[992,997] have a remarkable structure, determined by the necessity of the auric atom being 4-covalent. Gibson and his colleagues have shown[992] that they undergo a change on standing from a form which is soluble in benzene or chloroform to one which is not; and that this is due to the loss of paraffin, the successive reactions being, as expressed stoichiometrically,

$$2\,\mathrm{R_2AuCN} \rightarrow 2\,\mathrm{RAuCN} + \mathrm{R_2} \rightarrow 2\,\mathrm{AuCN} + 2\,\mathrm{R_2};$$

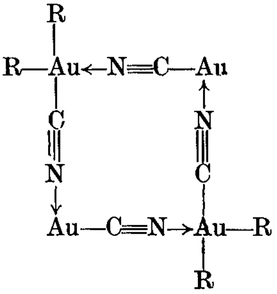
the first reaction goes slowly in the cold and rapidly on warming in solution, and the second above 100°; under some conditions these reactions may become explosive. It remains to discuss the structure of these substances.

The original auric dialkyl cyanide was proved by the freezing-points of its solutions in bromoform to have the tetrameric molecule $(\mathrm{Alk_2AuCN})_4$. Since the gold must be 4-covalent, and for stereochemical reasons the group of atoms Au—C≡N—X (whatever X may be) must be linear, it is clear that the compound has the 12-ring

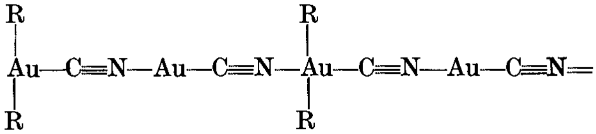


This structure was then established by X-ray analysis[996] of the dipropyl compound, which has a dipole moment of 1·47 D in carbon tetrachloride at 25°.[994] That the high polymerization is due to the stereochemistry of the CN group in co-ordination is shown by the fact that this compound reacts with ethylene diamine just like the dialkyl bromide to give the compound

The first product obtained by the loss of the hydrocarbon R_2 has the formula $(RAuCN)_n$; half the gold atoms must have lost their alkyl groups. It is much too insoluble for its molecular weight to be determined: it may retain the 12-ring, with the alkyl groups R removed from two opposite



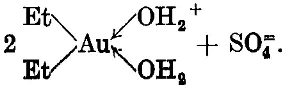
corners, two of the gold atoms being auric and two aurous. The auric atoms would thus keep their necessary covalency of 4, with the plane square structures, and the two aurous atoms have the preferred aurous covalency of 2; these would normally be linear, but we have evidence that the shared quartet is easily deformed (see under mercury). It may, however, have a linear structure



$$\underset{R}{\overset{R}{Au}}-C\equiv N-Au-C\equiv N-\underset{R}{\overset{R}{Au}}-C\equiv N-Au-C\equiv N=$$

like that of the aurous cyanide into which it is converted by further dealkylation.

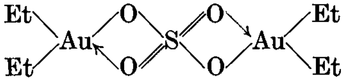
The sulphates are equally remarkable. Kharasch and Isbell[997] found that if di(phenyl-ethyl) auric bromide $(C_6H_5 \cdot CH_2 \cdot CH_2)_2AuBr$ is shaken in benzene solution with a large excess of silver sulphate, the bromine is removed as silver bromide and the filtered solution on evaporation leaves a crystalline residue of the composition $[(C_6H_5 \cdot CH_2 \cdot CH_2)_2Au]_2SO_4$. This is insoluble in water but soluble in chloroform, benzene, and ether, and so obviously covalent. Gibson and his colleagues[1024-5] investigated the ethyl compound $(Et_2Au)_2SO_4$ more fully, and found it was soluble in benzene, cyclohexane, acetone, ethyl acetate, alcohol, and also in water. In water it gives the reactions of sulphate ions, and its molecular weight by the freezing-point is a third of the formula weight, showing that it forms three ions, no doubt



In acetone by the boiling-point it is dimeric, corresponding to

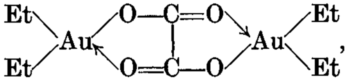
$$[(Et_2Au)_2SO_4]_2.$$

Ewens and Gibson[1025] discuss possible structures. The simple (Au_2) form

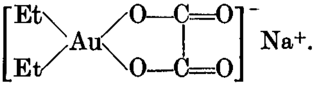


is no doubt excluded because it would require the valency angle of the gold to be reduced to 70°. It is difficult to find any structure that satisfies the requirements as to distances and valency angles, and also make the 4 gold atoms trivalent and 4-covalent.

From the sulphate the derivatives of dicarboxylic acids can be prepared. Sodium oxalate gives the oxalate



soluble and monomeric in cyclohexane and converted by excess of sodium oxalate into the salt

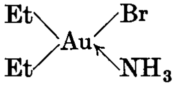


Higher homologues (malonic to suberic) give similar covalent derivatives, but these are dimeric (Au_4) and presumably correspond to the sulphate.[1024]

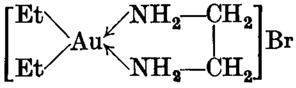
Of the dialkyl-halide type two cyclic derivatives were made[993] by the action of the Grignard reagent prepared from pentamethylene dibromide $Br(CH_2)_5Br$, which is known to contain, in addition to the magnesium derivative of the pentamethylene halide, that of the decamethylene dibromide $Br(CH_2)_{10}Br$. From this were made the gold compounds $(CH_2)_5AuBr$ and $(CH_2)_{10}AuBr$; their properties in general are very similar to those of the dialkyl gold compounds.

When diethyl gold bromide is treated with ammonia it breaks up to give a monammine $Et_2AuBr(NH_3)$ (formula I below), which is not a salt and is soluble in benzene. With ethylene diamine the second Au—N link may be to the same gold atom, which involves the expulsion of the bromine from the complex to yield a salt[988] (formula II), or under different conditions the link may be formed with a second gold atom[1024] (formula III).

The behaviour of the iodide of the methyl derivative of type II is curious. Hydrochloric acid removes all the ethylene diamine to form the parent dimethyl gold iodide, while hydriodic acid only carries the reaction half-way, giving an open-chain diamine derivative of type III. The ethyl and propyl derivatives of type III are monomeric in nitrobenzene.[991] As the following formulae show, the covalency of the gold retains the value of four throughout. The propyl compound of this last type (III) undergoes two curious reactions.[991] The chloroform solution on standing deposits crystals



I.



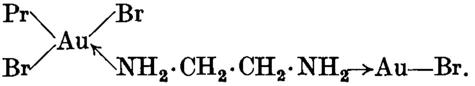
II.

III.

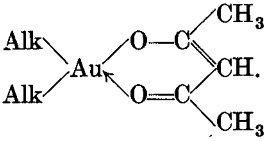
of the propyl analogue of salt II, leaving the dimeric dipropyl gold bromide in solution:

$$2\,\mathrm{Pr_2AuBr\cdot en\cdot AuBrPr_2} \rightleftharpoons 2\,[\mathrm{Pr_2Au\cdot en}]\mathrm{Br} + (\mathrm{Pr_2AuBr})_2.$$

If, however, its solution in benzene or chloroform is warmed, it loses hexane and colourless crystals separate of the aurous-auric compound

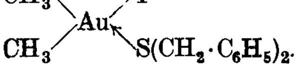


By treatment of the dialkyl bromide with thallous acetylacetonate the dialkyl gold acetylacetonate can be made



The methyl compound (Melting-point 84°) has a perceptible vapour-pressure even in the cold[995]; the ethyl, as often happens, has a much lower melting-point of 9–10°.[988]

Dibenzyl sulphide co-ordinates with gold in forming the complex



The Au—S link must, however, be rather weak, since the corresponding diethyl sulphide does not form a stable derivative. It is also of interest that a second molecule of dibenzyl sulphide cannot displace the halogen to form a salt.

The mono-alkyl derivatives, such as $(\mathrm{EtAuBr_2})_2$ (made by the action of bromine on the dialkyl derivatives), which are deep red, are much less stable than the dialkyls, and are reduced by hydroquinone or stannous chloride at once. They also are found to be dimeric by the freezing-points in bromoform[990]; they act as mixtures of the dialkyl compound and auric tribromide. Thus ethyl auric dibromide is converted by potassium bromide into potassium bromoaurate $K[AuBr_4]$ and diethyl gold bromide $(Et_2AuBr)_2$, and by ethylene diamine into a mixture of the diamine compounds of diethyl auric bromide and auric tribromide. Hence it is very probable that the two alkyl groups removed by the bromine come from one gold atom,[990] giving:

This conclusion is confirmed by the very high dipole moment of the propyl compound, $5{\cdot}5 \pm 0{\cdot}5$ D in carbon tetrachloride at 25° (compare the much smaller moments of Et_3SnCl 3·44 and Et_2SnCl_2 3·85 D).

Aryl Compounds

All the compounds so far described have had an aliphatic carbon atom attached to the gold. Kharasch and Isbell[997-8] have prepared a series of true aryl derivatives with the gold directly attached to the aromatic nucleus; these are all of the type $ArAuCl_2$: the diaryl compounds could not be made.

The Grignard reagent cannot here be used; when the magnesium is attached to an aryl group it does not react with gold trihalide. The aryl gold derivatives were made by the direct action of auric chloride on benzene at the ordinary temperature. If benzene is added to dry auric chloride, hydrogen chloride is violently evolved and aurous chloride is produced along with 1, 2, 4, 5-tetrachlorobenzene. If powdered auric chloride is slowly added to a large quantity of benzene, the reaction is quieter; hydrogen chloride is evolved, and the solution turns first red and then brown, with the formation of a brown precipitate, and shortly afterwards yellow crystals of aurous chloride separate, and the solution contains chlorinated benzene. The reaction can, however, be stopped at the point where the brown precipitate begins to appear by adding a few c.c. of ether, acetic acid, or ethyl acetate, and in that case no aurous chloride separates. If at this point (where the brown precipitate appears) ether is added and the solution evaporated, pale yellow crystals of phenyl auric dichloride $C_6H_5 \cdot AuCl_2$ separate, which can be freed from aurous chloride by washing with water and recrystallizing from alcohol. The effect of small quantities of ether in stopping the reaction of auric chloride with benzene is very remarkable: auric chloride has a visible reaction on one drop of benzene in 10 c.c. of ligroin, but liquid benzene will not react with solid auric chloride that has been moistened with ether. Presumably this is due to the formation of a co-ordination compound with the ether.

Various aryl auric dichlorides $ArAuCl_2$ were made; toluene and diphenyl react with auric chloride in the same way as benzene, and it seems that many aromatic hydrocarbons and their derivatives can be 'aurated' by this method. These compounds are at once reduced by hydroquinone and by stannous chloride; in fact they behave very like their alkyl analogues.

They are insoluble in water, but not decomposed by it; they are easily soluble in potassium chloride solution, in which no doubt they form complex salts.

AURIC COMPLEXES

The line between the simple and the complex compounds, which is often a difficult one to draw, scarcely exists at all in the auric series; the compounds are all really complex, though it is not always possible to say what their complex structures are. In comparison with the cupric and even the argentic complexes the auric present a very simple picture since they all without exception have a co-ordination number of 4. The tendency to co-ordinate is so strong that the trivalent halides will link up with almost any donor, and so an unusual number of mixed complexes are known.

A. *Open-chain Complexes*

Au—C *Complexes*

Most of these have already been described among the alkyl and aryl compounds; there remain only the complex cyanides.

Complex Cyanides

There is a well-marked series of double cyanides of the type

$$K[Au(CN)_4]^{1004}:$$

with strong acids they give the free acid $H[Au(CN)_4]$ in a hydrated form.

Au—N *Complexes: Ammines*

The pure auric ammines that have been prepared are relatively few; but Weitz[1005] has shown that by the action of ammonia on chloroauric acid $H[AuCl_4]$ in saturated ammonium sulphate solution, colourless tetrammine salts of the type $[Au(NH_3)_4]X_3$ are produced. These are very stable when the ion is that of an oxy-acid such as oxalic, nitric, phosphoric, chloric, perchloric, &c., and the ammonia groups cannot be removed by the action of the concentrated oxy-acids themselves; but the salts are at once decomposed by potassium chloride with the precipitation of the explosive gold-nitrogen compounds described above, whose instability is presumably due to the gold having a fifth covalency to the halogen.

Another class of nitrogen-co-ordination complexes is derived from the imides, especially succinimide (HSu). Trivalent gold, like divalent copper, readily replaces the imide hydrogen of these compounds; but whereas the cupric imides stabilize themselves by adding two amine molecules or the like, the auric atom forms a complex anion of the type of $M[Au(Su)_4]$. A series of alkaline and alkaline-earth salts of this type have been made by Kharasch and Isbell[1006]; they are mostly soluble in water. These salts are

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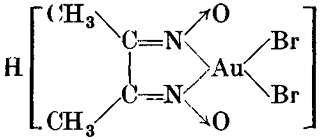
[1004] C. G. Lindbom, *Berl. Ber.* 1877, 1725.

[1005] E. Weitz, *Ann.* 1915, **410**, 117–222.

[1006] M. S. Kharasch and H. S. Isbell, *J.A.C.S.* 1931, **53**, 3059.

surprisingly stable; they are not affected by warm hydroquinone or stannous chloride or by cold concentrated acids or alkalies; the ammonium salt can be recrystallized unchanged from glacial acetic acid, whereas the cupric compound $Cu(Su)_2(NH_3)_2$ is decomposed even by dilute acetic acid. Saccharine (the imide of *o*-sulphobenzoic acid) forms similar salts. Other Au—N complexes are described by Gibson,[1026] including the glyoxime derivative



Phosphorus Complexes

Auric chloride and bromide form compounds with phosphorus tri- and pentachloride and with triaryl phosphine oxides[1007]; one of these, $AuCl_3, PCl_3$, is presumably a simple 4-covalent complex like a monammine, $Cl_3P \rightarrow AuCl_3$; but the others are more likely to be aurichlorides and are therefore discussed later.

F. G. Mann and D. Purdie[1008] find that 2-covalent aurous complexes like $Et_3P \rightarrow Au—Cl$ will take up a molecule of bromine or iodine to give planar molecules as $Et_3P \rightarrow AuCl(hal)_2$. These might be *cis* or *trans*, but only one form is known. We should expect that $Et_3P \rightarrow Au—Br + I_2$ would give the *trans*, and $Et_3P \rightarrow Au—I + IBr$ the *cis*; but only one form was found to be produced. This is probably due to the ease of the *cis*$\rightleftharpoons$*trans* change. The crystal structure of $Me_3P \rightarrow AuBr_3$ shows that the arrangement round the gold is planar; the Au—Br and Au—P distances are both 2·5 A[1009] (theory 2·64, 2·60).

Oxygen Complexes

The auric atom readily co-ordinates with oxygen; the so-called hydrate of auric chloride is no doubt really a complex acid $H[AuCl_3OH]$; and the aurates, of which even the potassium salt is hydrated, should be written as salts of $H[AuO_2]\ 2\,H_2O = H[Au(OH)_4]$.

This tendency also leads to the formation of double nitrates which seem to be truly complex.[1010] A solution of auric hydroxide $Au(OH)_3$ in concentrated nitric acid deposits crystals of $H[Au(NO_3)_4]$, $3\,H_2O$, and a series of salts (K, Rb, NH_4) of this are known; they are golden yellow. It is also possible to obtain a still more complex series of nitrates of the composition $M_2H[Au(NO_3)_6]$: the potassium, rubidium, and ammonium salts were made. These as they are written contain 6-covalent gold, which is very improbable; and the presence of an unreplaced hydrogen atom in all three salts suggests that their structure is more complicated than appears. In the absence of X-ray data it is useless to speculate on their constitution.

[1007] L. Lindet, *C.R.* 1884, **98**, 1382.

[1008] *J.C.S.* 1940, 1235.

[1009] M. F. Perutz and O. Weisz, ib. 1946, 438.

[1010] P. Schottländer, *Ann.* 1883, **217**, 356; Diss. 1884; *Jahresbericht*, 1884, p. 452.

Another rather unusual series of complex salts is that of the double acetates, such as $Mg[Au(O \cdot CO \cdot CH_3)_4]_2$ prepared by Weigand[1011] with various alkaline-earth cations. Auric gold is one of the few metals to give complex carboxylic salts of this type.

Various chelate complexes are described later.

Sulphur Complexes

Apart from the dibenzyl sulphide complex of dialkyl auric bromide (above, p. 186), these are almost unknown. Dibenzyl sulphide forms a compound $(C_6H_5 \cdot CH_2)S \rightarrow AuBr_3$, as well as a more complicated auric-aurous complex.[1012] Complex thiocyanates $M[Au(SCN)_4]$ are known,[1004] but they are relatively unstable.

Complex Halides

The attachment of the auric atom to the halogens in the 4-covalent complexes seems to be unusually strong, and these complexes occur in great variety, both pure, as in $M[AuCl_4]$, and with the fourth covalency supplied by any one of a whole series of donor atoms.

The pure tetrahalides of the types $M[AuCl_4]$, $M[AuBr_4]$, $M[AuI_4]$ are well known. On acidification they give the corresponding acids, in which the hydrogen is hydrated, as $H(OH_2)_2\,[AuBr_4]$, which forms purple crystals very soluble in water. The sodium salt $Na[AuCl_4]$, $2\,H_2O$ dissolves in ether, carrying its $2\,H_2O$ with it. On heating, the anhydrous aurichlorides evolve chlorine and are converted into the aurochlorides:

$$K[AuCl_4] = K[AuCl_2] + Cl_2.$$

The salt $K[AuBr_4]$, $2\,H_2O$ (purple: sol^y 19·5/18°, 208/67°) has been shown by X-ray analysis[1013] to have a plane $AuBr_4$ ion, with the 4 bromine atoms at the corners of a square.

As we have seen, the same type of $Au(hal)_4$ complex occurs in the dimeric molecules of auric chloride and bromide and in those of the mono-derivatives such as $(Et \cdot AuBr_2)_2$.

A remarkable mixed aurous-auric halide of the composition $CsAuCl_3$ has already been mentioned as apparently a divalent gold compound. It was discovered by H. L. Wells[1014] together with an analogue in which half the gold atoms are replaced by silver atoms, showing that the formulae should be doubled and written $Cs_2Au'Au'''Cl_6$ and $Cs_2Ag'Au'''Cl_6$. These salts are quite black, even in fine powder; they have been shown to be diamagnetic[1015] and so can only contain monovalent silver and gold and trivalent gold; the deep colour is common in compounds that contain the same element in different valency states. It has now been shown by X-ray analysis[1016] that the crystals contain linear $AgCl_2^-$ and $AuCl_2^-$ ions, and plane square $AuCl_4^-$.

[1011] F. Weigand, *Z. angew. Chem.* 1906, **19**, 139.

[1012] P. C. Ray and D. C. Sen, *J. Ind. Chem. Soc.* 1930, **7**, 67.

[1013] E. G. Cox and K. C. Webster, *J.C.S.* 1936, 1635.

[1014] *Amer. J. Sci.* 1922, **3**, 315, 417. [1015] N. Elliott, *J. Chem. Phys.* 1934, **2**, 419.

[1016] N. Elliott and L. Pauling, *J.A.C.S.* 1938, **60**, 1846.

A curious series of addition products of auric chloride with the halides of phosphorus and other elements should probably be referred to this group. Thus $PCl_5, AuCl_3$[1017] and $SCl_4, AuCl_3$[1018] presumably have the structures $[PCl_4]^+[AuCl_4]^-$ and $[SCl_3]^+[AuCl_4]^-$. Other compounds of auric chloride have been described with $SeCl_2$, $SiCl_4$, $SbCl_5$ (this should be analogous to the PCl_5 compound), $SnCl_4$, and $TiCl_4$, but little is known about them. The nitrosyl compound NOCl, $AuCl_3$[1019] is no doubt an aurichloride of the established cation $[NO]^+$ (see under Nitrogen, V. 684). The compounds of pyrone and dimethyl pyrone[1020] and of dimethyl chromone[1021] with auric chloride are presumably true salts (aurichlorides), but there is some complication in their structures, as they contain two (rarely three) organic molecules to one $AuCl_3$.

Some similar complication must occur in the compounds of aurichloric acid with a series of trialkyl and triaryl phosphine oxides[1022]; these all have the composition $(R_3PO)_2, HAuCl_4$, where R = methyl, ethyl, propyl, phenyl, and benzyl. They are formed in water and they are all soluble in water and crystalline.

Mixed Complexes

These are very numerous, especially when some of the co-ordinated atoms are halogens. The auric atom can probably form every stage of the fourfold complex from $[Au(OH)_4]^-$ to $[AuCl_4]^-$. An aqueous solution of auric chloride is really a solution of the acid $H[AuCl_3OH]$, and this is the molecule which ether extracts from the water, as was shown by Kharasch and Isbell,[997] who also point out that a solution of auric chloride in water is reduced by sulphanilic acid (aniline *p*-sulphonic acid), but not in presence of potassium chloride, which indicates that the $[AuCl_4]^-$ ion is more stable than $[AuCl_3OH]^-$.

A variety of ammine complexes obtainable from the alkyl gold compounds has already been described (p. 185). The corresponding auric halide derivatives are also known; they are all constructed on the same plan as the alkyl complexes. One nitrogen atom co-ordinates with the gold to form a non-ionized complex as in $[AuCl_3py]^\circ$ [1023] (yellow); two do so to give a monovalent cation as in $[AuCl_2(py)_2]Cl$[1023] (orange); an ethylene diamine can take the place of two amine molecules. Thus Gibson and Colles[989] have made such compounds as $[AuBr_3,py]^\circ$ (and the corresponding quinoline and isoquinoline derivatives) and $[AuBr_2(py)_2]Br$ (deep red).

Chelate Complexes

Examples of auric complexes chelated through nitrogen are the ethylene diamine compounds just mentioned (p. 186): through oxygen the acetyl-

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[1017] L. Lindet, *C.R.* 1884, **98**, 1382.

[1018] Id., ib. 1885, **101**, 1492.

[1019] J. J. Sudborough and J. H. Millar, *J.C.S.* 1891, **59**, 73, 270.

[1020] R. Willstätter and R. Pummerer, *Ber.* 1904, **37**, 3740.

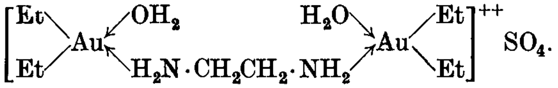
[1021] H. Simonis and A. Elias, ib. 1915, **48**, 1499.

[1022] R. H. Pickard and J. Kenyon, *J.C.S.* 1906, **89**, 262.

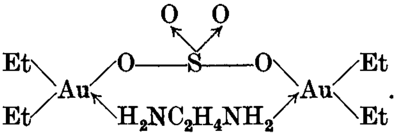
[1023] M. Francois, *C.R.* 1903, **136**, 1557.

acetonate of dimethyl gold (p. 186); and a few others have already been described.

The auric atom forms few 'ato' complexes. But some interesting alkyl compounds of this type (oxalato and sulphato) have recently been described by Gibson and Weller[1024] and by Ewens and Gibson.[1025] Gibson and Weller[1024] say that by shaking excess of silver sulphate with an acetone solution of diethyl auric bromide $(Et_2AuBr)_2$ a compound $Et_4Au_2SO_4$ is got (= I); the molecular weight is found by the boiling-point in acetone to be dimeric (Au_4); it is also soluble in alcohol, ethyl acetate, cyclohexane, and further in water, in which last it gives tests for sulphate ions, and behaves as $[Et_2Au(OH_2)_2]_2SO_4$. It will take up only one molecule of ethylene diamine; the product (II) in water gives the tests for SO_4'', and must be

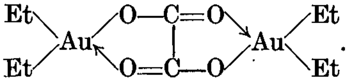


It also dissolves in bromoform, where it must be chelate:



A similar 2, 2′-dipyridyl compound occurs.

Of the compounds of type I, the propyl was very like the ethyl, but the butyl was very unstable. When the ethyl compound (I) is treated with sodium oxalate it gives III



which is soluble in ligroin and gives the right molecular weight in cyclohexane.[1026]

[1024] C. S. Gibson and W. T. Weller, *J.C.S.* 1941, 102.

[1025] R. V. G. Ewens and C. S. Gibson, ib. 109.

[1026] C. S. Gibson, *Brit. Assoc. Ann. Rep.* 1938, p. 35.

GROUP II

THE difference in properties between the two subgroups is less in Group II than in Group I, but is still very marked. In particular the abnormal high valencies which copper, silver, and gold can acquire through the breakdown of the external group of 18 electrons in the ion have no parallel in Group II B, where the 18 group is in an electric field of two positive charges, and so is too firm to be broken down by chemical attack. At the same time the opening of the penultimate group of electrons in the A subgroup which occurs in the transitional elements, and is able to reduce the valency, has not yet begun.

The only apparent departure from divalency, that of mercurous mercury, is due to the tendency, unique among metals, of mercury atoms to unite in pairs, using one valency electron each for this purpose, while the other is available for ionization as in $[Hg-Hg]^{++}$.

The radii of the atoms and ions are as follows:

	Be	Mg	Ca	Sr	Ba	Ra	Zn	Cd	Hg
Rad. of atom .	0·90	1·36	1·74	1·92	1·98	. .	1·31	1·48	1·48
Rad. of ion^{++} .	0·34	0·78	1·06	1·27	1·43	1·52[1]	0·83	1·03	1·12

The tendency to ionization is governed (1) by the size of the ions, and (2) by the effect of the 18 group in promoting covalency-formation in accordance with the Fajans principles. This is illustrated by the electrode potentials:

Be	Mg	Ca	Sr	Ba	Ra	Za	Cd	Hg
?	−2·54	−2·56	−2·77	−2·8	. .	−0·49	−0·40	+0·75 v.

These electrode potentials determine the electrochemical behaviour of the ions in water, and so are of great practical importance. But it is instructive to compare them with the energies required to ionize the metallic atom in the gaseous state, which can be determined from the spectrum. As the compounds are all divalent, the values we need are those for the conversion of the neutral atom into the divalent ion—for the removal of two electrons: they are, in electron-volts

Be	Mg	Ca	Sr	Ba	Ra	Zn	Cd	Hg
27·42	22·58	17·91	16·65	15·14	14·7	27·24	25·79	29·06

The general picture is much the same for both properties: the ease of ionization increases in typical and A elements with the atomic number, while in the B elements it is less, and diminishes with increase of atomic number, though less regularly, mercury being always characterized by its reluctance to assume the ionized state. In detail, however, there is a marked difference between the two curves. The fall in the A series is

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[1] G. E. R. Schultze, *Z. physikal. Chem.* 1936, B **32**, 430 (from RaF_2, fluorite lattice).

much less, and the rise in the B series much greater, for the electrode potential than for the ionization in the gas. Further, the excess of B over A is much less for the electrode potential. These differences can be explained in general terms by the fact that while the ionization potential in the vapour only involves one term—the energy of conversion of A into A^{++}—the electrode potential involves also a second term, the energy of hydration of the ion (and indeed a third, the lattice energy of the solid metal). The energy of solvation of the ion will obviously diminish with increase of the atomic size, and so may be expected to offset to some extent the increase in the ease of ionization, as it obviously does.

In general, these results illustrate the importance of the fourth rule of Fajans, that the tendency to covalency formation is greater with the B elements than with the A, and varies in quite a different way.

BERYLLIUM, MAGNESIUM, CALCIUM, STRONTIUM, BARIUM, RADIUM

THE typical and more especially the sub-typical elements have on the whole more analogies with the A subgroup, and are best treated in relation to it; they afford a good example of the general principle that the first (typical) element of a group has affinities with the second element of the next group (the diagonal relationship, here between beryllium and aluminium) and the second element of a group with its own B subgroup. Beryllium, however, is so peculiar in many ways, owing to its small size and correspondingly intense ionic field, and also to the limitation of its covalency to 4, that it is better treated separately; the same is true, though in a less degree, of magnesium. The general relations in the series are much the same as in I.A.: the most marked difference in properties is between beryllium and magnesium, and the next between magnesium and calcium; the series of alkaline earth metals from calcium to radium is one of the most regular in the Periodic Table.

As usual the tendency to form complexes, and to assume the covalency maximum, is greatest in the lightest element, and falls off as the atomic number increases: a covalency of 8 rarely occurs with strontium or barium.

The exceptional deforming power of the beryllium ion, and the steady fall of this property through the group, are shown, as Goldschmidt points out,[2] by the values of the field of the cation as measured by the ionic charge divided by the square of the ionic radius:

Be^{++}	Mg^{++}	Ca^{++}	Sr^{++}	Ba^{++}	Ra^{++}
17	3·3	1·8	1·2	1·0	0·87

With these we may compare the values for lithium^{+} (1·7), caesium^{+} (0·4), and aluminium^{+++} (9·2).

The most important differences to be observed in the series are:

With **hydrogen**: the rate of absorption by the metal rises with the atomic weight.

With **nitrogen**: the rate of combination again rises but the stability of the product falls.

With **oxygen**: the stability of the peroxides increases markedly with the rise of atomic number.

The stability of the *carbonates*, as shown by their reluctance to dissociate into carbon dioxide and the oxide, increases in the same way.

The tendency to complex formation falls off very markedly, especially between beryllium and magnesium. This is shown *inter alia* by the amount of hydration of the salts (see II. 221).

With elements like these, which are almost always ionized, the solubility of the salts is an important property. This is discussed in detail later

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[2] V. M. Goldschmidt, *Geochem. Verteilungsgesetze*, vii. 60 (Oslo, 1926).

under the alkaline earth metals (II. 220-1); the most striking differences between the first two elements and their successors are the much greater solubilities of the sulphate and selenates of both these elements, and of magnesium chromate, and the enormously greater solubilities of beryllium fluoride and oxalate.

BERYLLIUM

THE chemistry of beryllium is governed by the high field strength of the cation, due to the combined effects of the small radius and the double charge. It is just on the line between ionization and covalency formation, and has an extremely strong tendency to give covalent compounds with the maximum covalency of 4.

The divalent ion is colourless, and has a remarkably sweet taste (hence the alternative name of glucinum). It co-ordinates very readily, as is shown by the firmness with which the ion holds water and ammonia molecules, and the ease with which it forms complex halides and ato-compounds with beryllium in the anion. The viscosities, conductivities, and freezing-points of solutions of beryllium salts show[3] that the ion is more strongly hydrated than any other divalent cation. The ionic mobilities at 25° are:

Be	Mg	Ca	Sr	Ba	Ra
30	55·5	59·8	59·8	64·2	67

Its salts so uniformly have 4 molecules of water of crystallization for every beryllium atom that any compound which has not may be assumed not to contain beryllium ions, but either to have the metal in the form of a complex ion (as in the sulphate and oxalate) or not to be a salt at all (acetylacetonate, 'basic' acetate, etc.). Its ready passage into the covalent state also makes the hydroxide a weak base; the salts are considerably hydrolysed, giving no doubt largely the salts of the univalent ion $[Be \cdot OH]^+$. Another remarkable result of this tendency to covalency formation is that beryllium oxide, which is almost insoluble in water, is readily soluble in solutions of beryllium salts. It even expels carbon dioxide from the carbonate. The basic salts so formed can seldom be isolated in the pure state; on evaporation they often leave behind a gummy mass; probably in many cases the salt contains oxide in solid solution. It has been found that the solubility of the same is thereby increased, and it seems most probable that the dissolved oxide co-ordinates with the ion, replacing the water of hydration as in $Be{=}O{\rightarrow}Be$ (see $BeSO_4$, II. 210).

The beryllium salts of mineral acids are considerably hydrolysed in water: the degree of hydrolysis has been stated to be several per cent. at moderate dilutions.[4,5] It must, however, be remembered that the ordinary theory of hydrolysis, on which these determinations are based, assumes the absence of any molecular species other than the acid, the base, and their ions. If other species, such as a 'beryllated' ion $(BeO)_xBe^{++}$, are formed, this will upset the equilibrium, and lead to a greater separation of free acid than corresponds to the dissociation constant of the base; moreover, the basis of the calculation of the hydrolysis may be affected (see below, II. 204). Hence any quantitative statement of the degree of hydrolysis must be received with caution; but there is no doubt that beryllium salts hydrolyse very readily, and that for this reason the salts of weak acids, such as

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[3] R. Fricke and H. Schützdeller, *Z. anorg. Chem.* 1923, **131**, 132.

[4] H. Ley, *Z. physikal. Chem.* 1899, **30**, 199.

[5] L. Brunner, ib. 1900, **32**, 133.

carbonic, nitrous, hydrocyanic, and even hydrofluoric, either cannot be prepared at all or are decomposed by water. In this respect there is a marked difference between beryllium and the alkaline earth metals. Beryllium hydroxide is distinctly amphoteric in character, and gives rise to a series of beryllates containing the anions $[BeO \cdot OH]^{--}$ and $[BeO_2]^{---}$.

The 'diagonal' resemblance of beryllium to aluminium is so strong that it was for long supposed to be trivalent. This view appeared to be supported by the specific heat (Nilson and Pettersson, 1878), although, as Brauner pointed out (1878), no place could be found for a trivalent metal of atomic weight 13·5 in the Periodic Table. The specific heat argument was weakened by the discovery that boron and carbon gave similar low values, and that the specific heat of beryllium rose with rise of temperature (Nilson and Pettersson, 1880; Humpidge, 1883); but the question was not finally settled until in 1884 Nilson and Pettersson[6] determined the vapour density of beryllium chloride. This was subsequently supported by the vapour densities of the acetyl-acetonate[7] and the basic acetate $Be_4O(O \cdot CO \cdot CH_3)_6$.[8] Further evidence of the divalency if it is needed is given by the observation[9] that the flocculating power of beryllium for arsenic trisulphide sol is that of a divalent ion.

Beryllium occurs to the extent of about 0·006 per cent. (6 g. per ton) in the earth's crust. This is much less than would be expected from the general relation between frequency and atomic number (see V. M. Goldschmidt in Gerland's *Beiträge zur Geophysik*, 1926, **15**, 43). The defect is evidently due to the disruption of the beryllium atoms under natural bombardment into helium (see Gp. O. 4). This further explains the considerable amount of helium found in beryllium minerals (Rayleigh).

The chief source of beryllium is beryl, 3 BeO, Al_2O_3, 6 SiO_2, which contains 5 per cent. of beryllium.

Metallic Beryllium

Until recently the metal was scarcely known at all, owing to the difficulty of purifying it, and of obtaining it in the coherent state. The best method of preparation is that of Stock and Goldschmidt, the electrolysis of a fused mixture of the fluorides of sodium, beryllium, and barium, at a temperature above the melting-point of beryllium, usually at 1,350°. It is a steel-grey metal which can be polished; it is easily broken when cold, but ductile when hot; it is extremely light (density 1·84); its melting-point is 1,278°[10] and its boiling-point (extrapolated) 2,970° C.[11]

Beryllium foil can be used for the windows of X-ray tubes; foil 0·5 mm. thick has twice the transmission of Al foil 0·125 mm. thick, and is much

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[6] L. F. Nilson and O. Pettersson, *Ber.* 1884, **17**, 987.

[7] A. Combes, *C.R.* 1894, **119**, 1222.

[8] G. Urbain and H. Lacombe, ib. 1901, **133**, 875.

[9] A. Galecki, *Z. Elektrochem.* 1908, **14**, 767.

[10] G. Oesterheld, *Z. anorg. Chem.* 1916, **97**, 1.

[11] E. Baur and R. Brunner, *Helv. Chem. Acta*, 1934, **17**, 958.

stronger and less fusible.[12] Above its melting-point beryllium is miscible with aluminium, silver, copper, and iron but not with magnesium[10]; this may be due to the sizes of the atoms, of which the radii in the metal are

Be	Mg	Al	Cu	Ag	Fe
1·12	1·60	1·43	1·28	1·44	1·27

It forms some valuable alloys; the addition of 2·5 per cent. to copper (Be:Cu 1:5·5 atoms) gives an alloy 6 times as hard as copper, which is at first soft, and can then be hardened by heating. The addition of from 0·01 to 0·02 per cent. of beryllium to copper greatly increases its electrical conductivity, by removing traces of cuprous oxide. Beryllium is used in the highly permeable 'Lindemann glass' (IV. 601).

Metallic beryllium is not attacked by air in the cold, and on heating becomes covered with a protective film of oxide. The powdered metal burns brightly in air, and at high temperatures it is converted into a mixture of the oxide and nitride.[13] It does not react with hydrogen even at 1,000°[13,14] but when heated in nitrogen or ammonia it forms the nitride Be_3N_4. Halogens do not attack it in the cold. It dissolves in hydrochloric and sulphuric acids, but not in concentrated or dilute nitric acid, even when powdered. It dissolves in aqueous alkalies with evolution of hydrogen, which is a sign of the amphoteric character of the hydroxide.

Unlike the alkaline earth metals, but like magnesium, beryllium does not form a 'salt-like' hydride,[15] nor indeed any solid hydride: but the spectrum of the electric discharge between beryllium electrodes in hydrogen gives bands which are due to the molecules BeH and BeH^+, with interatomic distances (from the moments of inertia) which are for BeH 1·35 and for BeH^+ 1·29 A.[16]

Beryllium-Carbon Compounds

Beryllium carbide, Be_2C, is formed by heating beryllium with carbon or an organic substance to 1,300°, or by the action of carbon on beryllium oxide at 1,930°[17-20]; this last reaction does not take place at 1,700°, while above 2,100° the compound begins to decompose with separation of graphite. The carbide is brick-red, and forms regular octahedra; it is very slowly decomposed by water, rather slowly by mineral acids, and rapidly by alkalies, evolving methane.

Beryllium acetylide, BeC_2, is formed by the action of metallic beryllium on acetylene at 450°. Water and hydrochloric acid decompose it with evolution of acetylene.[21]

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[12] H. Brackney and Z. J. Atlee, *Rev. Sci. Instr.* 1943, **14**, 59.

[13] H. Borchers, *Metall-Wirt.* 1931, **10**, 863; *Chem. Centr.* 1932, **1**, 510.

[14] F. Fichter and K. Jablczynski, *Ber.* 1913, **46**, 1604.

[15] G. Kassner and B. Stempel, *Z. anorg. Chem.* 1929, **181**, 83.

[16] W. W. Watson, *Phys. Rev.* 1928, [ii] **31**, 1130; **32**, 600.

[17] P. Lebeau, *C.R.* 1895, **121**, 496; *Ann. Chim. Phys.* 1899, [7] **16**, 476, 479.

[18] C. Messerknecht and W. Biltz, *Z. anorg. Chem.* 1925, **148**, 153.

[19] J. M. Schmidt, *Bull. Soc. Chim.* 1928, [4] **43**, 49.

[20] F. Fichter and E. Brunner, *Z. anorg. Chem.* 1915, **93**, 91.

[21] J. F. Durand, *Bull. Soc. Chim.* 1924, [4] **35**, 1141.

Beryllium Alkyls and Aryls

These can be made by the action of metallic beryllium on mercury alkyls (Cahours, 1873), or better from beryllium halide and a Grignard reagent[22-5]; our knowledge of them is mainly due to Gilman and Schulze. They must be prepared in a stream of pure hydrogen or nitrogen, with the careful exclusion of air, moisture, and even carbon dioxide.

Beryllium dimethyl, $Be(CH_3)_2$, is a white crystalline substance which sublimes without melting at 200°, and is soluble in ether.[27] The diethyl is a colourless liquid boiling under 760 mm. at 180-240° with some decomposition, and at 110° under 16 mm.; the dipropyl and dibutyl are similar.[27]

Beryllium diphenyl and ditolyl can be made by treating the mercury diaryl with beryllium at 225° in presence of mercuric chloride.

All these compounds are extremely reactive. The dimethyl and the diethyl are spontaneously inflammable in air, even in concentrated ethereal solution. The dibutyl does not catch fire, but is rapidly oxidized, apparently to butyl alcohol. The solid methyl compound catches fire in carbon dioxide, but its ethereal solution reacts with the gas (as do the other alkyls) to give the acid $R \cdot COOH$. The compounds are quantitatively decomposed by water with some violence to give $Be(OH)_2$ and the hydrocarbon; if the diethyl is treated with a small quantity of water, the hydroxide formed remains dissolved in the liquid, presumably forming the group $Be{=}O{\rightarrow}Be$, as when the oxide dissolves in beryllium salt solutions (see below, p. 210).

The high melting- and boiling-points of the dialkyls show that they are considerably polymerized, as can be seen by comparing their boiling-points with those of the zinc dialkyls, whose molecular weights are, of course, 54 units greater:

$Be(CH_3)_2$	*ca.* 200°	$Zn(CH_3)_2$	46°
$Be(C_2H_5)_2$	*ca.* 200° (110°/16 mm.)	$Zn(C_2H_5)_2$	118°

The alkyl beryllium halides, such as $CH_3 \cdot Be \cdot I$, are also known[26]; they are less reactive even than the Grignard reagents; the reaction

$$BeAlk_2 + BeCl_2 \rightleftharpoons 2\ Alk \cdot Be \cdot Cl$$

is reversible.

Beryllium Cyanide

$Be(CN)_2$ seems to be formed when the iodide is heated in a stream of cyanogen[28]; it is almost completely hydrolysed by water (as we should expect) and hence beryllium hydroxide will not dissolve in aqueous hydrocyanic acid.

[22] E. Krause and B. Wendt, *Ber.* 1923, **56**, 467, Anm.

[23] H. Gilman, *J.A.C.S.* 1923, **45**, 2693.

[24] J. F. Durand, *C.R.* 1926, **182**, 1162.

[25] H. Gilman and F. Schulze, *J.A.C.S.* 1927, **49**, 2904.

[26] Id. *J.C.S.* 1927, 2663.

[27] Id. *Rec. Trav.* 1929, **48**, 1129.

[28] F. W. Bergstrom, *J.A.C.S.* 1928, **50**, 655.

Beryllium and Nitrogen

Beryllium nitride, Be_3N_2, can be made from the metal and nitrogen at 1,000° (the reaction begins at 900°[29]); from beryllium carbide and nitrogen at 1,250°[29]); or by the action of potassium cyanide on beryllium at 700°[30] according to the equation

$$3\,\mathrm{Be} + 2\,\mathrm{KCN} = \mathrm{Be_3N_2} + 2\,\mathrm{K} + 2\,\mathrm{C}.$$

It is a white crystalline powder, melting at 220±40°; it is volatile near its melting-point, and dissociates a little above it into $Be+N_2$. It is decomposed slowly by water and rapidly by acids and alkalies with evolution of ammonia.

An amide $Be(NH_2)_2$ and an imide $Be{=}NH$ have been described, but do not seem to exist.[28-9,31]

Beryllium azide $Be(N_3)_2$ can be prepared, but it is very highly hydrolysed by water.

Beryllium and Oxygen

Beryllium oxide, BeO, is made by heating the hydroxide to 440°, or better the basic carbonate to 1,100°. It has a wurtzite (4:1) lattice, showing that it is covalent in the solid state[32]; herein it differs from the oxides of the alkaline earths (including magnesium), which all have the ionized sodium chloride (6:1) structure; the difference is due to the smaller size and hence the greater deforming power of the beryllium ion.*

BeO melts at 2,570°.[33] It dissolves in acids, but more slowly the higher it has been heated. Fricke and Lüke[34] have shown from the heat of solution in hydrofluoric acid that the energy content of the solid is greater the lower the temperature of preparation, being 1·25 k. cals. per mole more when it is prepared at 440° than when it has been heated to 1,300°. This may be due to a more colloidal state of the low-temperature specimens (a larger surface of crystallites), the lattice becoming more complete after exposure to a high temperature; this view is supported by the X-ray examination.

Beryllium hydroxide, $Be(OH)_2$, is precipitated from solutions of beryllium salts by hydroxyl ion. The precipitate readily dissolves in excess of alkali, but beryllium hydroxide crystallizes out from the solution slowly on standing. This implies that there are two forms of the hydroxide, one more soluble and less stable than the other. This conclusion has been confirmed by direct measurement of the solubility.[35] The precipitate first

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* Pauling [*Chem. Bond*, p. 74] finds the Be-O link to have 63 per cent. ionic character. This shows how small a percentage of covalent character is sufficient to determine the covalent type of crystal structure.

[29] F. Fichter and E. Brunner, *Z. anorg. Chem.* 1915, **93**, 86.

[30] A. C. Vournasos, ib. 1912, **77**, 195.

[31] J. M. Schmidt, *Ann. Chim.* 1929, [10] **11**, 361.

[32] See further, G. v. Hevesy, *Z. physikal. Chem.* 1927, **127**, 408.

[33] H. v. Wartenberg and H. Werth, *Z. anorg. Chem.* 1930, **190**, 178.

[34] R. Fricke and J. Lüke, *Z. physikal. Chem.* 1933, B **23**, 319.

[35] R. Fricke and H. Humme, *Z. anorg. Chem.* 1929, **178**, 400.

formed is gelatinous, but this changes into an unstable crystalline α-form, and that on standing into a stable β-form, which is only about 1/25 as soluble. Contrary to earlier statements, neither the α- nor the β-form absorbs carbon dioxide. Even the β-form will dissolve in highly concentrated (10-normal) sodium hydroxide, with formation of the beryllates $NaHBeO_2$ or Na_2BeO_2.

Beryllium hydroxide dissolves readily in solutions of beryllium salts (see II. 210). It will not dissolve in solutions of ammonium salts, or of most amines, but it will in a solution of ethylene diamine. Beryllium, unlike all the other elements of Group II, will not form a peroxide.[36]

Beryllates. Potassium beryllate, $K_2[BeO_2]$, cannot be made in water, but is prepared by digesting freshly precipitated beryllium hydroxide with a solution of potassium hydroxide in absolute alcohol, in complete absence of carbon dioxide; it is very hygroscopic, and is hydrolysed by water. The sodium salt is similar.

Beryllium Sulphide

This can be made from the elements, but it is not formed by the action of sulphur on the oxide. It is best made by the continued action of hydrogen sulphide on beryllium chloride at a red heat.[37]

It has the zinc-blende structure and hence a covalent lattice; this is to be expected since beryllium oxide has a covalent lattice, and sulphur (and selenium and tellurium) are more deformable than oxygen. The interatomic distance is 2·10 A[38-41] (theory Be-S 1·94).

It burns in air to beryllium oxide and sulphur dioxide, but no sulphite or sulphate is formed. It is practically insoluble in water, and differs from all the alkaline earth sulphides and from aluminium sulphide in being very stable to water.[42-3] Even in boiling water very little hydrogen sulphide is evolved.

The existence of *polysulphides* of beryllium is doubtful.

Beryllium *selenide* and *telluride* have been made from their elements; they both have the wurtzite structure.[39,44]

Beryllium Halides

Beryllium Fluoride, BeF_2

Beryllium fluoride cannot be made by treating the hydroxide with hydrofluoric acid solution, as the salt hydrolyses on evaporation; but it is formed when beryllium oxide is ignited in a stream of gaseous hydrogen

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[36] T. R. Perkins, *J.C.S.* 1929, 1687.

[37] E. Tiede and F. Goldschmidt, *Ber.* 1929, **62**, 758.

[38] A. W. Zachariasen, *Z. physikal. Chem.* 1926, **119**, 210.

[39] V. M. Goldschmidt, *Skr. Akad. Oslo*, 1926, No. 2, p. 22; No. 8, p. 1.

[40] L. Pauling, *J.A.C.S.* 1927, **49**, 787.

[41] O. Stelling, *Z. Phys.* 1928, **50**, 506.

[42] K. Mieleitner and H. Steinmetz, *Z. anorg. Chem.* 1913, **82**, 94.

[43] W. Biltz, ib. 438.

[44] W. H. Zachariasen, *Z. physikal. Chem.* 1926, **124**, 277 (BeTe), 436 (BeSe).

fluoride, or when fluorine acts on beryllium or its carbide Be_2C. It is best prepared by heating ammonium fluoroberyllate $NH_4[BeF_4]$.[45] It has not yet been obtained in a definite crystalline state, but forms a glassy mass, whose X-ray diffraction pattern[46] is that of a 'random network' in which there are definite interatomic distances within the particles, but a random orientation of the particles themselves. It softens at about 800°, and begins to sublime at that temperature. The fused salt is a very bad conductor of electricity.[47]

Beryllium fluoride is hygroscopic and excessively soluble in water; it can thus be separated from the almost insoluble aluminium fluoride.[48] E.M.F. and conductivity measurements show[49] that there is a certain amount of auto-complex formation in the aqueous solution.

It does not dissolve in anhydrous hydrofluoric acid, and only very slightly in absolute alcohol.

Beryllium Chloride, $BeCl_2$

Beryllium chloride can be made by the action of chlorine or hydrogen chloride on the metal; of chlorine at a high temperature on a mixture of the oxide and carbon; by heating the oxide to about 800° in the vapour of sulphur chloride, phosphorus tri- or pentachloride, or carbon tetrachloride[50]; or by heating the carbide BeC_2 in chlorine to not above 300°.[51] It is a white crystalline substance. The melting and boiling or subliming points and the percentage of Be_2X_4 in the vapour at 564±2° are given for the three halides by Rahlfs and Fischer[52] as follows:

	M. pt.	*B. pt.*	*Subl. pt.*	%Be_2X_4
$BeCl_2$	405°	488°	..	23
$BeBr_2$	488°	..	473°	34
BeI_2	480°	488°	..	..

According to Nilson and Pettersson[53] the chloride is all monomeric at 745°. In pyridine solution it is monomolecular,[54] but here it certainly forms a co-ordination compound (see p. 209).

The specific conductivity of the fused substance is 0·00319 at 451°,[55-7] this being one of the very few chlorides whose conductivity near the

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[45] P. Lebeau, *C.R.* 1898, **126**, 1418.

[46] B. E. Warren and C. F. Hill, *Z. Krist.* 1934, **89**, 481.

[47] B. Neumann and H. Richter, *Z. Electrochem.* 1925, **31**, 484.

[48] W. Biltz and E. Rahlfs, *Z. anorg. Chem.* 1927, **166**, 355.

[49] M. Prytz, ib. 1937, **231**, 238.

[50] C. Matignon and M. Piettre, *C.R.* 1927, **184**, 853.

[51] J. Kielland and L. Tronstad, *Norsk. Vid. Selsk. Forh.* 1936, **8**, 147.

[52] O. Rahlfs and W. Fischer, *Z. anorg. Chem.* 1933, **211**, 349.

[53] L. F. Nilson and O. Pettersson, *Ber.* 1884, **17**, 987.

[54] A. Rosenheim and P. Woge, *Z. anorg. Chem.* 1897, **15**, 310.

[55] A. Voigt and W. Biltz, ib. 1924, **133**, 280.

[56] W. Biltz and W. Klemm, ib. 1926, **152**, 268.

[57] N. Bjerrum, *Ber.* 1929, **62**, 1091.

melting-point is not either greater than 0·1 in absolute units or less than 10^{-5}. As Hevesy points out,[58] this conductivity is about a thousandth of that of a fully ionized salt such as sodium chloride, and so indicates that in fused beryllium chloride about one molecule in a thousand is ionized; in the solid we may suppose there are even fewer.

Beryllium chloride dissolves very readily in water with a large evolution of heat, and crystallizes out as the tetrahydrate $BeCl_2, 4\,H_2O$. The anhydrous salt (but not the hydrate) is very soluble in many organic solvents; the saturated solution at 20° contains the following number of grammes of $BeCl_2$ per litre: methyl alcohol 256·7, ethyl alcohol 151·1, amyl alcohol 153·6, pyridine 133·3, ethyl bromide *ca.* 1. It is also easily soluble in ether, acetone, nitromethane, benzaldehyde, anisole, many amines and nitriles, but is insoluble in chloroform, carbon tetrachloride, carbon bisulphide, and benzene,[59] i.e. strictly non-donor solvents. With many of the solvents it forms co-ordination compounds, nearly all of the type $BeCl_2, 2\,A$.[60-1]

Beryllium chloride can be used for organic syntheses exactly like aluminium chloride, and is nearly but not quite as efficient; rather higher temperatures are needed, especially to break up the intermediate beryllium complexes.[62]

The tetrahydrate holds its water with great firmness, and does not lose an appreciable amount even on standing for 9 months over phosphorus pentoxide.[63] The aqueous solution has an acid reaction and is largely hydrolysed, but the quantitative measurements obtained by different methods do not agree. J. K. Wood,[64] by the hydrolysis of methyl formate at 25° and $V = 8$, found 6·5 per cent., while H. Ley[63] by the inversion of cane sugar found 5·2 per cent. at 99·7° and $V = 64$.

Beryllium Bromide

Its methods of formation and its properties are almost identical with those of the chloride. It melts at 488°, and sublimes below this temperature, having a vapour pressure of one atmosphere at 473°.[52] Thus it is more volatile than the chloride. The vapour at 566° contains 34 per cent. of Be_2Br_4 molecules.[52] The fused substance is practically a non-conductor of electricity.[65] Like aluminium bromide it catalyses the bromination of benzene.[66]

It dissolves very readily in water, and by saturating the concentrated

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[58] G. V. Hevesy, *Z. physikal. Chem.* 1927, **127**, 406.

[59] J. M. Schmidt, *Bull. Soc. Chim.* 1928, [iv] **43**, 49.

[60] R. Fricke and F. Ruschhaupt, *Z. anorg. Chem.* 1924, **146**, 103.

[61] R. Fricke and L. Havestadt, ib. 121.

[62] H. Bredereck, G. Lehmann, C. Schönfeld, and E. Fritsche, *Ber.* 1939, **72**, 1414.

[63] H. Ley, *Z. physikal. Chem.* 1899, **30**, 222.

[64] J. K. Wood, *J.C.S.* 1910, **97**, 878.

[65] P. Lebeau, *Ann. Chim. Phys.* 1899, [7] **16**, 498.

[66] M. F. Taboury and R. Pajeau, *C.R.* 1936, **202**, 328.

viscous solution with hydrogen bromide the tetrahydrate is obtained: this is also very soluble in water.

Beryllium bromide is soluble in ethyl alcohol: a saturated solution in anhydrous pyridine at 25° contains 185·6 g. per litre,[67] and in ethyl bromide about 1 g. per litre.[59]

Like the chloride it forms a large number of addition compounds with alcohols, amines, &c. See pp. 208 ff.

Beryllium Iodide

This is similar in general properties to the chloride and bromide, but much less stable. It is best made by the action of hydrogen iodide on beryllium carbide at 700°,[68-9] and can be purified by sublimation *in vacuo*; but owing to its extreme sensitiveness to water, moisture must be completely excluded.

It melts at 480° and boils at 488°. The fused substance does not conduct electricity.

Water acts violently upon it, evolving hydrogen iodide.[68,70] For this reason the expected tetrahydrate cannot be prepared.[71]

It readily absorbs ammonia, and dissolves in alcohols, amines, etc., with the formation of addition compounds.

Beryllium Derivatives of Oxy-acids

1. *Oxy-acids of Carbon*

Beryllium **ethoxide**, $Be(O \cdot C_2H_5)_2$, which may be mentioned here, has been made by the action of the metal on ethyl alcohol.[72]

The neutral **carbonate** is very unstable, owing to the weakness of the acid, and can only be prepared in an atmosphere of carbon dioxide; it forms a tetrahydrate $BeCO_3, 4\,H_2O$, sol^y. 21·2/15°.[73]

If a beryllium salt solution is treated with a soluble carbonate, carbon dioxide is evolved and a basic carbonate separates; several of these, containing from 2 to 5 molecules of $Be(OH)_2$, have been described; they are probably mixtures of $BeCO_3$ with $Be(OH)_2$.[75] The commercial 'basic beryllium carbonate', which is a mixture of some of these, is a convenient source for making beryllium compounds. On heating, these basic carbonates evolve H_2O and CO_2, and at 550° pure BeO is left.[74]

Carboxylates. $Be(OH)_2$ being a very weak base, its salts of organic acids

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[67] R. Müller, *Z. anorg. Chem.* 1925, **142**, 131.

[68] P. Lebeau, *C.R.* 1898, **126**, 1272; *Ann. Chim. Phys.* 1899, [7] **16**, 476, 490.

[69] C. Mosserknecht and W. Biltz, *Z. anorg. Chem.* 1925, **148**, 152.

[70] C. L. Parsons, *J.A.C.S.* 1904, **26**, 721.

[71] V. Cupr and H. Salansky, *Z. anorg. Chem.* 1928, **176**, 249.

[72] J. M. Schmidt, *Ann. Chim.* 1929, [10] **11**, 433.

[73] G. Klatzo, *J. prakt. Chem.* 1869, **106**, 227; *Bull. Soc. Chim.* 1869, [2] **12**, 132; *Jahresbericht*, 1868, 203.

[74] H. Copaux and C. Matignon, *Bull. Soc. Chim.* 1925, [4] **37**, 1359; *C.R.* 1925, **181**, 550.

[75] H. N. Terem, *C.R.* 1946, **222**, 1436.

are highly hydrolysed in water, though they are readily formed in its absence: thus anhydrous beryllium chloride reacts at the ordinary temperature with a benzene solution of a monocarboxylic acid, evolving hydrogen chloride[76]:

$$BeCl_2 + 2\,HO\cdot CO\cdot R = 2\,HCl + Be(O\cdot CO\cdot R)_2;$$

this is a good example of the way in which our ideas of weak and strong acids cease to hold when the acids and their derivatives are no longer ionized.

These carboxylates are obviously highly associated, and usually melt only with decomposition; they are hydrolysed by excess of water, but with small quantity of water they form the peculiar chelate complexes called 'basic salts', of the formula $Be_4O(O\cdot CO\cdot R)_6$ (see below, II. 213).

Beryllium formate. Owing to the greater strength of the acid, this salt, unlike its homologues, can be prepared[77] by dissolving the hydroxide in formic acid of 50 per cent. or above. It is anhydrous; on heating it decomposes without melting at 150°[76]; it is insoluble in ordinary organic solvents, and is only slowly hydrolysed by water. Hence it is no doubt polymerized, and has the covalency of the beryllium increased to 4.

Beryllium acetate, $Be(O\cdot CO\cdot CH_3)_2$, cannot be made from the aqueous acid, which only gives the 'basic' acetate; it can be made from beryllium chloride and the anhydrous acid[4] or from the basic salt with acetic anhydride at 140°. It melts with decomposition at 295°; it is initially insoluble in water, and only dissolves slowly (with hydrolysis) on boiling; it is insoluble in organic solvents.[78-80] The conductivity of an aqueous solution, made from beryllium sulphate and barium acetate, is abnormally low[80,81]; this cannot be due solely to hydrolysis, or the $Be(OH)_2$ would separate out.

The propionate is similar,[78] but it is hygroscopic, suggesting that the polymer is less stable. The benzoate and *o*-chlorobenzoate have been made[76]; they melt with decomposition at 308° and 247° respectively.

The salts of dibasic acids such as oxalic and malonic are really chelate ato-complexes, and as such are discussed later (II. 216).

II. *Oxy-acids of Nitrogen*

Beryllium nitrite cannot be prepared, owing to the weakness of the acid.[82]

Beryllium nitrate forms a tetrahydrate $Be(NO_3)_2, 4\,H_2O$, which is very soluble and melts in its own water of crystallization at 60·5°; a trihydrate has been described, but its existence has not been confirmed.[83] Several

[76] B. Feild, *J.A.C.S.* 1939, **61**, 1817.

[77] S. Tanatar, *Ber.* 1910, **43**, 1230.

[78] Id., *J. Russ. Phys.-Chem. Ges.* 1904, **36**, 82.

[79] S. Tanatar and E. Kurowski, ib. 1907, **39**, 936; *Chem. Centr.* 1908, **1**, 102.

[80] H. Steinmetz, *Z. anorg. Chem.* 1907, **54**, 219.

[81] N. V. Sidgwick and N. B. Lewis, *J.C.S.* 1926, 2539.

[82] F. Vogel, *Z. anorg. Chem.* 1903, **35**, 385.

[83] C. L. Parsons and G. J. Sargent, *J.A.C.S.* 1909, **31**, 1203.

indefinite basic nitrates have also been described, but they are probably solid solutions.[84]

Oxy-acids of Sulphur

Beryllium sulphite can be made from the hydroxide and sulphur dioxide in absolute alcohol,[85,86] but it is decomposed by water with the separation of basic sulphites.

Beryllium sulphate, $BeSO_4$, can be got in the anhydrous state by dehydrating its tetrahydrate at 400°, or by precipitation from concentrated sulphuric acid. It is very stable and does not begin to lose sulphur trioxide below 580°. The normal hydrate is $BeSO_4$, $4\,H_2O$; higher hydrates with 6 and $7\,H_2O$ have been described, but not confirmed.[87,88,90] Schreiner and Sieverts[88] found no (stable) solid phases in the system $BeSO_4$—H_2O down to the eutectic point at $-18°$ except $BeSO_4$, the tetrahydrate, and ice. A pentahydrate, stable below $-16°$, has, however, been prepared,[89] and tensimetric observations[87] indicate that a di-hydrate can be obtained. The sol^y of the tetrahydrate in water is 42·5/25° and 37·0/$-18°$.[88] The crystal structure has a tetrahedral arrangement of 4 O's round each S, and of $4\,H_2O$'s round each Be.[91]

The aqueous solution of beryllium sulphate will dissolve large quantities of beryllium oxide, and on evaporation solids can be obtained of the composition of basic salts, $BeSO_4$, xBeO, $y H_2O$; they are probably not definite individuals; their possible constitution is discussed later (II. 210).

Beryllium selenate, $BeSeO_4$, $4\,H_2O$, is isomorphous with the sulphate, and at 100° is converted into a dihydrate which will lose the rest of its water on drying at 300°; all these forms are very soluble in water, and at 25° the sol^y of the tetrahydrate is 56·7. The aqueous solution readily dissolves beryllium oxide.

According to Berzelius, beryllium tellurate can also be made.

Oxy-acids of the Halogens

There is little recent work on these salts.

A soluble chlorate can be prepared, but it decomposes on keeping, and the solution decomposes on evaporation.[92]

Beryllium perchlorate, $Be(ClO_4)_2$, $4\,H_2O$, loses none of its water up to the temperature at which the anion begins to decompose. It is very hygroscopic: sol^y 148·6/25°.[93]

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[84] C. L. Parsons and W. O. Robinson, *J.A.C.S.* 1906, **28**, 568.

[85] G. Krüsz and H. Moraht, *Ber.* 1890, **23**, 734.

[86] Id., *Ann.* 1890, **260**, 178.

[87] F. Krauss and H. Gerlach, *Z. anorg. Chem.* 1924, **140**, 61.

[88] L. Schreiner and A. Sieverts, ib. 1935, **224**, 167.

[89] R. Rohmer, *Bull. Soc. Chim.* 1943, [v] **10**, 468.

[90] W. Schröder, E. Neumann, and J. Altdorf, *Z. anorg. Chem.* 1936, **228**, 129; A. V. Novoselova and M. E. Levina, *J. Gen. Chem. Russ.* 1938, **8**, 1143.

[91] C. A. Beevers and H. Lipson, *Z. Krist.* 1932, **82**, 297.

[92] V. Cupr, *Coll. trav. chim. Tschekoslav.* 1929, **1**, 377; *Chem. Centr.* **29**, ii. 1637.

[93] N. V. Sidgwick and N. B. Lewis, *J.C.S.* 1926, 1290.

A hypobromite does not seem to exist; the bromate is known to be very soluble, but it has not been isolated. The iodate is also very soluble, and crystallizes with $4\,H_2O$; a periodate $Be(IO_4)_2, 8\,H_2O$ has also been made.[94]

Complex Beryllium Compounds

As a result of its small size and its double charge, the beryllium ion has a very strong tendency to covalency formation; similarly the neutral beryllium atom in its covalent compounds A—Be—A tends to increase its group of 4 shared electrons to the full octet, and so acquire its maximum covalency of 4.

The complexes thus produced can be classified according to the nature of the atoms attached to the beryllium. Complexes in which this atom is carbon do not seem to occur.

Nitrogen Complexes

These are essentially derivatives of ammonia and the amines, and of the nitriles.

Ammines

Beryllium salts, especially the chloride bromide and iodide, readily take up ammonia to form ammines. Those of the chloride have been examined by Ephraim[95-6] and others,[97] and especially by Biltz.[98-9] The vapour pressures of the system salt $+NH_3$ show that all three halides give compounds with 4, 6, and $12\,NH_3$, and the iodide even with 13. But of these only the tetrammines are stable at the ordinary temperature, and they are unusually stable; thus the dissociation pressures of $BeCl_2$ ammines are:

	Liq. NH_3	$BeCl_2, 12\,NH_3$	$BeCl_2, 6\,NH_3$	$BeCl_2, 4\,NH_3$
Temp.	$-50°$	$-50°$	$-50°$	$+156°$
Press.	306 mm.	168 mm.	90 mm.	6 mm.

The bromide and iodide are similar. $BeCl_2, 2\,NH_3$ seems to exist, but if ammonia is removed from the tetrammine, there is some decomposition with loss of ammonium chloride.

It is to be noticed that though the tetrammine is so exceptionally stable to heat, it is decomposed by water, which shows that while the affinity of the beryllium ion for ammonia is very strong, its affinity for water is higher still.

Other beryllium salts form ammines, but less readily. Beryllium

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[94] V. A. Biber, I. A. Neuman, and A. A. Bragina, *J. Gen. Chem. Russ.* 1941, **11**, 861.

[95] F. Ephraim, *Ber.* 1912, **45**, 1323, 1330.

[96] Id., *Z. physikal. Chem.* 1913, **81**, 532.

[97] K. Mieleitner and H. Steinmetz, *Z. anorg. Chem.* 1913, **80**, 73.

[98] W. Biltz and C. Messerknecht, ib. 1925, **148**, 157.

[99] W. Biltz, K. A. Klatte, and E. Rahlfs, ib. 1927, **166**, 341.

fluoride only gives a monammine BeF_2, NH_3, and even this is stable only at low temperature.[99] Beryllium sulphate forms in the cold a diammine, which still retains one NH_3 at 235°.[100]

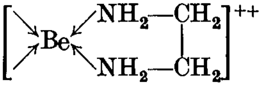
Beryllium chloride also combines with a variety of amines (Fricke *et al.*[101–6]); the compounds are unusually made in ether. Most of them are only diammines. This may be partly due to the undoubtedly weaker power of co-ordination of amines compared with ammonia; but steric effects of the groups attached to the N probably contribute. Thus only ammonia and methylamine give tetrammines, the rest only diammines. In the same way, while prussic acid forms $BeCl_2$, 4 HCN, the nitriles only form $BeCl_2$, 2 $R \cdot CN$. So, too, with oxygen: water forms a tetrad complex, aldehydes ketones and ethers only diad, and the ether compounds are much the least stable of the three.

Fricke *et al.* have got complexes $BeCl_2$, 2 B for B = Et_2NH, $BuNH_2$,[106] o-toluidine, quinoline,[103] pyridine (m. pt. 152°)[101,110]; methylamine alone forms a tetrammine.[102] Of phenyl hydrazine and hydrazine 3 molecules are very readily taken up, but the formation of a complex with 4 is doubtful with hydrazine, and though it occurs with phenyl hydrazine the latter gives a very unstable product. The suggestion that in these complexes both the N atoms of the hydrazine are engaged is improbable, both for steric reasons and because of the extreme weakness of the second nitrogen atom.

A singular complex $BeCl_2$, 2 NH_3, 4 $CH_3 \cdot CO \cdot CH_3$ is formed with acetone[102]; in dry air it loses acetone but not NH_3; a rather similar complex $BeCl_2$, 2 acetone, 4 benzene is known (see later, II. 212).

The benzidine complex alone contains 2 molecules of $BeCl_2$: it is 2 $BeCl_2$, 3 benzidine; evidently the 2 NH_2 groups, being unable to form a chelate ring, attach themselves to 2 beryllium atoms.[104]

The chelate N-complexes are rather few. Beryllium hydroxide will dissolve in aqueous ethylene diamine, though not in a solution of a monamine[107]; it must form the ring



If a solution of $BeCl_2$ in ether is treated with 2 equivalents of *en*, the solutes are wholly precipitated as the salt $[Be(en)_2]Cl_2$, which is quite insoluble in water.[104]

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[100] F. Ephraim, *Ber.* 1926, **59**, 1230.

[101] R. Fricke and F. Ruschhaupt, *Z. anorg. Chem.* 1924, **146**, 103.

[102] R. F. and L. Havestadt, ib. 121.

[103] R. F. and O. Rode, ib. 1926, **152**, 347.

[104] R. F. and L. Havestadt, ib. 357.

[105] R. F. and O. Rode, ib. 1927, **163**, 31.

[106] R. F. and F. Röbke, ib. 1928, **170**, 25.

[107] E. J. Fischer, *Wiss. Veröff. Siemens-Konzern*, 1925, **4**, ii. 171.

Nitrile Complexes

Beryllium chloride will also combine readily with nitriles.[101,103,105] It forms a tetra-addition compound only with prussic acid, of the composition $BeCl_2, 4\ HCN$; all the organic nitriles examined—those of acetic, propionic, caproic, benzoic, *p*-toluic, phenylacetic, and naphthoic acids—gave compounds only of the type $BeCl_2, 2\ R \cdot CN$. These are very slightly soluble in organic solvents, and are decomposed by water.

A succinonitrile complex $BeCl_2,(CH_2CN)_2$ is claimed by Fricke,[103] but its structure and even its composition are doubtful.

Oxygen Complexes

These are by far the most numerous of the complexes of beryllium. The most obvious are the hydrated salts. Nearly all the inorganic beryllium salts form tetrahydrates as their highest hydrates: the carbonate, nitrate, sulphate (above −16°), selenate, chloride, bromate, and perchlorate do so; supposed higher hydrates of these salts have been found not to exist. Salts with less than 4 H_2O to one Be as a maximum (like the oxalate) can be shown to be complex, and supposed salts which do not hydrate at all, such as the 'basic' acetate, are demonstrably covalent compounds. The stability of some of these hydrates is remarkable (see $BeCl_2, 4\ H_2O$, II. 204 and $Be(ClO_4)_2, 4\ H_2O$, II. 207).

The evidence for the hydration of the beryllium ion in solution is also very strong. Fricke[108] concludes from the high viscosity of beryllium salt solutions, from the small mobility of the beryllium ion, and from the depressions of the freezing-point as compared with those produced by similar salts, that Be^{++} is the most strongly hydrated of all divalent ions.

This tendency of the beryllium ion to co-ordinate is illustrated in a peculiar way by its power of combining with beryllium oxide.

The aqueous solution of any soluble salt of beryllium can dissolve considerable amounts (up to several molecular proportions) of beryllium oxide or hydroxide. The affinity is so strong that a concentrated solution of the beryllium salt of a strong acid continues to dissolve the basic carbonate with a brisk effervescence even after one mole of base has been added for each mole of salt. The ratio of oxide to Be ion increases with the concentration of the salt, and if a concentrated salt solution saturated with oxide is diluted, the hydroxide or a basic salt is precipitated. On evaporation these solutions deposit more or less colloidal solids. It has been shown by Parsons[109–12] that the compositions of these are not definite, but vary continuously with the conditions of their formation; he considers that they are solid solutions. This may be true of the solids, but it does not explain the presence of the (normally insoluble) oxide in the solution.

[108] R. Fricke and H. Schützdeller, *Z. anorg. Chem.* 1923, **131**, 130.

[109] C. L. Parsons, *J.A.C.S.* 1904, **26**, 1437.

[110] Id., *Z. anorg. Chem.* 1904, **42**, 258.

[111] C. L. Parsons and W. O. Robinson, *Science*, 1906, **24**, 202.

[112] C. L. Parsons, W. O. Robinson, and C. T. Fuller, *J. Phys. Chem.* 1907, **11**, 651.

There are three possible explanations of this phenomenon[113]: (1) that the oxide is in the colloidal form: (2) that a salt of the half ion $[Be{-}OH]^+$ is formed, and (3) that the BeO replaces the water in the hydrated ion to form the complex grouping $Be \leftarrow O{=}Be$.

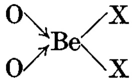
(1) This may be partly true: the strongest solutions are turbid and highly viscous, and may contain colloidal matter, though it cannot be separated by dialysis. But solutions can be made up with 5 moles of BeO per litre, which is far beyond the concentrations given by other colloidal metallic hydroxides. Also this would not explain the stability of these solutions to heat, and to the presence of electrolytes (which is indeed a condition of their formation). Britton has shown[114] that more than one mole of NaOH can be added to one mole of $BeSO_4$ in solution without precipitation occurring, and that the resulting solution is not coagulated by electrolytes, and 'shows no signs of colloidality'. Hence at least most of the oxide must be present in some other form.

(2) The formation of basic salts of an ion $[BeOH]^+$ would only account for the addition of one mole of oxide to one of salt, whereas much stronger solutions can be prepared; the addition should also lower the freezing-point whereas it slightly raises it.

(3) This view, that the oxide co-ordinates with the Be ion to form complex ion $[Be(OBe)_x]^{++}$, or more probably $[Be(OBe)_x(OH_2)_{4-x}]^{++}$, agrees with all the facts. It accounts for the small change in conductivity (3 to 7 per cent.),[112-13] since the number of ions will not alter, but the 'beryllated' ion may move rather quicker; it is compatible with the slight (*ca.* 10 per cent.) increase in the freezing-point depression.[112] It also accounts for the fact that the solubilities in water of the sulphate and selenate are increased by the addition of the oxide in proportion to the amount of the latter, the molecular ratio of the BeO dissolved to the extra salt dissolved being almost exactly 4 for both salts over a range of the ratio (BeO dissolved)/(total salt) from 0·1 to 0·87. If we could assume the salts to be fully dissociated at these high concentrations, this would be direct evidence of the presence of an ion $[Be(OBe)_4]^{++}$, and though this assumption is not justified, the facts do indicate that the oxide replaces more or less completely the water of the complex $[Be(OH_2)_4]^{++}$ ion.

Addition compounds with alcohols and phenols, which are numerous with the magnesium and calcium halides, do not seem to be known with beryllium.

On the other hand, aldehydes and ketones add on to Be atoms readily, usually to form covalent molecules of the



type. Ethyl ether evolves heat with anhydrous beryllium chloride, and

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[113] N. V. Sidgwick and N. B. Lewis, *J.C.S.* 1926, 1287.

[114] H. T. S. Britton, ib. 1925, **127**, 2121.

two liquid layers are formed; the lower, which is very viscous, solidifies to a mass of crystals of $BeCl_2, 2\ Et_2O$[101]; m. pt. 330°.[106] This dissolves in ether and benzene, and other complexes can be made from its solution, as the ether is readily displaced by ketones, amines, etc. In this way compounds of $BeCl_2$ with 2 molecules of acetone, benzophenone, benzaldehyde, cinnamaldehyde, and nitrobenzene have been prepared. Most of them are very slightly soluble in solvents other than alcohol and water, which decompose them; indeed the materials for their preparation must be very carefully dried, since beryllium has a much stronger affinity for water than for the other addenda.

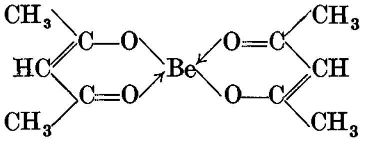
The acetone compound shows an exceptional sol^y in benzene[102,106] and at 5° colourless crystals separate, of $BeCl_2$, 2 acetone, 4 benzene, m. pt. 40°, which loses its benzene very readily, much more so than its acetone; this is perhaps a van der Waals compound or crystal aggregate; a similar solid, with ammonia in place of acetone, and acetone in place of benzene, has been described above (II. 209).

Neutral Chelate Compounds

The complexes with chelate rings formed through oxygen are numerous and stable; they can be neutral or negatively charged. The former kind are (1) derivatives of hydroxy-keto-compounds, β-keto-enols, β-keto-esters, hydroxyquinones, and (2) a series of covalent derivatives of carboxylic acids, of the general formula $Be_4O(O \cdot CO \cdot R)_6$, which are almost but not quite peculiar to beryllium. The complex anions are 'ato' compounds, derived from catechol, *o*-hydroxy-aromatic acids, and dibasic acids both organic and inorganic: there is also one remarkable open-chain 'ato' compound, the complex ethylate $M[Be(O \cdot Et)_4]$.

Derivatives of β-keto-enols and β-keto-esters

Beryllium acetylacetonate



was discovered in 1894 by Combes,[115] who found that it was volatile, and by a determination of its vapour density confirmed the atomic weight of beryllium. It is made by the action of acetylacetone on a solution of $Be(OH)_2$ in dilute acetic acid or on a solution of $BeCl_2$ in presence of ammonia.[116-20] It melts at 108° and boils undecomposed at 270°; it is scarcely soluble even in hot water, but is hydrolysed by it on boiling; it

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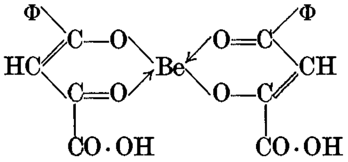
[115] A. Combes, *C.R.* 1894, **119**, 1222.
[116] W. Biltz, *Ann.* 1904, **331**, 336.
[117] Id., *Z. anorg. Chem.* 1913, **82**, 439.
[118] C. L. Parsons, *J.A.C.S.* 1904, **26**, 732.
[119] Id., *Z. anorg. Chem.* 1904, **40**, 400.
[120] F. M. Jaeger, *Rec. Trav.* 1914, **33**, 394.

dissolves readily in organic solvents, including carbon disulphide and benzene. Werner,[121] in 1901, recognized that these acetylacetonates are non-ionized ring compounds; that the beryllium has its maximum covalency of 4 is shown by the fact that it does not hydrate or take up ammonia.[117] Various other β-diketone derivatives have been prepared, for example from benzoylacetone (m. pt. 211°),[122-3] dibenzoylmethane (214-15°),[123] and *m*- and *p*-nitrobenzoylacetone (m. pts. 207-8° and 243-4°).[124]

The tetrahedral arrangement of the valencies of 4-covalent Be was established by means of compounds of this type; Lowry[125-6] found that the beryllium derivative of benzoyl camphor showed mutarotation, which made it probable that the beryllium formed a second centre of asymmetry; Mills and Gotts[127] established the conclusion beyond doubt by resolving the Be derivative of benzoyl-pyruvic acid; the active dimethyl-ammonium salt was found to racemize in 15′.



β-ketoesters such as ethyl acetocetate[123] and salicylate[128] form similar complexes. Of the same type also are the insoluble beryllium 'Lakes' formed by 1-hydroxy-anthraquinone derivatives, which can often be used as tests for beryllium; thus the blue colloidal lake given by 1, 2, 5, 8-hydroxy-anthraquinone will detect 0·01 per cent. of Be in 0·1 g. of a mineral,[129-30] and others are used in the same way.[131]

'Basic' Carboxylic Complexes

The monobasic carboxylic acids give rise to a remarkable series of complex beryllium derivative of the composition $Be_4O(O \cdot CO \cdot R)_6$, which are non-ionized, soluble in hydrocarbons, and volatile.

The best known is the acetate $Be_4O(O \cdot COCH_3)_6$, made by Urbain and Lacombe in 1901[132-3.135] by treating the hydroxide or carbonate with

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[121] A. Werner, *Ber.* 1901, **34**, 2584.

[122] R. W. Bailey, F. M. Brewer, and H. M. Powell, *J.C.S.* 1933, 1546.

[123] H. S. Booth and D. G. Pierce, *J. Phys. Chem.* 1933, **37**, 59.

[124] H. Burgess, *J.C.S.* 1927, 2017.

[125] H. Burgess and T. M. Lowry, ib. 1924, **125**, 2081.

[126] T. M. Lowry and R. C. Traill, *Proc. Roy. Soc.* 1931, **132**, 398, 416.

[127] W. H. Mills and R. A. Gotts, *J.C.S.* 1926, 3121.

[128] A. Rosenheim and F. Lehmann, *Ann.* 1924, **440**, 153.

[129] I. Kolthoff, *J.A.C.S.* 1928, **50**, 393.

[130] G. Rienäcker, *Z. anal. Chem.* 1932, **88**, 29.

[131] C. E. White and C. S. Lowe, *Ind. Eng. Chem.* [*Anal.*] 1941, **13**, 809.

[132] G. Urbain and H. Lacombe, *C.R.* 1901, **133**, 874.

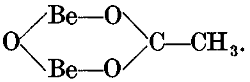
[133] H. Lacombe, ib. 1902, **134**, 772.

[134] S. Tanatar, *J. Russ. Phys. Chem. Ges.* 1904, **36**, 82 (*Chem. Centr.* 04. i. 1192).

[135] F. Haber and G. van Oordt, *Z. anorg. Chem.* 1904, **40**, 465.

acetic acid; it crystallizes from chloroform in tetrahedra, m. pt. 285-6°, b. pt. 330-1°. It is monomeric in the vapour and in solution in benzene and in acetic acid.[134] It is soluble in all ordinary organic solvents except alcohol and ether; it is insoluble in cold water and hydrolysed by hot, or by dilute acids. It has no tendency to combine with ammonia,[132] and though it can take up 3 molecules of pyridine,[142] this is very loosely held.

The crystal structure has been examined by Bragg and Astbury[138-9] and by Pauling and Sherman[141]; the molecule has tetrahedral symmetry, the central oxygen atom being surrounded tetrahedrally by 4 Be atoms, and the 6 acetate groups attached symmetrically to the 6 edges of this tetrahedron; this involves the formation of chelate 6-rings of the form



The co-ordinate links are not marked, because the ordinary structural symbols are insufficient to express so complicated a structure, but on examination it can be seen that it gives complete octets to all the oxygen, beryllium, and carbon atoms: that the central oxygen and the 4 beryllium atoms are all 4-covalent: and the oxygen of the carboxyl groups are in the same state as those in an acetyl acetonate (see ref. [140]). The molecule is interesting as a sixfold complex in which no atom can have a covalency of more than 4 (see, for another example, the borotungstates, III. 385).

A similar zinc compound $Zn_4O(O{\cdot}CO{\cdot}CH_3)_6$ has been obtained (see II. 283); it also is volatile, but it differs from the beryllium compound in being immediately hydrolysed by water, obviously because the 4-covalent zinc, unlike the 4-covalent beryllium, is covalently unsaturated, so that it can co-ordinate a water molecule, which initiates the hydrolysis. An analogous series of zirconyl compounds $(O{=}Zr)_4O(O{\cdot}CO{\cdot}R)_6$ is also known (see under Zr. IV. 642).

A large number of beryllium compounds of this type have been made; Feild[143] has recently shown that they can be prepared by the action of beryllium chloride on a benzene solution of the acid in presence of a trace of water, which partially hydrolyses the simple carboxylate first produced:

$$4\,Be(OCO{\cdot}R)_2 + H_2O = Be_4O(OCO{\cdot}R)_6 = 2\,HO{\cdot}CO{\cdot}R.$$

The formate is made by heating the normal compound $Be(O{\cdot}CO{\cdot}H)_2$ under reduced pressure. It sublimes unchanged on heating. The other compounds are all similar in properties, though the crystalline form

[136] S. Tanatar and E. Kurowski, *J. Russ. Phys. Chem. Ges.* 1907, **39**, 937 (*Chem. Centr.* 08. i. 102).

[137] S. Tanatar, *Ber.* 1910, **43**, 1230.

[138] W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.* 1923, **104**, 437.

[139] G. T. Morgan and W. T. Astbury, ib. 1926, **112**, 441.

[140] N. V. Sidgwick, *Nature*, 1923, **111**, 808.

[141] L. Pauling and J. Sherman, *Proc. Nat. Acad. Sci.* 1934, **20**, 340.

[142] H. Steinmetz, *Z. anorg. Chem.* 1907, **54**, 217.

[143] B. Feild, *J.A.C.S.* 1939, **61**, 1817.

becomes less symmetrical as the radicals lengthen. They are all monomeric in the vapour or in solution, and are remarkably stable, as their boiling-points show.

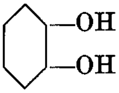
$Be_4O(O\cdot CO\cdot R)_6$ *Compounds*

Acyl	*M. pt.*	*B. pt.*	*Monomeric by*	*References*
Formate$_6$	. .	Subl.	. .	133 136 137
Acetate$_6$	283°	330°	v.d.; cry.	133 137 143
Propionate$_6$	134°	340°	v.d. (480°)	133 134
Acet.$_3$ Prop.$_3$	141°	330°	cry.	137 138
n-Butyrate$_6$	26°	239°/19 mm.	cry.	133 139
Isobutyrate$_6$	88–9°	336–7°	cry.	133 139
Acet.$_2$, isobut.$_4$	—15°	351°	cry.	134 136
Isovalerate$_6$	Liq.	254°/19 mm.	cry.	133
Trimethylacetate$_6$	163°	. .	. .	139
Crotonate$_6$	. .	. .	cry.	136
Levulinate$_6$	. .	. .	cry.	136
Benzoate$_6$	317°	. .	. .	143
o-chlorobenzoate$_6$	255·6°	. .	. .	143

Ato Complexes

In these the stable 4-covalency of the beryllium is secured by the replacement of 4 hydroxylic hydrogens, involving the assumption by the beryllium of two negative charges. Such compounds are nearly always derived from dibasic acids, as in this way the molecule secures the extra stability due to ring formation; but beryllium also gives a remarkable open-chain complex anion in the complex ethoxide $K_2[Be(O\cdot C_2H_5)_4]$.[144]

Catechol



forms chelate rings very readily by the replacement of its two hydroxylic hydrogen atoms. The stable beryllium complex must have two such rings (since each involves two covalencies), and hence have 4 hydrogens replaced by one beryllium atom; this is only possible if the beryllium has acquired two electrons, so that the complex appears as a divalent anion. Alkaline salts of this anion, of the formula $M_2[Be(C_6H_4O_2)_2]$, $x\ H_2O$, can be obtained by dissolving $Be(OH)_2$ in alkaline solutions of catechol; the NH_4, Na, K, and Ba salts are known.[145] In the preparation of these and other complex beryllium salts it is often found that with excess of $Be(OH)_2$ more basic complexes are formed, for example,

$$(NH_4)_2[Be_2O(C_6H_4O_2)_2],\ 5\ H_2O$$

(i.e. the dichelate salt+1 BeO). The constitution of these basic salts is obscure: they cannot be due to 'beryllation' since the Be is already 4-covalent.

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[144] H. Merwein and T. Bersin, *Ann.* 1929, 476, 128.

[145] A. Rosenheim and F. Lehmann, *Ann.* 1924, 440, 153.

Similar derivatives are known of salicylic and of *o*-hydroxy-toluic acids, which behave as dibasic acids.[145] Beryllium salicylate itself is really a salt of this kind. Bury[146] shows that it has the composition

$$Be(C_6H_4O \cdot CO_2),\ 2\,H_2O;$$

the presence of only 2 H_2O shows that it is not a simple salt, but in the dimeric form $Be[BeSal_2]$, 4 H_2O the cation has the necessary 4 molecules. Bury finds that this formulation is supported by the conductivity of the solution, which is small and changes little with the concentration; for the meaning of this see below.

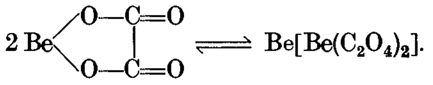
Oxalato- and Malonato-complexes

These acids form auto-complex salts $Be[BeA_2]$ with beryllium itself.[151] The most remarkable is the oxalate; it has the composition BeC_2O_4, 3 H_2O, and so has less than the normal 4 H_2O to each Be: it is the only oxalate of a divalent metal that is readily soluble in water (27·8 per cent. anhydrous salt at 25°); the oxalates of the other elements of Group II (see list, II. 221), and those of divalent Sn, Cr, Mn, Fe, and Co, are scarcely, if at all, soluble. The molecular conductivity is less than a quarter of that of the sulphate, and is almost constant over a large range of concentrations, as the following values (corrected for viscosity) show ($BeSO_4$ added for comparison):

Mol. normality . . .	0·65	0·166	0·032	$BeSO_4$ 0·03
$\Lambda\eta/25°$ . . .	11·00	10·22 (min.)	11·13	62

Again the depression of the freezing-point of water indicates very little dissociation, the van 't Hoff *i* being between 1·10 and 1·20 for mol. normalities of 0·18 to 0·02.

All these abnormalities can be explained if we assume that in the solution we have mainly an equilibrium between a non-ionized (hydrated) monochelate compound and a highly dissociated dichelate complex salt:



Each oxalate-group will probably carry one H_2O (compare K_2Ox,H_2O: $(NH_4)_2Ox,H_2O$: $(NH_4)_2[HgOx_2]$, 2 H_2O: the K_3 and $(NH_4)_3$ salts

$$M_3[CrOx_3],\ 3\,H_2O:$$

all salts of cations that are rarely if ever hydrated), so that BeOx will have 3 H_2O, and $Be[BeOx_2]6H_2O$—both 3 H_2O per Be. The van 't Hoff *i* is near unity, since on either side of the equation we have one molecule per Be atom; the molecular conductivity is independent of dilution as the number of molecules on the two sides of the equation is the same. The existence of a non-ionized form of the oxalate explains why oxalic acid is able[147] to form a solid solution with its beryllium salt.

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[146] F. E. Jones, W. E. Hamer, C. W. Davies, and C. R. Bury, *J. Phys. Chem.* 1930, **34**, 563.

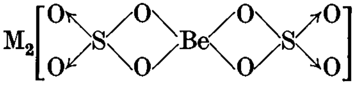
[147] N. V. Sidgwick and N. B. Lewis, *J.C.S.* 1926, 1287, 2538.

The existence of a complex ion $[BeOx_2]^{--}$ is supported by that of series of double oxalates of this type, such as $Na_2[BeOx_2],H_2O$.[149,150]

Beryllium malonate behaves similarly[147]; its conductivity is low and constant. Double malonates $M_2[Be(mal)_2], x\ H_2O$ have been obtained.[150]

Sulphato-Complexes

Beryllium sulphate behaves as a normal electrolyte; it has the crystal structure[160] to be expected of the salt $[Be(OH_2)_4]\cdot(SO_4)$, and there is no evidence of the occurrence of any considerable amount of complex ions in the solution; the same is true of the selenate. Double sulphates of beryllium occur, but this does not show that they are complex: the alums are known not to be complex and the double salts of the vitriols, such as the familiar $(NH_4)_2SO_4$, $FeSO_4$, $6\ H_2O$, are probably not so either. Those of beryllium, however, are of another type,[154-6], M_2SO_4, $BeSO_4$, $2\ H_2O$ (and also anhydrous); the NH_4 and K salts have been obtained,[152-3,157-9] the latter being formed over a considerable range of concentrations. The low hydration is good evidence of the absence of Be cations, which would require $4\ H_2O$. The salts are no doubt of dichelate structure, with the $2\ H_2O$ attached to the SO_4 as in so many sulphates.



Sulphur Complexes

Considering the strong tendency of beryllium to combine with water, it is remarkable that it has scarcely any affinity for hydrogen sulphide. The only co-ordination compound with sulphur that has been described is $BeBr_2$, $2\ H_2S$,[161] and even this is comparatively unstable. It is only formed at low temperature, and its dissociation tension is 94·5 mm. at 0° (1/84 of that of liquid H_2S at 0°).

Complex Halides

Beryllium forms a well-marked series of complex fluorides, the fluoroberyllates, derived from the acid H_2BeF_4. Salts of a lower fluoride, such

[148] H. Ley, *Z. phys. Chem.* 1899, **30**, 245.

[149] G. N. Wyrouboff, *Bull. Soc. Min.* 1902, **25**, 83; *Z. Krist.* 1904, **39**, 310.

[150] A. Rosenheim and P. Woge, *Z. anorg. Chem.* 1897, **15**, 292.

[151] J. Meyer and E. Mantel, ib. 1922, **123**, 43.

[152] H. T. S. Britton and A. J. Allmand, *J.C.S.* 1921, **119**, 1463.

[153] H. T. S. Britton, ib. 1922, **121**, 2612.

[154] W. Schröder, E. Neumann, and J. Altdorf, *Z. anorg. Chem.* 1936, **228**, 129.

[155] W. Schröder, J. Hahnrath, and E. Kehren, ib. 1938, **239**, 39.

[156] W. Schröder, H. Hompesch, and P. Mirbach, ib. 225.

[157] W. Schröder and W. Kleese, ib. 399.

[158] W. Schröder and H. Schwedt, *Z. anorg. Chem.* 1939, **240**, 50.

[159] W. Schröder, U. Beckmann, and W. Ausel, ib. 1939, **241**, 179.

[160] C. A. Beevers and H. Lipson, *Z. Krist.* 1932, **82**, 297.

[161] W. Biltz and G. Keunecke, *Z. anorg. Chem.* 1925, **147**, 185.

as $KBeF_3$, can be got by using excess of BeF_2, but they are unstable, and on recrystallization from water are converted into the tetra-compounds. The fluoroberyllates have long been known[162-3]; they can usually be recrystallized from water, and though the solution gives reactions for the simple ions, showing that it is to some extent dissociated, the beryllium goes on electrolysis to the anode. They can be made by dissolving beryllium oxide in the acid fluoride, or in the dry way[164] by heating sodium fluosilicate with beryllium oxide at 700-800°. For the crystal structure of K_2BeF_4 see reference.[165]

In their solubilities the fluoroberyllates are very like the sulphates. The alkaline salts are very soluble, and those of the alkaline earths relatively insoluble. The Co″, Ni, and Zn salts[167] are soluble, crystallize with 6 and 7 H_2O like the vitriols, and like them form with the alkalis double salts $M'_2M''(BeF_4)_2$, 6 H_2O; it is even possible to get mixed salts, such as $K_2Ni(BeF_4,SO_4)6H_2O$; cupric fluoroberyllate has 5 H_2O. There are, however, some differences; Ag_2BeF_4 is very soluble, while Ag_2SO_4 is relatively insoluble. These similarities are evidently due[166] to these two series of salts having anions of the same valency and structure, and nearly the same size. Other examples of such similarities will be found later (see, for example, III. 410; VI. 1044; VII. 1297).

The corresponding complex chlorides $M'_2[BeCl_4]$ and $M''[BeCl_4]$ are much less stable, and our only evidence of their existence is derived from the freezing-point diagrams of mixtures of beryllium chloride with other chlorides[168-9]; these show the formation of the double salts Li_2BeCl_4, Na_2BeCl_4, Tl_2BeCl_4, and $BaBeCl_4$; the corresponding salts of silver, lead, and cadmium do not seem to be formed.

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[162] G. Krüss and H. Moraht, *Ann.* 1890, **260**, 161.

[163] N. N. Ray, *Z. anorg. Chem.* 1931, **201**, 289; 1932, **205**, 257; **206**, 209; 1936, **227**, 32, 103; 1939, **241**, 165.

[164] A. V. Novoselova, O. I. Vorobieva, and N. D. Nagorskaja, *J. Gen. Chem. Russ.* 1937, **7**, 2789.

[165] R. Hultgren, *Z. Krist.* 1934, **88**, 233.

[166] N. N. Ray, *Z. anorg. Chem.* 1932, **205**, 257.

[167] J. M. Schmidt, *Bull. Soc. Chim.* 1926, [iv] **39**, 1686.

[168] Id., *Ann. Chim.* 1929, [x] **11**, 351.

[169] H. O'Daniel and L. Tscheischwili, *Z. Krist.* 1942, **104**, 124.

MAGNESIUM, CALCIUM, STRONTIUM, BARIUM, RADIUM

THE gap between magnesium and the succeeding elements is sufficient to make it desirable to treat the magnesium compounds separately; but in the general discussion we may include it along with the alkaline-earth metals proper, the elements from calcium to radium.

In all these elements the tendency to ionization predominates, increasing of course with the atomic number; hence, from the practical point of view, their chemistry is mainly the chemistry of the salts, that is, of the divalent cations. The most important properties of these, as of all salts, are the solubilities in water and the hydration. The values of these properties for the more important salts of all the metals including beryllium are given in Tables I, II, and III (pp. 220–1). Table I gives the solubilities in g. (or mg.) of anhydrous salt to 100 g. of water at a temperature not far from 20°; Table II the same expressed as moles of salt to 100 moles of water (for diluter solutions this is 1·8 times the molarity); Table III gives the number of moles of water of crystallization.

With the solubilities we have to consider the variations (*a*) with a change of anion, and (*b*) with a change of cation. We may divide the salts into (1) the very soluble, where the molecular solubility (molarity) is 1 or more, (2) the fairly soluble, where it is between 1 and 0·01, and (3) the slightly soluble where it is less than 0·01. Taking as our standard the barium salts whose solubility is usually the least and never much more than the least, we have the following results, where S is the molecular solubility:

$S > 1$	$1 > S > 0{\cdot}01$	$S < 0{\cdot}01$
Chloride	Hydroxide	Carbonate
Bromide	Fluoride	Oxalate
Iodide	Malonate	Fluosilicate
Azide	Succinate	Sulphite
Formate	Benzoate	Sulphate
Acetate	Nitrate	Selenate
Nitrite	Bromate	Chromate
Chlorate		Iodate
Perchlorate		

Secondly, we have the influence of the cation on the solubility. For the alkaline earth metals proper, this is almost always in the order Ca>Sr>Ba. This holds (if we disregard small departures from the regular order) for the chlorides, bromides, iodides, azides, succinates, fluosilicates, nitrates, nitrites, sulphites, sulphates, selenates, chromates, chlorates, bromates, and iodates. Of the few radium salts whose solubilities are known the chloride, bromide, and sulphate fall into line, being less soluble than their barium analogues; the nitrate is slightly more soluble than the barium salt.

The only salts which show the reverse order (Ca < Ba) are the hydroxides, fluorides, and oxalates (we do not have the distinction between the salts of strong and those of weak acids which occurs in the alkali metal salts). The perchlorates (including those of beryllium and magnesium) differ but little in solubility, and the same is true of most of the organic salts (formates, acetates, malonates, benzoates). The magnesium salts usually fall into line with the rest, or nearly so; sometimes the excess of solubility is larger than we should expect: this is especially marked in the sulphate, selenate, and chromate. With the oxalates the order is reversed by magnesium and beryllium, the relative solubilities being approximately

Be 55000; Mg 43; Ca 1; Sr 3·8; Ba 8.

Comparatively few of the beryllium salts have had their solubilities determined (only 7 out of the 24 in the table); their only noticeable departures from regularity are the high solubilities of the oxalate (already mentioned) and of the fluoride, which is nearly 3,000 times as soluble in water as magnesium fluoride.

The values of the hydration in the solid salts (Table III) are a measure of the tendency of the ions to co-ordinate with oxygen; with regard to beryllium it must be remembered that its covalency limit is 4, and that its salts have been much less thoroughly investigated than those of the other elements.

TABLE I. *Solubilities in G. or Mg(m.) Anhydrous Salt to 100 G. Water, at 20°±5° C. (Temp. 25° unless otherwise stated)*

	Be	Mg	Ca	Sr	Ba	Ra
$M(OH)_2$	0·055 m./18°	1·89 m./18°	0·131/18°	0·89/25°	4·18/25°	
MF_2	*ca.* 50/o.t.	12·0 m./18	2·53 m./18	11·7 m./18	0·209 g./18	
MCl_2	Large	54·1/20°	81·5/20°	55·5/20	37·2	24·5
MBr_2	Large	102·5	140·0	99·7	104·1/20°	70·6
MI_2	Large	140·0/20	204/20	179·6/20	205·3/20	
$M(N_3)_2$	..	..	44·9/15°	45·8/16°	17·4/17°	
MCO_3	..	1·13 m.	(0·62 m./39°)	0·59 m./18	0·86 m./18	
M Formate	..	8·1/o.t.	17·0	9·47/20	31·3/20°	
M Acetate	..	63·4/20°	34·7/20°	40·8/20	72·8/22°	
M Oxalate	33·1	0·030/18	0·80 m./18	4·16 m./18	11·2 m./18°	
M Malonate	..	..	0·371	0·524	0·227	
M Succinate	..	32·2/15°	1·25/25	0·382	0·406	
M Benzoate	..	6·36	3·11	5·4	4·5	
MSiF	..	61·0	10·6	..	0·025	
$M(NO_2)_2$	..	92·0	98·2/20	68·6/20	67·5/20	
$M(NO_3)_2$	108·4	75·1	121/18°	70·8/20	9·1/20	13·9/20°
MSO_3	..	0·65	0·167/15°	3·3 m./18	2·17 m./18°	
MSO_4	42·2	35·8/20	0·107	11·4 m./18°	0·222 m.	0·002 m.
$MSeO_4$	56·8	37·9	7·39	..	8·15 m./18°	
$MCrO_4$	..	72·4	2·28/20	0·096	0·319 m.	
MS_2O_6	..	52·9	27·9	14·8	20·9	
$M(ClO_3)_2$	..	146·9	194·5	174·9/18	33·8/20	
$M(BrO_3)_2$	..	48/ca. 18	ca. 90/18	31/15	0·652/20°	
$M(IO_3)_2$	—b	8·55	0·307	0·026/15°	0·0422	
$M(ClO_4)_2$	146·9	99·8	188·6	309·7	198·3	

TABLE II. *Solubilities in Moles of Salt to 100 Moles Water at the same Temperatures* (X^{-5} *stands for* $X \times 10^{-5}$)

	Be	Mg	Ca	Sr	Ba	Ra
$M(OH)_2$	2·31^{-5}	58·4^{-5}	3,170^{-5}	15,500^{-5}	49,000^{-5} (0·49)	
MF_2	10	346^{-5}	58·4^{-5}	168^{-5}	2,140^{-5} (0·02)	
MCl_2	Large	10·2	13·2	6·30	3·22	1·49
MBr_2	Large	10·0	12·6	7·25	6·31	3·30
MI_2	Large	9·06	12·5	9·48	9·45	
$M(N_3)_2$	..	..	6·51	4·80	1·14	
MCO_3	..	24·1^{-5}	11·1^{-5}	7·21^{-5}	7·85^{-5}	
M Formate	..	1·28	2·35	0·96	2·48	
M Acetate	..	8·02	3·95	3·56	5·13	
M Oxalate	6·14	480^{-5}	1·2^{-5}	42·6^{-5}	89·5^{-5}	
M Malonate	..	..	0·047	0·0498	0·0171	
M Succinate	..	4·13	0·144	0·0338	0·0288	
M Benzoate	..	0·430	0·198	0·295	0·214	
$MSiF_6$	..	6·61	1·05	..	161^{-5}	
$M(NO_2)_2$	..	14·2	13·4	6·87	5·30	
$M(NO_3)_2$	14·7	9·12	13·3	6·03	0·627	0·715
MSO_3	..	0·112	0·0250	35^{-5}	18^{-5}	
MSO_4	7·22	5·35	1,410^{-5}	112^{-5}	1·71^{-5}	0·0117^{-5}
$MSeO_4$	6·72	4·07	0·727	..	0·000523	
$MCrO_4$	..	9·29	0·263	0·0085	2·27^{-5}	
$M(ClO_3)_2$	..	13·83	17·4	12·36	2·00	
$M(BrO_3)_2$	..	2·8	5·5	1·6	0·029	
$M(IO_3)_2$	..	0·412	0·0142	107^{-5}	156^{-5}	
$M(ClO_4)_2$	12·7	8·05	14·21	19·46	10·61	

TABLE III. *Water of Crystallization of Salts*

	Be	Mg	Ca	Sr	Ba	Ra
$M(OH)_2$	0	0	0	8, 2, 1	8, 1	
MO_2	..	?	8	8	8	
MCl_2	4	12, 8, 6, 4	6, 4, 2, 1	6, 2, 1	2	2
MBr_2	4	10, 6, 4	6	6, 2	2, 1	2
MI_2	..	10, 8, 6	6	6, 2, 1	7·5, 2, 1	
MCO_3	4	5, 3, 1	6, 1	0	0	
M Formate	0	2	0	2	0	
M Acetate	..	4	2, 1	4, 1/2	3, 1	
M Oxalate	3	2	0	2·5, 1	3·5, 2, 0·5	
$M(NO_2)_2$	..	9, 6, 3	1	1	1	
$M(NO_3)_2$	4	9, 6, 2	4, 3, 2	4	0	
MSO_3	..	6, 3	2	0	0	
MSO_4	4, 2	12, 7, 6, 1	2, 0·5	0	0	
$MSeO_4$	4	7, 6, 2, 1	..	0	0	
$M(ClO_3)_2$	..	6, 4	2	? 3	1	
$M(BrO_3)_2$	..	6	1	1	1	
$M(IO_3)_2$	..	10, 4	6, 1	6, 1	1	
$M(ClO_4)_2$	4	6, 4, 3, 2	0	4, 2, 2/3	3, 1	
$M(IO_4)_2$	..	10	..	6	0	
Mean highest (and no. of salts)	3·4 (9)	7 (18)	3·0 (17)	3 8 (18)	2·3 (18)	2·0 (2)

MAGNESIUM

MAGNESIUM is one of the commonest elements in the earth's crust, of which it forms 2·1 per cent., and is very widely distributed, being found in the animal and vegetable kingdoms as well as in rocks, and also in the sea, which last contains on the average about 0·13 per cent., and from which it is extracted commercially.[170]

There has been much argument[171] as to whether magnesium has the properties of a member of Group II A (alkaline earth metals) or II B (zinc, cadmium, mercury); in fact of course it has resemblances to both. It is found in nature rather with the A elements than with the B. In its chemistry it shows analogies to both subgroups: in its power of complex formation it stands between the two, and seems to come nearer to B than to A, but this is a natural result of its small size, which gives it a deforming power that partly offsets the effect of the inert gas structure of the ion.

The ion Mg^{++} is that of a strong base, whose salts are relatively little hydrolysed, and when they are derived from strong acids have a neutral reaction. It has a distinct tendency to form complexes, as is shown by the numerous hydrated salts, and by the fall in the transport number as the concentration increases (e.g. for magnesium chloride 0·37 in a 0·05 equivalent normal solution and 0·29 in a normal solution).

Metallic Magnesium

Technically, magnesium is by far the most important metal of the subgroup. It is commonly made by the electrolysis of fused anhydrous magnesium chloride, obtained from carnallite ($MgCl_2$, KCl, 6 H_2O) or in other ways, at temperatures above the melting-point of magnesium, with a graphite anode and an iron cathode.

Metallic magnesium melts at 650° and boils at 1,100° C.[172] It is stable in cold dry air, but in moist air it is slowly oxidized; it burns with the familiar bright flame, whose brightness is partly due to the large evolution of heat (145·8 k.cals.[173]) and partly to the presence of the non-volatile oxide. It is said to give out 10 per cent. of the energy as visible radiation.

Magnesium has a potential to the normal hydrogen electrode of 1·31 volts; according to the Nernst equation it would be in equilibrium with hydrogen under a pressure of 10^{45} atmospheres. It reduces carbon monoxide, carbon dioxide, sulphur dioxide, nitric oxide, and nitrous oxide at a red heat, and combines directly with nitrogen, sulphur, the halogens, phosphorus, and arsenic; at 200° it reacts with methyl alcohol to give magnesium methylate $Mg(O \cdot CH_3)_2$.

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[170] The Dow Chemical Co. Inc. has built a 5-million dollar plant for the extraction of magnesium from sea-water at Freeport, Texas (*J. Ind. Eng. Chem.*, News Edn. 1940, **18**, 420).

[171] See, for example, P. Pfeiffer, *Z. angew. Chem.* 1924, **37**, 41.

[172] H. Hartmann and R. Schneider, *Z. anorg. Chem.* 1929, **180**, 282; W. Leitgebel, ib. 1931, **202**, 305.

[173] W. A. Roth and G. Becker, *Z. physikal. Chem.* 1932, **159**, 1.

Magnesium is of great value as a constituent of light alloys, such as magnalium, a magnesium-aluminium alloy with a density of 2·0 to 2·5, and Griesheim electron-metal (80 per cent. of magnesium with small amounts of aluminium, zinc, copper, and manganese) of density 1·8. Like magnesium itself, these alloys are all stable in air under a thin protective layer of oxide, but are not permanent under water.

Magnesium Hydride

The spectrum of magnesium vapour in hydrogen at low pressures gives bands which are due to a hydride MgH, and the spectrum of the corresponding deuteride MgD has also been obtained. But of the existence of a solid isolable hydride MgH_2 there is no satisfactory evidence.[174-5]

Magnesium and Carbon

Under this head are included the binary carbides of magnesium, and also the very large and important group of alkyl and aryl magnesium halides (the Grignard reagents) together with the magnesium dialkyls and diaryls.

There are two binary carbides of magnesium, which cannot be got pure enough for analysis, but from their behaviour must have the compositions MgC_2 and Mg_2C_3. Neither can be made by heating magnesium or its oxide with carbon to a high temperature, and both are thermodynamically unstable above 800°. They can only be made[176] by heating the metal with acetylene or other hydrocarbons. With acetylene magnesium begins to react at about 400° to form the carbide MgC_2, of which a maximum yield of some 30 per cent. is got at 500°. This carbide on treatment with water is at once decomposed into acetylene and magnesium hydroxide:

$$MgC_2 + 2\,H_2O = Mg(OH)_2 + C_2H_2,$$

and is no doubt the magnesium salt of acetylene $Mg[C{\equiv}C]$, corresponding to calcium carbide. Its spontaneous formation from

$$Br\cdot Mg{-}C{\equiv}C{-}Mg\cdot Br$$

is described later (II. 231).

The second carbide Mg_2C_3, which is of a unique type, is also formed from the metal and acetylene, but at a higher temperature (about 600°); it is, however, best made by heating the magnesium with methane or pentane instead of acetylene; the action begins about 700° and the temperature should not rise above 800°; in this reaction practically no MgC_2 is formed. These two carbides give quite different X-ray powder diagrams.[177] The second carbide, like the first, cannot be got pure enough for analysis; its composition is inferred from the fact that it reacts with water to give allylene (methyl acetylene):

$$Mg_2C_3 + 4\,H_2O = 2\,Mg(OH)_2 + CH_3{-}C{\equiv}C{-}H.$$

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[174] W. H. Zartmann and H. Adkins, *J.A.C.S.* 1932, **54**, 3398.

[175] H. Gilman, A. L. Jacoby, and H. Ludeman, *J.A.C.S.* 1938, **60**, 2336.

[176] J. Novak, *Z. physikal. Chem.* 1910, **73**, 513.

[177] H. H. Franck, M. A. Bredig, and Kin Hsing Kou, *Z. anorg. Chem.* 1937, **232**, 110.

The production of this hydrocarbon is very remarkable. The carbide itself must be supposed to be the salt of the symmetrical anion $[C{=}C{=}C]^{4-}$, and would be expected to give on hydrolysis not allylene $CH_3\cdot C{\equiv}C\cdot H$ but allene; there are, however, other indications that the interconversion of allylene and allene

$$CH_3\cdot C{\equiv}C\cdot H \rightleftharpoons H_2C{=}C{=}CH_2$$

is easy. The spectra show that the proportion of allene is 6 per cent. at 82° and 19 per cent. at 600°.[178-9] If sodium is heated with an ethereal solution of allene at 100° it is converted into a white powder which evolves allylene on treatment with water[180] and may be supposed to be or to contain the sodium salt $[CH_3\cdot C{\equiv}C]Na$.

Magnesium Alkyl and Aryl Compounds

This group includes the dialkyl and diaryl compounds, and also the mono-alkyl and aryl* halides, which are of great importance owing to their use in the multifarious Grignard syntheses; this latter class may be considered first.

Magnesium Alkyl and Aryl Halides

These compounds were discovered by Grignard in 1900[181]; they have since been the subject of innumerable investigations,† owing to their great value in organic synthesis. The results have been summarized in numerous monographs and elsewhere[182]; an admirable account on a rather smaller scale is given by Krause and v. Grosse.[183]

The magnesium alkyl and aryl halides (generally known as 'Grignard reagents') are easy to prepare and to use; they are formed by the action of metallic magnesium on the alkyl or aryl halide in ethereal solution:

$$Mg + R\cdot hal = R\cdot Mg\cdot hal.$$

---

* There is no very marked difference between the alkyl and aryl compounds; as no one has invented a term to cover both kinds of radicals, the word alkyl will be used here to include aryl as well unless the contrary is stated [or is obvious].

† In the first 8 years after their discovery more than 800 papers on the subject were published.

[178] D. A. Frank-Kamenetski and V. G. Markovitsch, *Acta. Phys.-Chem. U.R.S.S.* 1942, **17**, 308.

[179] Id. *J. Gen. Chem. Russ.* 1942, **12**, 619.

[180] G. Gustavson and N. I. Demjanoff, *J. prakt. Chem.* 1888, [2] **38**, 201.

[181] V. Grignard, *C.R.* 1900, **130**, 1322; 1901, **132**, 336, 558, 560; *Ann. Chim. Phys.* 1901, **24**, 437.

[182] For example, Julius Schmidt, *Ahrens Sammlung*, x (1905), xiii (1908); F. Runge, *Organische Magnesium-Verbindungen*, Stuttgart, 1932; W. Schlenk in Houben-Weyl's *Methoden d. organ. Chemie*, ed. **2**, Bd. iv. 777–895.

[183] E. Krause and A. v. Grosse, *Chemie d. Metall-organischen Verbindungen*, Berlin, 1937, pp. 14–59.

In this solution they are but slightly oxidized by the air, being to some extent protected by the layer of ether vapour over the liquid, so that as a rule it is not necessary to use an indifferent gas; the material must be dried with care, but ordinary care is sufficient.

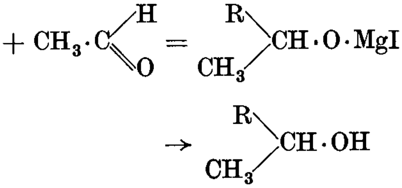
In most cases the original magnesium compound is not isolated, but the solution immediately used for the synthesis, the second organic component, usually dissolved in ether or benzene, being added as soon as the magnesium has gone into solution. The reactivity essentially depends on the fact that magnesium has a much weaker affinity for carbon than for oxygen, nitrogen, or the halogens, so that it very readily exchanges its hydrocarbon radical for one of the other elements. The number of reactions which the Grignard reagents can undergo is enormous[184]; the following are a few of the more important, classed under the element which replaces the carbon on the magnesium atom:

Oxygen

$$\mathrm{R\cdot Mg\cdot I} \quad + \mathrm{H_2O} = \mathrm{R\cdot H} + \mathrm{MgIOH}$$

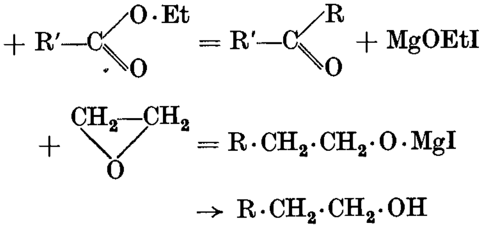
$$+ \mathrm{H_2CO} = \mathrm{R\cdot CH_2\cdot O\cdot MgI}$$

$$\rightarrow \mathrm{R\cdot CH_2OH}$$



$$+ \mathrm{CH_3\cdot C}{<}^{\mathrm{H}}_{\mathrm{O}} = {}^{\mathrm{R}}_{\mathrm{CH_3}}{>}\mathrm{CH\cdot O\cdot MgI} \rightarrow {}^{\mathrm{R}}_{\mathrm{CH_3}}{>}\mathrm{CH\cdot OH}$$

$$+ \mathrm{(CH_3)_2C{=}O} = \mathrm{R(CH_3)_2C\cdot OH}$$

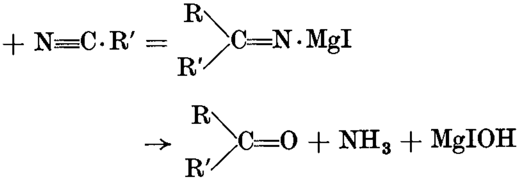


$$+ \mathrm{R'{-}C}{<}^{\mathrm{O\cdot Et}}_{\mathrm{O}} = \mathrm{R'{-}C}{<}^{\mathrm{R}}_{\mathrm{O}} + \mathrm{MgOEtI}$$

$$+ \mathrm{CH_2{-}CH_2}\ (\mathrm{O}) = \mathrm{R\cdot CH_2\cdot CH_2\cdot O\cdot MgI} \rightarrow \mathrm{R\cdot CH_2\cdot CH_2\cdot OH}$$

Nitrogen

$$\mathrm{R\cdot Mg\cdot I} + \mathrm{NH_3} = \mathrm{R\cdot H} + \mathrm{I\cdot Mg\cdot NH_2}$$



$$+ \mathrm{N{\equiv}C\cdot R'} = {}^{\mathrm{R}}_{\mathrm{R'}}{>}\mathrm{C{=}N\cdot MgI} \rightarrow {}^{\mathrm{R}}_{\mathrm{R'}}{>}\mathrm{C{=}O} + \mathrm{NH_3} + \mathrm{MgIOH}$$

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[184] For a full list see Krause and v. Grosse, pp. 47-59.

Halogens

$$\begin{aligned} \mathrm{R{\cdot}Mg{\cdot}I} + \mathrm{HCl} &= \mathrm{R{\cdot}H} + \mathrm{ClMgI} \\ + \mathrm{R'Br} &= \mathrm{R{-}R'} + \mathrm{BrMgI} \end{aligned}$$

The Grignard reagents can also be used to make the alkyl derivatives of many other metals, for example:

$$\mathrm{AuBr_3} + 2\,\mathrm{C_2H_5{\cdot}MgBr} = \mathrm{(C_2H_5)_2AuBr} + 2\,\mathrm{MgBr_2}.$$

Some further points in connexion with their preparation and reactions may be mentioned. They are usually prepared in solution in diethyl ether. Other ethers than diethyl ether can be used, especially when it is desirable to work at higher temperatures (di-isoamyl ether boils at 176°). It is theoretically interesting that tertiary amines such as dimethyl aniline or pyridine can be used as solvents in their preparation, and even the dialkyl ethers of sulphur selenium and tellurium.[185]

The rate of formation of the Grignard reagent increases with the atomic weight of the halogen in the order $\mathrm{F} \ll \mathrm{Cl} < \mathrm{Br} < \mathrm{I}$ (the heats of formation of the links to carbon are C—F 103·4; C—Cl 78·0; CBr 65·5; C—I 57·0 k.cals.). The fluorides will scarcely react with magnesium at all; Gilman has found[186] that phenyl fluoride must be left with magnesium in the cold for 18 months before it gives any test for phenyl magnesium fluoride $\Phi{\cdot}\mathrm{Mg{\cdot}F}$, and if the solution is boiled this is at once converted into magnesium difluoride and diphenyl: even after phenyl fluoride had been heated with magnesium in a sealed tube to 300° for 200 hours the amount of diphenyl formed was only small. The reactivity of the other halogens is of quite a different order.

Among the chlorides only the alkyl derivatives give satisfactory results; the aryls are very sluggish. The bromides are on the whole the most commonly used; the iodides are, in fact, often too reactive, and have a strong tendency to react further, with the production of the hydrocarbon, either directly[187]

$$\mathrm{Mg} + 2\,\mathrm{R{\cdot}I} = \mathrm{R{-}R} + \mathrm{MgI_2}$$

or by its action on the Grignard reagent already formed:

$$\mathrm{R{\cdot}I} + \mathrm{R{\cdot}Mg{\cdot}I} = \mathrm{R{-}R} + \mathrm{MgI_2}.$$

The rate of formation of the alkyl-halide compound from the metal depends on the precise conditions; the reaction is heterogeneous, and the stirring of the liquid and the state of the metallic surface have a great influence on the results. The influence of the surface is shown by the nature of the catalysts which are found to hasten the reaction. The most usual of these is a trace of iodine (bromine can also be used), which obviously serves to remove a layer of oxide from the surface; a previous treatment of the metal with a small quantity of a particularly active halide such as ethyl bromide often has the same effect.

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[185] H. Hepworth, *J.C.S.* 1921, **119**, 1249.

[186] H. Gilman and L. L. Heck, *J.A.C.S.* 1931, **53**, 377.

[187] G. O. Johnson and H. Adkins, ib. 1932, **54**, 1943.

The percentage yield of alkyl-magnesium halide obtainable under the best conditions has been determined for many of the halides by Gilman and his co-workers[188]; more recently Houben, Boedler, and Fischer[189] have examined the same question. Since the reaction with the metal is not reversible, the yield is really a measure of the absence of by-reactions, and in particular of the so-called Wurtz-Fittig reaction, the formation of the hydrocarbon R—R; unless air and moisture are completely excluded, there is an increasing tendency with the heavier alkyls for this reaction to interfere, as Grignard found.[178]

The rate of formation of the Grignard reagents has been examined (under conditions of stirring, etc., that were standardized as far as possible) by Gilman and his colleagues.[190] The effects of the nature of the halogen, and of the length and structure of the carbon chain in the alkyl, is shown by the following figures, which give the percentage yield formed in 45 seconds at 40°:

n—C_4H_9Cl	*n*—C_4H_9Br	*n*—C_4H_9I
5·9	59·1	47·2

n—C_3H_7Br	*n*—C_4H_9Br	*n*—$C_5H_{11}Br$	*n*—$C_6H_{13}Br$
58·0	59·1	51·1	44·3

n—C_4H_9Br	*iso*—C_4H_9Br	tert. C_4H_9Br
59·1	50·2	46·1

They also find that the rate of reaction is greater with the simpler alkyl halides than with the simpler aryl halides. The fall in the rate (shown above) on passing from the bromide to the chloride is surprising.

It has recently been shown that the Grignard reagents are present in the ethereal solution as equilibrium mixtures with the dialkyl magnesium and the dihalide:

$$2\,\mathrm{R\cdot Mg\cdot hal} \rightleftharpoons \mathrm{MgR_2} + \mathrm{Mg(hal)_2}.$$

This may for the present be disregarded; the mixed alkyl magnesium halides undoubtedly exist in solution and in the solid state, the solids in a solvated and an unsolvated form. In the solvated form—as etherates[191]—they usually have the composition $\mathrm{R\cdot Mg\cdot X}$, 2 Et_2O, though compounds with one and even with three molecules of ether to one magnesium atom are known. Examples are $\mathrm{Et\cdot Mg\cdot I}$, 2 Et_2O; $\mathrm{C_6H_5\cdot Mg\cdot Br}$, 2 Et_2O; α—$\mathrm{C_{10}H_7\cdot Mg\cdot Br}$, Et_2O. We have already seen that the ethyl ether can be replaced by other ethers, by their sulphur, selenium, and tellurium analogues, and by tertiary amines, including pyridine and quinoline, that

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[188] H. Gilman, *et al.*, ib. 1923, **45**, 159, 2462: H. Gilman and R. McCracken, *Rec. Trav.* 1927, **46**, 463: H. Gilman and E. A. Zoellner, *J.A.C.S.* 1928, **50**, 425; *Rec. Trav.* 1928, **47**, 1058; E. A. Zoellner, *Iowa State Coll. J. Sci.* 1934, **9**, 213: H. Gilman, E. A. Zoellner, W. M. Selby, and C. Boatner, *Rec. Trav.* 1935, **54**, 584.

[189] J. Houben, J. Boedler, and W. Fischer, *Ber.* 1936, **69**, 1766.

[190] H. Gilman, E. A. Zoellner, J. B. Dickey, and W. M. Selby, *J.A.C.S.* 1935, **57**, 1061.

[191] W. Schlenk and W. Schlenk Jr., *Ber.* 1929, **62**, 921.

is. by other donor solvents. The etherates are often low melting and very soluble in ether, and some of them when concentrated form two liquid layers with the solvent.

It has been said that the etherates are dimeric in solution, but the very careful measurements by Meisenheimer[192] of boiling-points in ether show that the association is not large, and varies continuously with the concentration, the association factor being about 1·5 in 2—4 per cent. solution, and rising to 2 at about 10 per cent. As ether is an associating solvent, this behaviour is not surprising, and it is compatible with the minute ionization (much less than 1 per cent.) required by the conductivity (see below).

The non-solvated form of the alkyl magnesium halides can be made by driving off ether from the etherates, and also by preparing the compounds in the absence of a donor solvent such as ether. Tschelinzeff has shown[193] that magnesium will react with organic halides in solvents such as benzene, toluene, and ligroin. The yields obtained with a benzene solution have been determined by Schlenk[191] with rather remarkable results. He finds the following percentage yields after two months' shaking of the metal with a benzene solution of the alkyl iodide:

R.I : R = CH_3	Et	Pr	*n*—Bu	*n*—Hept	*n*—Oct
% yield 0	11	1	96	3	96

This curious alternation in the size of the yields, which are much greater when the alkyl contains an even number of carbon atoms, is obviously related to the solubilities of the products, Alk·Mg·hal, which are relatively insoluble in the benzene, and separate in voluminous white flocks. The alkyl-halide is also formed in the absence of any solvent, but very slowly, and the product must be continuously removed by stirring or other mechanical means from the surface of the metal.[194] Aryl halides practically do not react at all with magnesium in the cold if no solvent is used, except on heating.[195]

These compounds are not volatile in a vacuum but, curiously, can be distilled in a stream of ether vapour, which suggests that the etherate must be somewhat volatile.[196] They are remarkably stable to heat: ethyl magnesium bromide only suffers about 14 per cent. decomposition in an hour at 300°.[197] They combine with ether with great readiness, and a considerable evolution of heat; the heat effect of increasing quantities of ether shows that two molecules are taken up[198]:

n—C_3H_7MgI +	1 Et_2O	2 Et_2O	3 Et_2O
Heat in k.cals:	6·63	12·30	12·80

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[192] J. Moisenheimer and W. Schlichenmaier, *Ber.* 1928, **61**, 720.

[193] W. Tschelintzeff, ib. 1904, **37** 4534: 1905, **38**, 3664; 1906, **39**, 773, 1674, 1682, 1686; 1907, **40**, 1487; *C.R.* 1907, **144**, 88.

[194] W. Schlenk Jr., *Ber.* 1931, **64**, 739.

[195] P. Schorigin *et al.*, ib. 1931, **64**, 2584.

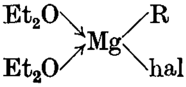
[196] H. Gilman and R. E. Brown, *J.A.C.S.* 1930, **52**, 4480.

[197] H. Gilman and J. M. Peterson, *Rec. Trav.* 1929, **48**, 247.

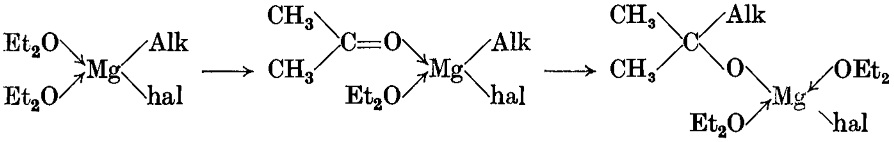
[198] I. Lifschitz and O. E. Kalberer, *Z. physikal. Chem.* 1922, **102**, 393.

The relative ease of reaction of a particular Grignard reagent in a variety of syntheses has been examined by Entemann and Johnson[199] and that of various Grignard reagents with benzonitrile by Gilman *et al.*[200]

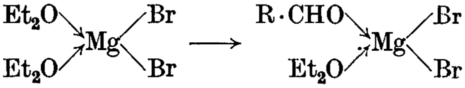
To explain the structure of these etherates various suggestions, some very improbable, have been put forward; but the true solution is now clear; it was first advanced by Meisenheimer in 1921.[201] The two ether molecules co-ordinate through the oxygen with the magnesium atom of the covalent alkyl-halide molecule, completing its octet, and giving, for example,



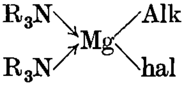
The Grignard synthesis, for instance with acetone, is then simply explained. The ketone first replaces one of the ether molecules (doubly linked oxygen is normally a more active donor than singly linked), and the alkyl group then migrates to the carbonyl carbon, its place being taken by another ether molecule:



This view is supported by the observation[202] that magnesium bromide and iodide crystallizes with two molecules of ether, and that the product when treated with an aldehyde has one molecule of ether replaced by a molecule of the aldehyde:



The tertiary amines which can be used in the Grignard reaction in the place of ether must form similar compounds



There is no reason to doubt the covalent structure of these molecules in the solid state, and for the most part in solution; but in their solutions, either in ether or in a mixture of ether and benzene, they give indications of the presence of ions, and behave to some extent as electrolytes. The solutions have been shown to have measurable conductivities[203-4] and

[199] C. E. Entemann and J. R. Johnson, *J.A.C.S.* 1933, **55**, 2900.

[200] H. Gilman, E. L. and N. B. St. John, and M. Lichtenwalter, *Rec. Trav.* 1936, **55**, 577–590.

[201] J. Meisenheimer and J. Casper, *Ber.* 1921, **54**, 1655.

[202] F. B. Ahrens and A. Stapler, ib. 1905, **38**, 3265.

[203] W. V. Evans and F. H. Lee, *J.A.C.S.* 1933, **55**, 1474.

[204] Id., ib. 1934, **56**, 654.

decomposition potentials,[205-6] and on electrolysis they break up into the metal and an equimolecular mixture of paraffin and olefine (for example, $Et\cdot Mg\cdot Br$ gives $Mg+C_2H_6+C_2H_4$), in the quantities required by Faraday's law.[207-9] These facts make it clear that the solute is to some extent ionized, but the value of the conductivity shows that the extent must be very small: the specific conductivity of a normal solution of ethyl magnesium bromide in ether at 20°[203,210] is only $6{\cdot}14\times 10^{-5}$, which is about a thousandth of that of an aqueous solution of potassium chloride at the same dilution, in spite of the fluidity of ether being nearly 4 times (3·82 times) that of water. It is to be presumed that the ions are $[R\cdot Mg]^+$ and $[Br]^-$, no doubt to some extent solvated. Since the solution contains magnesium dialkyl and magnesium dihalide as well as alkyl magnesium halide, it might be supposed that the ionized molecule was the dihalide, but it is found[203] that a normal solution of ethyl magnesium bromide in ether at 20° conducts more than 3 times as well as one of magnesium dibromide. Now the normal ethyl magnesium bromide solution is known to contain 0·4 normal ethyl magnesium bromide, 0·3 normal magnesium diethyl (which presumably does not conduct), and 0·3 normal magnesium bromide; if the dissociation of the magnesium bromide is the same here as in a normal solution, the specific conductivity of ethyl magnesium bromide must be some 7 times as great as that of magnesium dibromide.

Where a hydrocarbon has a peculiarly active or acidic hydrogen atom (like acetylene and cyclopentadiene and their derivatives), the magnesium compound can be made by the action of the hydrocarbon itself on an alkyl magnesium halide; thus if acetylene is passed into a solution of ethyl magnesium bromide[211] the reaction

$$2\,EtMgBr + HC{\equiv}CH = 2\,C_2H_6 + Br\cdot Mg\cdot C{\equiv}C\cdot Mg\cdot Br$$

takes place. This acetylene derivative, and the corresponding iodide, behave in a very remarkable way.[212] When first prepared the compound separates as a viscous oil, which is quite free from ether; this has the usual reactions of the Grignard reagents with all kind of organic and inorganic substances. But on standing for several weeks this oil changes into a solid crystalline mass, which does not melt below a very high temperature, and has lost all its reactivity except with water, with which it regenerates acetylene, showing that the $C{\equiv}C$ group has not been fundamentally altered. This change occurs in a few hours in solution in bromobenzene or allyl bromide, and in a few minutes on warming to 50°.

[205] W. V. Evans, F. H. Lee, and C. H. Lee, *J.A.C.S.* 1935, **57**, 489.
[206] W. V. Evans, R. Pearson, and D. Braithwaite, ib. 1941, **63**, 2574.
[207] L. W. Gaddum and H. E. French, ib. 1927, **49**, 1295.
[208] W. V. Evans and D. Braithwaite, ib. 1939, **61**, 898.
[209] W. V. Evans, D. Braithwaite, and E. Field, ib. 1940, **62**, 534.
[210] N. V. Kondyrev. and A. K. Ssusi, *Ber.* 1929, **62**, 1856.
[211] A. Wohl and B. Mydo, ib. 1922, **55**, 322.
[212] H. Kleinfeller, ib. 1929, **62**, 2736.

It is evident that the same disproportionation has taken place here as occurs with the alkyl magnesium halides:

$$Br \cdot Mg—C \equiv C—Mg \cdot Br \longrightarrow MgBr_2 + MgC_2:$$

but that what corresponds to the dialkyl is here the carbide, which goes over, as we should expect, into the ionized form, and so loses the reactivity, which depends on the presence of the metal-carbon link. In solution the disproportionation leads to an equilibrium, but in this case, where the products are solid, the reaction necessarily proceeds to completion. It is evident that the original viscous liquid contained a substance in which the acetylene carbons were covalently linked to magnesium, but why this compound does not form an etherate, like all others with this link, has not been explained. Cyclopentadiene, indene, and fluorene will displace the ethyl group from the Grignard reagent in the same way as acetylene.[213]

According to Gilman and Kirby[214] alkyl magnesium bromides can add on to compounds with conjugated double links either in the 1, 2 or in the 1, 4 positions.

A property of these Grignard solutions which is of great practical importance is their reaction with atmospheric oxygen. While they are by no means so sensitive to air as the zinc alkyls, and do not as a rule require their reactions to be carried out in an indifferent atmosphere, the Grignard reagents are slowly oxidized by air, mainly to alcohols and phenols, probably with the intermediate production of peroxides[215-17] (see later under zinc alkyls, II. 266):

$$R \cdot Mg \cdot Br + \tfrac{1}{2} O_2 = R \cdot O \cdot Mg \cdot Br \longrightarrow R \cdot OH.$$

The layer of ether vapour usually protects the solution from this reaction, but it has been pointed out[218] that at 0° or below this vapour is much less effective, and serious losses through oxidation may occur. It was found that one sample in ethereal solution was completely oxidized at room temperature in an hour, and at 0°, with slow stirring, in 3-8 minutes.

The oxidation is accompanied by a faint chemi-luminescence[219-21]; the heat of oxidation is about 60 k.cals.

A delicate colour test for the Grignard reagents in solution was found by Gilman[222-5] using Michler's ketone.

[213] C. Courtot, *Ann. Chim.* 1915, [9] **4**, 58.
[214] H. Gilman and R. H. Kirby, *J.A.C.S.* 1941, **63**, 2046.
[215] J. Meisenheimer, *Ber.* 1928, **61**, 708.
[216] C. W. Porter and C. Steel, *J.A.C.S.* 1920, **42**, 2650.
[217] H. Wuyts, *C.R.* 1909, **148**, 930.
[218] M. T. Goebel and C. S. Marvel, *J.A.C.S.* 1933, **55**, 1693.
[219] J. Schmidlin, *Ber.* 1912, **45**, 3172.
[220] R. T. Dufford, *J.A.C.S.* 1928, **50**, 1822.
[221] I. Lifschitz and O. E. Kalberer, *Z. physikal. Chem.* 1922, **102**, 393.
[222] H. Gilman and F. Schulze, *J.A.C.S.* 1925, **47**, 2002.
[223] Id.; *Bull. Soc. Chim.* 1927, [iv] **41**, 1479.
[224] H. Gilman and L. L. Heck, *Rec. Trav.* 1929, **48**, 193.
[225] H. Gilman and R. G. Jones, *J.A.C.S.* 1940, **62**, 1243.

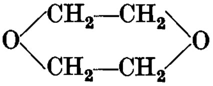
Equilibrium of Dialkyls and Alkyl-halides

The equilibrium

$$2\,\mathrm{R{\cdot}Mg{\cdot}hal} \rightleftharpoons \mathrm{MgR_2} + \mathrm{Mg(hal)_2}$$

was first suggested by Quelet[228] and investigated by the Schlenks[226-7]; it has since been confirmed in other ways by Cope.[226]

The Schlenks showed that dioxane



in solution gives insoluble addition products not only with magnesium dihalides, but also with alkyl magnesium halides. If a solution of a Grignard reagent is treated with dioxane, the whole of the halogen is precipitated in these two forms, but a certain amount of magnesium remains in solution as the dialkyl. That the dioxane causes no fundamental change, but merely replaces the ether as a co-ordinated molecule, is shown by the fact that the precipitated R·Mg·hal product still gives all the usual Grignard reactions.

Thus by precipitating with dioxane, filtering and analysing the filtrate, we can ascertain the proportions of the dialkyl, the alkyl-halide, and the dihalide, in the solutions.

The Schlenks were able to show (1) that both the mono- and the dialkyl derivatives are able to give the characteristic synthetic reactions. Thus a solution of phenyl magnesium bromide reacts with benzophenone to give the derivative of diphenyl magnesium $\Phi_3C{-}O{-}Mg{-}O{-}C\Phi_3$, while with fluorenone it gives the mono-phenyl magnesium derivative $R{-}O{-}Mg{\cdot}Br$. (2) The disproportionation is not an instantaneous reaction, but may need some hours at the ordinary temperature to reach equilibrium. (3) The proportions at equilibrium are not affected by a change in concentration in the ratio of 10 to 1, from which it follows that the alkyl halide compound must be monomeric ($R{\cdot}Mg{\cdot}X$) and not dimeric (as in MgR_2, MgX_2). (4) The effect on the proportions of the nature of the halogen and also of the hydrocarbon radical were examined by Schlenk[227] and also by Johnson and Adkins[230]; their more important results are given in the following table, which states the molecular percentage of dialkyl magnesium MgR_2 present in the solution.

Percentages of MgR_2 *at equilibrium at* 20°

R	R·Mg·Cl	R·Mg·Br	R·Mg·I
CH_3	..	..	6·5
Et	42·5	29·5	28·5
Pr	41·5	38	38
Bu	46	45	43
Ter. Bu	39	28	..
Phenyl	..	35	31

Apart from the methyl compound the variations are not large.

The question has been further examined by Cope,[231] who confirms the previous conclusions in general, and extends them by showing that the percentage of dialkyl magnesium at equilibrium is greater at higher temperatures, and is less in butyl than in ethyl ether.

Magnesium Dialkyls and Diaryls

Magnesium diethyl $Mg(C_2H_5)_2$ was obtained in 1866 by Wanklyn, who made it from zinc ethyl through the sodium and mercury compounds, and again by Lohr (1891) and Fleck (1893), who also prepared the diphenyl compound; but their products were impure. The pure diethyl and diphenyl compounds were made by W. Schlenk Jr.,[227] by the action of the metal on a solution of mercury diethyl or diphenyl in ether.

Magnesium diethyl is thus obtained as a mono-etherate $MgEt_2, Et_2O$, which is solid at 0° but liquid at the ordinary temperature. It is spontaneously inflammable in air, and reacts explosively with water.

The etherates lose their ether on heating *in vacuo*, leaving the dialkyl compounds $Mg(alk)_2$.

A whole series of these dialkyls (methyl, ethyl, propyl, butyl) have been made in the ether-free state; they are all white substances and scarcely volatile even in a vacuum, so that they are presumably much more highly polymerized than the beryllium alkyls. The methyl compound is, however, perceptibly volatile, and if methyl magnesium chloride is heated to 190° under 0·2 mm. pressure, dimethyl magnesium sublimes away[232]; the higher homologues seem to be quite non-volatile.[233-4] They are insoluble in all ordinary solvents other than ether, and, like the Grignard reagents themselves, are remarkably stable to heat; they can be heated without decomposition to temperatures from 200° to 250°; but they are extraordinarily reactive, and so readily oxidized that they catch fire even in carbon dioxide: they can be used only in an atmosphere of dry nitrogen or hydrogen. They are violently decomposed by water, alcohols, and ammonia, with liberation of the hydrocarbon R·H; with halogens they give first the alkyl magnesium halide

$$MgR_2 + X_2 = R \cdot Mg \cdot X + R \cdot X,$$

and then magnesium dihalide. They form etherates which usually have low melting-points (much lower than many of the etherates of the alkyl-halides) and are excessively soluble in ether: even the methyl compound $Mg(CH_3)_2$ gives a 16 per cent. solution in cold ether.

Magnesium diphenyl can be made by the action of magnesium on a

[226] W. Schlenk and W. Schlenk Jr., *Ber.* 1929, **62**, 920.
[227] W. Schlenk Jr., ib. 1931, **64**, 734, 736.
[228] R. Quelet, *Bull. Soc. Chim.* 1927, [iv] **41**, 933.
[229] A. C. Cope, *J.A.C.S.* 1934, **56**, 1578.
[230] G. O. Johnson and H. Adkins, ib. 1932, **54**, 1943.
[231] A. C. Cope, ib. 1935, **57**, 2238.
[232] H. Gilman and R. E. Brown, *Rec. Trav.* 1929, **48**, 1133.
[233] Id., ib. 1930, **49**, 724.
[234] Id., *J.A.C.S.* 1930, **52**, 5045.

solution of mercury diphenyl in ether at the ordinary temperature,[227] or in the absence of a solvent at 200°,[235] in an atmosphere of dry nitrogen. In the non-solvated state it is a colourless substance which on heating does not decompose until 280°, where it dissociates into magnesium and diphenyl. It is extremely reactive; it catches fire in moist though not in dry air, and is violently decomposed by water.

Magnesium and Nitrogen

Magnesium (like lithium and beryllium) combines very readily with nitrogen; it begins to absorb it at about 300°, forming its only nitride (other than the azide $Mg[N_3]_2$) Mg_3N_2, the dissociation tension of which is only 2-3 mm. at 670-727° and 67 mm. at 1,040°.[236] If magnesium is heated in air, it combines with the nitrogen as well as the oxygen; the oxygen is much more rapidly absorbed, but with a limited supply of air a good deal of nitride is formed; it can also be made by heating magnesium or a mixture of magnesium oxide and carbon in nitrogen or ammonia. The purest nitride (practically 100 per cent.) is made by heating pure magnesium in pure nitrogen for 4–5 hours at 800-850°.[237]

Mg_3N_2 is a colourless crystalline compound, and like the phosphide Mg_3P_2 has the crystal lattice of a third-group oxide of the C type (such as C—Sm_2O_3).[238-9] It burns to the oxide if it is heated in air, and is very readily decomposed by water to give the hydroxide $Mg(OH)_2$ and ammonia.

The phosphide, arsenide, antimonide, and bismuthide, all the type Mg_3X_2, are similar; but it has been shown[238] that while the phosphide and arsenide, like the nitride, have the crystal structure of a C-sesquioxide, the antimonide and bismuthide have the lattice of an A-sesquioxide such as A—Sm_2O_3.

Magnesium Diamide, $Mg(NH_2)_2$

The (usually impure) diamide can be made by the action of ammonia on magnesium activated with iodine at 350–400°[240]; very slowly from the pale blue solution of magnesium in liquid ammonia on standing; by heating magnesium with sodamide or potassamide, when the alkali metal separates[241]; or by the action of ammonia on an ethereal solution of magnesium diethyl.[242] The last method seems to give the purest and most active form; this is a white powder which decomposes on heating, catches fire in air, and reacts violently with water evolving ammonia. At a red heat it is converted into the nitride Mg_3N_2 and ammonia:

$$3\,Mg(NH_2)_2 = Mg_3N_2 + 4\,NH_3$$

[235] H. Gilman and R. E. Brown, *Rec. Trav.* 1930, **49**, 202.

[236] P. Laffitte, E. Elchardus, and P. Grandadam, *Rev. Ind. Min.* 1936, 861 (*B.C.A.* 1939, i. 90).

[237] B. Neuman, C. Kröger, and H. Kunz, *Z. anorg. Chem.* 1932, **207**, 139.

[238] E. Zintl and E. Husemann, *Z. physikal. Chem.* 1933, B **21**, 138.

[239] M. v. Stackelberg and R. Paulus, ib. 1933, B **22**, 305.

[240] A. P. Terentiew, *Z. anorg. Chem.* 1927, **162**, 351.

[241] F. W. Bergstrom, *J.A.C.S.* 1923, **45**, 2789; 1926, **48**, 2852.

[242] W. Schlenk Jr., *Ber.* 1931, **64**, 736.

It reacts with pyrrol at 100°, expelling ammonia and forming magnesium pyrrol.[240]

Substituted diamides can also be made; thus aniline acts on activated magnesium, or on magnesium diethyl, to give a colourless compound which decomposes on heating, and is no doubt the dianilide

$$\mathrm{Mg(NH\cdot C_6H_5)_2}.$$[240-1]

Magnesium Oxide

A suboxide Mg_2O has been described, but it is very unlikely that it exists.[243-4]

Magnesium oxide MgO can be made by the oxidation of the metal, or by heating any easily decomposed oxy-compound of magnesium, such as the hydroxide or oxalate, or particularly the carbonate. It has a sodium chloride lattice,[245] like the monoxides of calcium strontium and barium, but unlike that of beryllium, showing that it is ionized in the solid state. It is very stable to heat; it melts at 2,800°, and its dissociation tension as calculated by the Nernst equation, is 230 mm. at 2,700°. It readily absorbs moisture and carbon dioxide from the air, to form the hydroxide $Mg(OH)_2$ and the carbonate $MgCO_3$.

Its reactivity and its energy content (as determined by its heat of solution in hydrochloric acid) vary considerably with the method of preparation, being smaller the higher the temperature to which it has been exposed; this change is not accompanied by any change in the X-ray diagram, and is due to an increase in particle size.[246-7]

Magnesium Hydroxide, $Mg(OH)_2$

This occurs in nature as the mineral brucite; it can be made by the action of water on the oxide or of alkalies on a solution of a magnesium salt. It is a stable compound and does not lose its water readily (though more easily than the hydroxides of the alkaline earths*); at 300° the dissociation tension of water is only 10 mm. It is very slightly soluble in water; at the ordinary temperature the saturated solution is about 3×10^{-4} normal (19 mg. per litre at 18°); it is a strong electrolyte. X-ray photographs indicate that there are no solid phases other than MgO and $Mg(OH)_2$.[246]

Magnesium Peroxide

Magnesium like beryllium oxide has no tendency to combine with elementary oxygen, but by treating it with hydrogen peroxide solids can be produced which appear to contain a hydrated peroxide (or perhaps a peroxidated oxide); their composition varies according to the method of

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* See below, p. 248.

[243] Cl. Winkler, ib. 1890, **23**, 122.

[244] H. G. Grimm and K. F. Herzfeld, *Z. Phys.* 1923, **19**, 156.

[245] R. W. G. Wyckoff, *Amer. J. Sci.* 1921, [v] **1**, 138.

[246] G. F. Hüttig and W. Frankenstein, *Z. anorg. Chem.* 1930, **185**, 403.

[247] K. Taylor and L. S. Wells, *J. Res. Nat. Bur. Stand.* 1938, **21**, 133.

preparation. Ruff and Geisel find[248] that the most highly oxidized material is that which is freshly precipitated by sodium hydroxide from magnesium sulphate solution in presence of hydrogen peroxide; if this is analysed while still moist it has the composition MgO, MgO_2, aq. If it is dried at the ordinary temperature it loses part of its oxygen, and after three weeks has the composition MgO_2, 3 MgO, aq.

Magnesium and Sulphur

MgS, the only solid sulphide of magnesium, can be made by the action of sulphur vapour on the metal above 600°, or on a mixture of magnesium oxide and carbon: or by igniting the oxide or better the sulphate $MgSO_4$ in the vapour of carbon bisulphide, mixed with nitrogen, at 700-900°.[249]

It is a colourless crystalline substance with a sodium chloride lattice[250]; it melts above 2,000°.[251] It is rapidly decomposed by water to a mixture of the hydrosulphide $Mg(SH)_2$, which is only known in solution, and the hydroxide. If the solution is boiled, the hydrolysis is complete: the sulphur is expelled as hydrogen sulphide, and only magnesium hydroxide remains.

Magnesium selenide is similar, and also has the sodium chloride lattice.[253]

Magnesium telluride is again similar; it is formed from its elements at a red heat, with an almost explosive evolution of energy. Unlike magnesium oxide, sulphide, and selenide, it has a zinc blende lattice,[252-3] showing that it forms a giant molecule of the covalent type. This is due to the larger telluride anion being more deformable.

Magnesium Halides

The magnesium derivatives of acids, including the halogen hydrides, are nearly all salts, and their properties are essentially those of the ions, so that as a rule there is little to say about them apart from their hydration and their solubility.

The 'subhalides' MgX can be shown to occur with every halogen in the gaseous state, and to give a characteristic band spectrum, but in no case is there any satisfactory evidence of their occurring in any other state.

Magnesium Fluoride, MgF_2

Dry hydrogen fluoride does not act on the metal, but the fluoride can easily be made from the aqueous acid. It has a rutile lattice with and Mg—F distance of 2·05 A.U. (calculated for the ionic link 2·11, for the covalent 2·00 A.) It melts at 1,260°. It is distinguished from the other halides by its very slight solubility in water and acids; at 18°, 100 g. of water will dissolve 12 mg.[254]

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[248] O. Ruff and E. Geisel, *Ber.* 1904, **37**, 3683.

[249] E. Tiede and F. Richter, ib. 1922, **55**, 69.

[250] S. Holgersson, *Z. anorg. Chem.* 1923, **126**, 179.

[251] E. Tiede and A. Schleede, *Ber.* 1920, **53**, 1721.

[252] W. H. Zachariasen, *Z. physikal. Chem.* 1927, **128**, 417.

[253] V. M. Goldschmidt, *Trans. Far. Soc.* 1929, **25**, 277.

[254] Landholt-Börnstein, 1923, p. 1184.

Magnesium Chloride, $MgCl_2$

The anhydrous salt can be made from its elements, or by passing a mixture of chlorine and carbon monoxide over magnesium oxide at 750°.[255] The dehydration of the hydrated chloride is best effected by heating the double salt $NH_4Cl, MgCl_2, 6\,H_2O$. Anhydrous magnesium chloride melts at 715° (550° lower than the fluoride) and has a vapour pressure of 25 mm. at 1,000°; its extrapolated boiling-point is 1,410°, and it can be distilled in a current of hydrogen.

It is very soluble in water, and gives hydrates with 12, 8, 6, and 4 H_2O; the hexahydrate is the most stable, its range being from $-3{\cdot}4°$ to 116·7°. Sol^y 54·1/20°.

Various basic chlorides or oxychlorides are known, though no very definite individuals have been isolated.[256] They are much used for making cements and 'artificial marble'. Thus 'Soret Cement' is made by adding two parts of ignited magnesium oxide to a concentrated solution of 1 part magnesium chloride; the whole sets on stirring to a solid mass.

Magnesium Bromide, $MgBr_2$

This is very similar to the chloride. It melts at 700°. It is extraordinarily hygroscopic: its cryohydric point is $-42{\cdot}7°$, and it forms hydrates with 10·6, and 4 H_2O[257-8]. Sol^y 102·5/25°. The salt is also readily soluble in a variety of oxygenated organic solvents (alcohols, ketones, ethers), with many of which it forms solid addition compounds such as $MgBr_2(C_2H_5OH)_6$.

Magnesium Iodide, MgI_2

The pure salt is best made by treating magnesium with excess of iodine vapour at 600°, and removing the excess by sublimation.[259] It forms hydrates with 10, 8, and 6 molecules of water. The decahydrate has the sol^y 140/20°.

Magnesium iodide is even more soluble than the bromide in various oxygenated organic solvents (alcohols, acids, amides, ethers, ketones, etc.). It forms two liquid layers with ether (critical solution temperature 38°) and with acetone.

Oxy-salts of Carbon

Magnesium carbonate occurs as the mineral magnesite. It can be precipitated from a solution of a magnesium salt with alkaline carbonate, but unless there is excess of carbon dioxide, a basic carbonate is liable to separate.

Magnesium carbonate is more readily dissociated by heat than any of the alkaline earth carbonates, though less than the beryllium salt (see

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[255] W. D. Treadwell, A. Cohen, and T. Zürrer, *Helv. Chim. Acta*, 1939, **22**, 449.

[256] W. Feitknecht and F. Held, ib. 1944, **27**, 1480.

[257] F. H. Getman, *Rec. Trav.* 1935, **54**, 866. [258] Id., ib. 1938, **57**, 847.

[259] W. Biltz and G. F. Hüttig, *Z. anorg. Chem.* 1921, **119**, 117.

below, II. 253). Its solubility in water is very small (11·3 mg./25°),[260] but it forms hydrates with 5, 3, and 1 H_2O. It is more soluble in presence of carbon dioxide, owing to the formation of an acid carbonate $Mg(CO_3H)_2$.

Dolomite, the natural carbonate of magnesium and calcium, was formerly regarded as a solid solution or isomorphous mixture; but this cannot be so as it always has approximately the composition $MgCO_3$, $CaCO_3$, and is not isomorphous with either of its components. It is formed from its components at any temperature above $-34°$ with a loss of free energy.[260]

Magnesium alkylates, $Mg(O \cdot Alk)_2$, can be made by the action of magnesium amalgam, or of magnesium activated by iodine, on the alcohol[261]; an example is $Mg(O \cdot C_2H_5)_2$, which is a white powder soluble in alcohol, and no doubt is a salt.

Magnesium cyanide, $Mg(CN)_2$, cannot be obtained directly from water since it is hydrolysed, but if a concentrated solution of a salt such as magnesium nitrate is treated with prussic acid in the presence of ammonia, an ammine $Mg(NH_3)_2(CN)_2$ separates out, and if this is heated *in vacuo* it gives the cyanide $Mg(CN)_2$.

The compound is not very stable, even in the absence of water; above 200° it is converted into magnesium cyanamide $Mg[N{-}C{\equiv}N]$.

Magnesium formate, $Mg[O \cdot CHO]_2$, $2\,H_2O$, can be hydrated at 110°. Sol^{y} 8·1/15°; it is less soluble in alcohol.

Magnesium acetate. This forms a tetrahydrate melting at 65°; sol^{y} 63·4/20°. The anhydrous salt is best made by heating the nitrate

$$Mg(NO_3)_2,\ 6\,H_2O$$

with acetic anhydride, washing the precipitate with ether, and drying at 60°; it melts at 323°.[262]

There are strong reasons for thinking that magnesium acetate forms auto-complexes both in solution and in the solid state. The solid takes a very long time to dry, retaining acetic acid obstinately, and apparently in combination. Rivett has shown[263-4] that the concentrated aqueous solution has an enormous viscosity, 155 times that of water when the salt is 5·4 molar; neither magnesium chloride nor sodium acetate behaves in this way. The lowering of the freezing-point of a 2-molar magnesium acetate solution is only one-third of that of a 2-molar magnesium chloride solution; measurements of the vapour pressure by a dew-point method confirmed this.[266] The conductivity of the solution has a maximum at 1-normal; that of the chloride has a maximum at 2·5 normal, where it is 5 times as great as the maximum of the acetate. These effects fall off rapidly on

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[260] F. Halla and F. Ritter, *Z. physikal. Chem.* 1935, **175**, 63.

[261] V. Cerchez, *Bull. Soc. Chim.* 1928, [iv] **43**, 762.

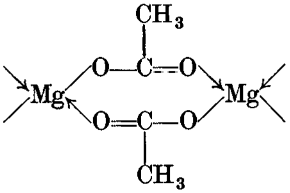
[262] E. Späth, *Mon.* 1912, **33**, 240. [263] A. C. D. Rivett, *J.C.S.* 1926, 1063.

[264] E. A. Goode, N. S. Bayliss, and A. C. D. Rivett, ib. 1928, 1950.

[265] R. Scholder, *Ber.* 1927, **60**, 1510.

[266] F. Kohlrausch and F. Mylius, *Sitz.-ber. Berl. Acad.* 1904, 1223; F. Kohlrausch, *Z. physikal. Chem.* 1908, **64**, 164.

dilution. This behaviour certainly points to some kind of auto-complex formation, and Rivett suggests that polymerization occurs through the formation of chains of chelate rings of the type



Magnesium oxalate is reasonably stable. It forms a dihydrate

$$MgC_2O_4, 2\,H_2O$$

which, like the oxalates of nearly all divalent metals except beryllium, is extremely insoluble in water, sol^y 0·03/18°. There is evidence of auto-complex formation in the solution.[265] The salt (like other salts with polyvalent cations and polyvalent anions) shows a remarkable power of supersaturation: magnesium oxide will dissolve in a solution of oxalic acid up to 300 times its saturation concentration without any solid salt separating.[266]

Oxy-salts of Nitrogen

Magnesium Nitrite

This forms hydrates with 9, 6, and 3 H_2O; sol^y (of the hexahydrate) 92/25°. The solution is not much hydrolysed in the cold (beryllium nitrite (II. 206) is too highly hydrolysed to be prepared); but at 60° and above it evolves oxides of nitrogen.

Magnesium Nitrate, $Mg(NO_3)_2$

This is a very stable salt; it forms hydrates with 9, 6, and 2 H_2O, the last two congruent (m. pts. 6 aq. 90°; 2 aq. 131°); above 130° it is anhydrous. Sol^y (of 6 aq.) 75·1/25°. The hydrates lose water on heating, but above 90° they begin to lose nitric acid as well, and basic nitrates separate. The anhydrous salt can be made by drying the hexahydrate over phosphorus pentoxide in the cold to the dihydrate, and drying this *in vacuo* with constant pumping for months,[267] or from the lower hydrates in a stream of nitric acid vapour at 180-190°.[268]

Oxy-salts of Sulphur

Magnesium Sulphite

It forms a hexahydrate, which goes over at 40° to a trihydrate; sol^y 0·65/25°. The solution is slowly oxidized by air.

Magnesium sulphate

The anhydrous salt is very stable to heat, and has a strong affinity for water. It is formed from the monohydrate at 200°; it is stable up to

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[267] W. W. Ewing, E. Klinger, and J. D. Bradner, *J.A.C.S.* 1934, **56**, 1054.

[268] A. Sieverts and W. Petzold, *Z. anorg. Chem.* **1932**, **205**, 119.

a white heat, where it evolves oxygen, sulphur dioxide and trioxide, and leaves magnesium oxide behind. It melts with decomposition, and if it is rapidly heated does so at 1,120°.

Like many sulphates, especially of polyvalent metals, it only takes up water slowly; it forms a series of hydrates, which, with their transition points,[269] are:

$$\text{(ice)} \underset{-4^\circ}{\rightleftharpoons} 12\text{ aq.} \underset{+1{\cdot}8^\circ}{\rightleftharpoons} 7\text{ aq.} \underset{48{\cdot}3^\circ}{\rightleftharpoons} 6\text{ aq.} \underset{68^\circ}{\rightleftharpoons} 1\text{ aq.} \underset{200^\circ}{\rightleftharpoons} \text{(anhyd.)}$$

The heptahydrate is Epsom Salts; it is a vitriol isomorphous with the corresponding sulphates of divalent iron, cobalt, nickel, and zinc. Sol^y (of heptahydrate) 35·8/20°. The solubility of the monohydrate falls from 68° to 200°.[269]

Anhydrous magnesium sulphate is slightly soluble in alcohols, the values at 25° being methyl alcohol 0·224; ethyl alcohol 0·023[270]; in both these solvents the solubility falls as the temperature rises.

Numerous double salts of magnesium sulphate are known, but in none is there any evidence of complexity. Examples are Schönite, K_2SO_4, $MgSO_4$, $6\,H_2O$; Astrakanite Na_2SO_4, $MgSO_4$, $4\,H_2O$; and Kainite, KCl, $MgSO_4$, $3\,H_2O$.

Magnesium selenate is very like the sulphate; it forms hydrates with 7, 6, 2, and 1 H_2O; sol^y (of the $6\,H_2O$) 37·9/25°.[271]

Magnesium tellurate was prepared by Berzelius, but very little is known about it.

Magnesium dichromate has two hydrates, $MgCr_2O_7$, 5 and $7\,H_2O$, with a transition point at 89·4°.[272]

Oxy-salts of the Halogens

Magnesium hypochlorite, hypobromite, and hypoiodite are only known in solution.

Magnesium chlorate, $Mg(ClO_3)_2$, is formed at once if chlorine is passed into cold water with magnesium oxide in suspension. It is hygroscopic, and forms a hexahydrate which passes into a tetrahydrate about 40°; sol^y 146·9/25°.

Magnesium bromate, $Mg(BrO_3)_2$, is known only as the hexahydrate; the anhydrous salt cannot be prepared. Sol^y about 43/ord. temp.

Magnesium iodate, $Mg(IO_3)_2$, crystallizes with 10, 4, and 0 molecules of water. Sol^y (of the tetrahydrate) 9·31/25°.

Magnesium perchlorate, $Mg(ClO_4)_2$. This is a very stable salt with an extremely strong affinity for water. The anhydrous salt can be obtained from the hydrate only by heating to 250°; a little above this temperature

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[269] See Gmelin, *Magnesium*, B, p. 217.

[270] G. C. Gibson, J. O.'L. Driscoll, and W. J. Jones, *J.C.S.* 1929, 1441.

[271] For the system $MgSeO_4$, H_2SeO_4, H_2O at 30° see H. Furukawa and G. B. King, *J. Phys. Chem.* 1944, 48, 174.

[272] W. H. Hartford, *J.A.C.S.* 1946, 68, 2192.

it decomposes, giving mainly the oxide and the chloride MgO and $MgCl_2$. It forms hydrates with 6, 4 (probably not 3), and 2 H_2O, the heats of hydration being[273]

$O \rightarrow 2$ aq. 13·5; $O \rightarrow 4$, 24·7; $O \rightarrow 6$, 32·7 k.cals.
Heat per 1 H_2O 6·75 6·2 5·4

It is largely used as a dehydrating agent, the anhydrous salt being known as 'anhydrone', and the trihydrate (actually in all probability a mixture of the di- and tetrahydrates) as 'dehydrite'; even the latter is almost as effective a drying agent at ordinary temperatures as phosphorus pentoxide,[274] and it has the advantage of being less likely to react with the material to be dried, of being able to be regenerated by heat after use, and of taking up more water: 100 g. of anhydrous $Mg(ClO_4)_2$ take up 48 g. of water, and 100 g. of the trihydrate 19 g. of water to form the hexahydrate, while 100 g. of phosphorus pentoxide only absorb 12·7 g. in conversion into metaphosphoric acid.

Sol^{y} (of the hexahydrate) 99·8/25°[275]; it is also soluble in numerous oxygenated organic solvents (alcohols, ethers, ethyl acetate, acetone; for values of the solubilities see under perchloric acid, VII. 1233).

Magnesium periodate. The metaperiodate $Mg(IO_4)$, 10 H_2O is easily soluble in water. A variety of more complicated periodates (such as the di-meso-periodate $Mg_3I_2O_9$, 3 H_2O) are known.

Complex Magnesium Compounds

These are fairly numerous,[276] but not very stable. They are nearly all complexes of the divalent magnesium cation Mg^{++}, and the great majority have the metal linked to oxygen; the link to nitrogen is much weaker, and there seem to be no complexes in which magnesium is directly co-ordinated to carbon or the halogens. The co-ordination number varies, but often reaches its maximum value of 6.

Magnesium-Nitrogen Complexes

Nearly all magnesium salts take up ammonia, and some of the resulting ammines are very stable to heat, as the following examples show (the dissociation tensions at the specified temperatures are given in brackets): $MgCl_2$, 6 NH_3, 4 NH_3, 2 NH_3 (the last has 18 mm./181°); the other halides behave in the same way. Further examples are $Mg(ClO_4)_2$, 6 NH_3 (1 atm./227°), and 2 NH_3 (10 mm./260°).

Aromatic amines and pyridine can replace ammonia, as in $Mg(NO_3)_2$, 2 $C_6H_5NH_2$; $Mg(NO_3)_2$ 2 py., 4 aq. (AQ); $MgBr_2$, 2 Et_2O, 4 py.; MgI_2, Et_2O, 5 py.

[273] G. F. Smith, O. W. Rees, and V. R. Hardy, *J.A.C.S.* 1932, **54**, 3520.

[274] J. H. Bower, *Bur. Stand. J. Res.* 1934, **12**, 241.

[275] H. H. Willard and G. F. Smith, *J.A.C.S.* 1923, **45**, 295.

[276] A number of them are quoted in Pfeiffer, *Organische Molekül-verbindungen*, ed. 2, Stuttgart, 1927. Others will be found in Gmelin, *Magnesium B.*, under the respective simple salts.

Addition compounds are also formed by nitriles, as in $MgBr_2$, 3 and 4 $CH_3 \cdot CN$; MgI_2, 6 $CH_3 \cdot CN$.

All these complexes seem to be broken down by water.

Magnesium-Oxygen Complexes

These are very common, and it is clear that the link of the magnesium ion to oxygen is a strong one, as is shown, for example, by the dehydrating power of the perchlorate.

The magnesium salts have a stronger tendency to hydrate than any of the salts of the heavier metals of the subgroup; of the nineteen salts of magnesium which have just been described, all but two (the very insoluble fluoride, and the cyanide which is decomposed by water) form hydrates, usually with a large number of water molecules; the values have been given in Table III, p. 221.

The ion is equally ready to co-ordinate with organic compounds of oxygen. Pfeiffer quotes compounds of the magnesium halides with varying numbers of molecules up to 6 (6 and 4 being the most usual) of twenty-five different organic substances, alcohols, ethers, aldehydes, ketones, esters, acid chlorides, acid anhydrides, and amides; and other magnesium salts behave in the same way. Most of these compounds have only been isolated and analysed: their salt character has not been established, but it may fairly be assumed.

On the other hand, the number of neutral co-ordination compounds of magnesium is very small. The etherates of the magnesium dialkyls no doubt belong to this class, and so probably do the solvation products of the Grignard reagents with tertiary amines, or dialkyl sulphides, selenides, or tellurides. Otherwise we only have the acetonylacetate $Mg(C_5H_7O_2)_2$, of which very little is known. It is described[277] as being anhydrous and easily soluble in alcohol; its molecular weight as determined by the boiling-point in alcohol is normal, which implies that the deforming power of the magnesium atom is sufficient to keep it in the covalent form in that solvent.

The (presumably complex) double fluorides $MMgF_3$ and M_2MgF_4 have been obtained from both of the systems KF—MgF_2 and RbF—MgF_2.[278]

CALCIUM, STRONTIUM, BARIUM, RADIUM

THE general relations of these elements have already been discussed (p. 219); they form a closely related series. Radium, apart from its radioactivity, falls into line with the rest; its salts are, of course, relatively little known, and the remarks that follow apply primarily to calcium, strontium, and barium; the radium salts are mentioned when their properties have been examined.

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[277] S. Tanatar and E. Kurowski, *Chem. Centr.* 1908, ii. 1096.

[278] H. Remy and W. Seemann, *Rec. Trav.* 1940, 59, 516.

The Elements

Calcium is the commonest metal in the earth's crust (3·63 per cent.) after aluminium (8·8 per cent.) and iron (5·1 per cent.); it is widely distributed also in the more solid structures of the animal kingdom, being found in bones, teeth, eggshells, coral, etc.

Strontium, though the amount (0·042 per cent.) is only about 1 per cent. of that of calcium, is nearly as abundant as chlorine or sulphur; its most important minerals are celestine ($SrSO_4$) and strontianite ($SrCO_4$). The isotopes of ordinary strontium have the mass numbers 86 (10 per cent.), 87 (6·6 per cent.), and 88 (84·3 per cent.). The production of ^{87}Sr by the β-radioactive decay of ^{87}Rb has already been mentioned, and the fact that the strontium isolated from a Canadian mica rich in rubidium was found to contain 99 per cent. of this isotope (I. 63).

Barium is nearly as abundant as strontium (0·039 per cent.), and is by far the commonest of those elements whose atomic numbers are greater than 38 (Sr). It has the highest electroaffinity and the least tendency to complex formation of all the alkaline earth metals (except perhaps radium).

Radium. Its discovery by the Curies[279] was due to the fact that while the radioactivity of uranium compounds is usually proportional to the amount of uranium they contain, there are some uranium minerals which are far more active, showing that they must contain a substance of greater activity than uranium. The amount of radium in a normal uranium mineral is proportional to its half-life as compared with that of uranium (1,691 years: $4{\cdot}5 \times 10^9$ years), and is 0·38 g. per ton of uranium, or about 1 g. in 7 tons of pitch-blende.

The method of concentration consists essentially in separating the radium with the barium and some other elements as an insoluble sulphate residue, which after further purification contains only the radium and barium salts; these are then converted into the chlorides (originally by boiling with sodium carbonate solution: now sometimes by reduction to sulphides or in other ways), and it only remains to separate the radium from the barium. In the original separation this was effected by the fractional crystallization of the chlorides, the radium salt being the less soluble, and the fraction

$$\frac{Ra_{\text{cryst}}}{Ba_{\text{cryst}}} \div \frac{Ra_{\text{soln.}}}{Ba_{\text{soln.}}}$$

being 4·5; as the quantities got smaller, increasing amounts of hydrochloric acid were added to the solution, which diminishes the solubility without much affecting the ratio.[280] The total amount of radium isolated up to date is supposed to be more than a kilogram.

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[279] 26 December 1898; see P. Curie, M. Curie, and G. Bémont, *C.R.* 1898, **127**, 1215.

[280] See further, W. B. Pletenpol, *J. Chem. Phys.* 1942, **10**, 211.

There are four natural isotopes of No. 88, of which radium alone has been isolated in quantity; their atomic weights and half-life periods are:

	Actinium X	*Thorium X*	*Radium*	*Mesothorium 1*
At. wt.	223	224	226·05	228
Half-life	11·2 days	3·64 days	1,691 years.	6·7 years.

Hahn and Donath[281] have examined a variety of barium minerals for an inactive isotope of radium, but in vain; if any such isotope is present it must be less than 0·2 mg. to every ton of barium.

Metals

The melting- and boiling-points of the metals of this subgroup are:

	Be	Mg	Ca	Sr	Ba	Ra
M. pt.	1,278°	649°	810°	752°	830°	700° C.
B. pt.[a]	2,970°	1,100°	1,439°	1,366°	1,737°	< 1,737° C.

a = [282]

The irregularity of the melting-points is explained by the differences in crystal structure; beryllium and magnesium have a close-packed hexagonal structure, calcium and strontium a face-centred cubic, and barium a space-centred cubic.

The metals are all white (the supposed yellow colour of barium is due to impurities), and are very readily oxidized by air, but in the massive state are usually protected by a film of oxide or nitride.

Calcium is a soft metal (not as soft as lead) which is trimorphic. In the air it becomes covered with a film of nitride, and if it is heated in air it burns largely to the nitride.

Strontium is best made by reducing the oxide with aluminium *in vacuo* at a temperature at which the strontium distils off; it is softer than calcium and decomposes water more violently, but does not absorb nitrogen below 380°.

Barium is very similar to strontium, and is made from the oxide and aluminium in the same way; under a pressure of 10^{-4} mm. it can be distilled at 950°. It reacts with water more readily than strontium or calcium, but less so than sodium. It soon oxidizes in air.

Calcium and strontium form a continuous series of mixed crystals, but calcium+barium and strontium+barium both show two series separated by a two-phase region.[283-4]

Radium. This was made[285] by the electrolysis of an aqueous solution of

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[281] O. Hahn and K. Donath, *Z. physikal. Chem.* 1928, **139**, 143.

[282] B. pts. of Mg, Ca, Sr, and Ba are from H. Hartmann and R. Schneider, *Z. anorg. Chem.* 1929, **180**, 282.

[283] W. Klemm and G. Mika, ib. 1941, **248**, 155.

[284] A. J. King, *J.A.C.S.* 1942, **64**, 1226.

[285] P. Curie and A. Debierne, *C.R.* 1910, **151**, 523; *Radium*, 1910, **7**, 309.

radium chloride, with a mercury cathode, the mercury being afterwards distilled off. It melts at about 700° and is more volatile than barium; it is very unstable in air, and turns black at once, probably from the formation of a nitride. Radium salts give a carmine red colour to a flame.

Hydrides

Subhydrides of these elements, or at least of the first three, of the formula MH, can be shown by their spectra to be formed in a vacuum tube containing the vapour of the metal and hydrogen; but the evidence for their occurrence in the solid state is very weak.[286-8]

The normal hydrides MH_2 are formed by all three alkaline earths, but with increasing difficulty as the atomic weight rises. With calcium the rate of combination of the metal with hydrogen depends on the state of the metal[288]; the very fine powder got by evaporating a solution of calcium in liquid ammonia begins to absorb hydrogen at 0°, but normally the reaction does not begin below 250°. The dissociation tension of the hydrogen[282] shows that at 780-800° solid solutions of calcium in calcium hydride containing from 0 to 20 per cent. and from 90 to 100 per cent. of the metal are formed.

Strontium hydride is similar, but like the barium and unlike the calcium compound it can absorb more hydrogen at 0° up to a composition MH_4: much of this extra hydrogen can be pumped off.[289,290]

Barium hydride, BaH_2, is formed at a higher temperature than the others, best by heating barium amalgam in hydrogen up to 1,400°. It melts at 1,200° and can be distilled in a stream of hydrogen at 1,400°. It is less stable than the hydrides of calcium and strontium, but more than those of the alkali metals. All these hydrides, which are undoubtedly salts of the negative hydrogen ion, are very readily converted by water into the hydroxide and hydrogen.

The following are the heats of formation (I: Hf) of the solid hydrides from the solid metal and hydrogen gas, and (II:Ha) the gaseous hydrides from their atoms[291]:

	Solid Hf	*Solid* Ha
CaH_2 . .	46	197·6 k.cals.
SrH_2 . .	42	192·9 ,,
BaH_2 . .	40·8	193·6 ,,

Radium hydride, RaH_2, has not been prepared.

[286] C. B. Hurd and K. E. Walker, *J.A.C.S.* 1931, **53**, 1681.

[287] P. Remy-Génneté, *Ann. Chim.* 1933, [x] **19**, 363.

[288] W. C. Jones, M. F. Stubbs, A. E. Sidwell, and A. Pechukas, *J.A.C.S.* 1939, **61**. 318.

[289] M. Gautier, *C.R.* 1902, **134**, 100.

[290] W. Biltz and G. F. Hüttig, *Z. anorg. Chem.* 1920, **114**, 262.

[291] F. R. Bichowsky and F. D. Rossini, *Thermo-chemistry*, 1936.

Carbides

Calcium carbide, CaC_2, was discovered by Moissan,[292] who made it by heating lime and carbon in the electric furnace; it can also be made by heating calcium carbonate or metallic calcium with carbon, but not below 2,000° C. The crystal structure[293-4] shows that it is the calcium salt of the $[C\equiv C]^{--}$ ion. Its decomposition by water to lime and acetylene is familiar. It is useful for reducing metallic oxides, with evolution of carbon monoxide and dioxide. At a red heat it absorbs atmospheric nitrogen with separation of carbon and production of calcium cyanamide $CaCN_2$, which has the formula $Ca[\overset{=}{N}{-}C\equiv N]$, or is a resonance hybrid between this and other forms such as $Ca[\bar{N}{=}C{=}\bar{N}]$; this reaction is an important source of combined nitrogen.

Calcium carbide has a very high melting-point. The strontium and barium compounds are very similar; the melting-points fall in the order Ca > Sr > Ba, but even barium carbide has a higher melting-point than platinum (Moissan). Barium carbide absorbs atmospheric nitrogen, but the main product is the cyanide $Ba(CN)_2$.[295]

Alkyl and Aryl Compounds

These are but little known. No dialkyl or diaryl compounds of any of these metals have been prepared, and indeed no alkyl or aryl derivatives of any kind have been isolated, but there is good evidence that calcium,[296-7,301] strontium,[298,300-2] and barium[297,299,301-2] will form alkyl and aryl metallic halides corresponding to the Grignard reagents, and resembling them in behaviour.

These are formed in the same way as the magnesium compounds, but much more slowly. Thus, with barium,[299] ethyl iodide reacts only just enough to give the Gilman colour test (II. 231), and methyl iodide and butyl iodide will not react at all; the phenyl compound is more easily made, but even this requires that the metal should be shaken with an ethereal solution of phenyl iodide in the cold for 50 hours.

The products have not been isolated, but the reactions of the resulting solutions, for example, the formation of carboxylic acids by the addition of carbon dioxide, are sufficient to establish their structures.

The calcium, strontium, and barium alkyls have recently[300-2] been

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[292] H. Moissan, *C.R.* 1894, **118**, 501.

[293] U. Dehlinger and R. Glocker, *Z. Krist.* 1926, **64**, 296.

[294] M. v. Stackelberg, *Z. physikal. Chem.* 1930, B **9**, 460.

[295] See O. Kuhling and O. Berkold, *Z. angew. Chem.* 1909, **22**, 193.

[296] E. Beckmann, *Ber.* 1905, **38**, 904.

[297] H. Gilman and F. Schulze, *J.A.C.S.* 1926, **48**, 2643.

[298] C. Gruttner, Inaug.-Diss. Berlin, 1914.

[299] H. Gilman and F. Schulze, *Bull. Soc. Chim.* 1927, **41**, 1833.

[300] H. Gilman, R. N. Meals, G. O'Donnell, and L. Woods, *J.A.C.S.* 1943, **65**, 268.

[301] H. Gilman and L. A. Woods, *J.A.C.S.* 1945, **67**, 520.

[302] H. Gilman, A. H. Haubein, and L. A. Woods, ib. 922.

re-examined by Gilman *et al.* They have not actually isolated the alkyls; they show that if zinc ethyl is boiled with the metal in the absence of air, and the solvent benzene and the excess of zinc ethyl evaporated the double compound $Et_2Sr\text{-}ZnEt_2$, or its calcium or barium analogue, separates as colourless crystals. Solutions of this double compound in ether give reactions of the strongest alkyls, which zinc ethyl alone will not do.

Nitrides

Nitrides of the type M_3N_2 are formed by all three alkaline earth metals on heating in nitrogen. Calcium nitride, Ca_3N_2, was made in this way by Moissan; it melts at 1,195°[303]: it is not decomposed by carbon except in the electric furnace. Its dissociation tension[304] shows that its heat of formation is 108·2 k.cals.

Strontium nitride, Sr_3N_2, is similar, and is made in the same way.

Barium nitride, Ba_3N_2, is also similar; it does not decompose below its melting-point of 1,000°.

All these nitrides are very readily decomposed by water with evolution of ammonia.

Oxides. Peroxides

The alkaline earth metals all form oxides MO, hydroxides $M(OH)_2$ and their hydrates, and peroxides MO_2 and their hydrates.

Oxides

The oxides MO all have the sodium chloride lattice[305]; they have very high melting-points, and their vapour pressures at high temperatures have been determined by the rates of evaporation[306] to be as follows:

	CaO	SrO	BaO
Temp.	1,728°	1,635°	1,475°
V.p. in mm. $\times 10^6$	1·80	4·0	33·0

Calcium oxide, m. pt. 2,572°; b. pt. 2,850°, is remarkable for its inactivity in the ordinary dry state as quicklime; in this condition it will not react in the cold with chlorine, hydrogen sulphide, carbon dioxide, sulphur dioxide, or nitrogen peroxide.[307] In the same way the conversion of barium oxide into the peroxide by heating in air is much hastened by the addition of small quantities of water.

Strontium oxide, SrO, is similar, but it needs a higher temperature than the calcium compound to prepare it either from the carbonate or from the hydroxide. It melts at 2,430°, which is below lime and above barium oxide.

[303] A. v. Antropoff and E. Falk, *Z. anorg. Chem.* 1930, **187**, 405.

[304] S. Satoh, *Bull. Inst. Phys. Chem. Res. Japan*, 1939, **18**, 548.

[305] V. M. Goldschmidt, *Trans. Far. Soc.* 1929, **25**, 277.

[306] E. Preston, *J. Soc. Glass Technol.* 1933, **17**, 118.

[307] V. H. Veley, *J.C.S.* 1893, **63**, 821; 1894, **65**, 1.

Barium oxide, BaO, cannot be made by heating the carbonate, as that is too stable (see below II. 253), but it can be prepared from the nitrate or iodate, or from the hydroxide by several hours heating at 800°, or from the peroxide at 1,150°. It is usually made by heating a mixture of barium carbonate and carbon; this causes an evolution of carbon monoxide and leaves behind a porous mass of barium oxide which is very reactive.

Hydroxides

Calcium hydroxide, $Ca(OH)_2$, is the familiar slaked lime. In the reaction

$$CaO + H_2O = Ca(OH)_2$$

the volume of the slaked lime produced is twice that of the quicklime, and this fact can be made use of for splitting wood or rock.

All these hydroxides lose water on heating and are converted into the oxides; but their stability increases with the atomic number of the metal, the temperatures at which the dissociation tension of the water is 10 mm. being:

$Mg(OH)_2$	$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$
300°	390°	466°	700°

Calcium hydroxide is capable of taking up more water, but tensimetric and X-ray measurements indicate that this excess is very lightly held, and that no definite hydrate beyond CaO, H_2O, or $Ca(OH)_2$ is formed.[308] The dissociation tension is 1 atmosphere at 513°.[309]

The solubility in water is small, and falls with a rise in temperature, the values (in g. per 100 g. water)[310] being at 0° 0·136, at 50° 0·098, and at 100° 0·060. In presence of alkalies this is very much reduced, being only 0·002 g. to 100 g. of a 0·8 per cent. sodium hydroxide solution[311] at 20°.

Strontium hydroxide, $Sr(OH)_2$, which is similar, forms hydrates with 8, 1, and probably 2 molecules of water.[312] It is much more soluble than the calcium compounds: sol^y 0·89/25°. On heating it loses water to form the oxide, the dissociation pressure being 1 atmosphere at 1,051°.[313]

Barium hydroxide, $Ba(OH)_2$. Hüttig and Arbes find[314] by tensimetric and X-ray measurements that the only solid phases in the system BaO: H_2O are ice, $Ba(OH)_2$ 8 H_2O; 1 H_2O: $Ba(OH)_2$ anhydrous; and BaO. Sol^y (octahydrate) 4·181/25°.[315-16] The anhydrous hydroxide melts at 408°; its heat of fusion is 3·40 k.cals/mole[317]; it has a dissociation tension of water vapour amounting to 1 atmosphere at 998°.[313]

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[308] G. F. Hüttig and A. Arbes, *Z. anorg. Chem.* 1930, **191**, 161.

[309] S. Tamaru and K. Siomi, *Z. physikal. Chem.* 1932, **161**, 421.

[310] A. Guthrie, *J. Soc. Chem. Ind.* 1901, **20**, 223.

[311] A. d'Anselme, *Bull. Soc. Chim.* 1903, [3] **29**, 936.

[312] G. F. Hüttig and A. Arbes, *Z. anorg. Chem.* 1930, **192**, 233.

[313] J. Johnston, *J.A.C.S.* 1908, **30**, 1357; *Z. physikal. Chem.* 1908, **62**, 330; 1909, **65**, 740.

[314] *Z. anorg. Chem.* 1931, **196**, 409.

[315] H. F. Sill, *J.A.C.S.* 1916, **38**, 2639.

[316] K. Nishizawa and Y. Hachihama, *Z. Elektrochem.* 1929, **35**, 386.

Peroxides MO_2 *and* MO_2 *aq.*

The ease of formation and stability of these compounds increase very markedly with the rise in the atomic number of the metal throughout the whole subgroup from beryllium to barium (see below, p. 202).

Calcium peroxide CaO_2, like the magnesium compound, cannot be made by the direct action of oxygen on the metal or the monoxide, but only by treating lime water with hydrogen peroxide, or a calcium salt with sodium peroxide, when the hydrate $CaO_2, 8\,H_2O$ (isomorphous with the strontium and barium compounds) is precipitated. At 130° it loses its water to form CaO_2, which decomposes into calcium oxide and oxygen at a red heat. Another hydrate $CaO_2, 2\,H_2O$ (or perhaps $Ca(OH)_2, H_2O_2$) can be isolated.[318]

Strontium peroxide, SrO_2, can be formed by the direct action of oxygen on the monoxide, but only under considerable pressure; even under 12 atmospheres no peroxide is produced, but Fischer and Ploetze[319] obtained a 15 per cent. yield at 400° under 100 atmospheres; it has recently been found that at 350–400° and 200-50 atmospheres the reaction is reversible: the dissociation tension of strontium peroxide is 1 atmosphere at 357°.[320] It is usually made by the action of hydrogen peroxide or sodium peroxide on a solution of a strontium salt. It forms an octahydrate, which is only slightly soluble in water.

Barium peroxide, BaO_2, the most stable compound of the series, can be made by heating barium oxide in oxygen or air; the dissociation tension is half an atmosphere at 740° and 1 atmosphere at 840°[321]; the interaction does not, however, occur in the complete absence of water. This reaction was formerly used for the commercial preparation of oxygen, barium oxide being converted into the peroxide by heating in air under pressure, and then the pressure lowered and the extra oxygen pumped off (Brin's Oxygen Process). Barium peroxide is now used for bleaching (straw, silk, etc.) and for the preparation of hydrogen peroxide.

Barium peroxide is more soluble in water than the calcium and strontium analogues, 100 g. of water dissolving at the ordinary temperature about 0·1 g. barium peroxide as the octahydrate. It has a peculiar reaction with potassium ferricyanide, the two substances reducing one another with evolution of oxygen:

$$BaO_2 + 2\,K_3Fe(CN)_6 = K_6Ba[Fe(CN)_6]_2 + O_2.$$

The reaction is quantitative, and can be used to determine the peroxide content of the impure material.[322-3]

The stability of the peroxides increases steadily along the series; beryllium forms none (p. 202); magnesium only compounds of the oxide with

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[317] R. P. Seward, *J.A.C.S.* 1945, **67**, 1189.

[318] R. de Forcrand, *C.R.* 1900, **130**, 1250, 1308, 1388.

[319] F. Fischer and H. Ploetze, *Z. anorg. Chem.* 1912, **75**, 10.

[320] C. Holtermann and P. Laffitte, *C.R.* 1939, **208**, 517.

[321] J. H. Hildebrand, *J.A.C.S.* 1912, **34**, 256.

[322] J. Quincke, *Z. anal. Chem.* 1892, **31**, 28.

[323] A. Baumann, *Z. angew. Chem.* 1892, **5**, 116.

hydrogen peroxide, which may be peroxidated hydroxides: calcium peroxide can only be got by dehydrating the hydrogen peroxide compound, and not by the action of oxygen on the monoxide: strontium peroxide can be made directly, but only under a high pressure of oxygen: barium peroxide can be made under the ordinary pressure.

The hydroxides and peroxides of the alkaline earths have a strong tendency to crystallize with 8 molecules of water, irrespective of the covalency maximum of the cation; thus we have octahydrates of strontium and barium hydroxides, and of the peroxides of all three metals, calcium, strontium, and barium, these last three hydrates being isomorphous. Octahydrates are formed by some other salts of calcium also, such as the chloroplatinates: by several magnesium salts, the chloride, iodide, and complex bismuth chloride $MgBiCl_5$: and even by beryllium platinichloride $BePtCl_6$ (the presence of a large anion obviously assists the hydration of the cation). With the beryllium, magnesium, and calcium salts, where the covalency maximum is 4 or 6, we must suppose (except on the very improbable hypothesis that the anion takes up two molecules of water—or with beryllium four) that the water is in the form of double molecules, as Werner originally suggested. The crystal structure of these octahydrates seems to be unknown.

Sulphides

The sulphides of these elements are as a rule insoluble in water as such, but readily converted by it into the very soluble hydrosulphides $M(SH)_2$, aq.

Calcium sulphide, CaS, can be made by the reduction of the sulphate with carbon, and in other ways. It is a white crystalline substance (the m. pt. is apparently unknown) which is easily oxidized by air, and is practically insoluble in water; so far as it dissolves it is largely hydrolysed with the production of SH^- anions and so of the hydrosulphide $Ca(SH)_2$, which is very easily soluble in water and crystallizes with 6 H_2O.

Polysulphides are known, but they seem very indefinite.

Strontium sulphide, SrS, which can be made in the same way, is a colourless crystalline compound whose melting-point is above 2,000°; it has a sodium chloride lattice[315]; it is practically insoluble in water, but on warming readily forms the hydrosulphide $Sr(SH)_2$ and the hydroxide, and on cooling the latter crystallizes out. Strontium hydrosulphide forms a tetrahydrate, with sol^y 42·2/20°.[325]

A polysulphide SrS_4, 4 and 2 H_2O, can be obtained by boiling strontium sulphide with sulphur and evaporating down the solution *in vacuo* in the cold.

Barium sulphide, BaS,[326] can be made by reducing barium sulphate with carbon; it has a sodium chloride lattice.[324] It is easily soluble in water, as it is at once converted into a mixture of barium hydrosulphide and hydroxide; the mixed salt Ba(SH)OH can also probably be isolated. The

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[324] S. Holgersson, *Z. anorg. Chem.* 1923, **126**, 182.

[325] E. Terres and K. Brückner, *Z. Elektrochem.* 1920, **26**, 27.

[326] Id. ib. **26**, 1.

solution rapidly turns yellow in air, from its oxidation and the formation of the polysulphide BaS_4, H_2O, a red solid which is yellow when powdered or in dilute solution; it is readily soluble in water (41/15°) to give a red solution with an alkaline reaction.

Alkaline Earth Halides

Fluorides

The only fluorides of these elements that can be isolated are the normal divalent salts MF_2; but with all three elements the mixed vapours of the metal and the difluoride in a vacuum tube, give a band spectrum of the subfluoride MF; with calcium it is possible that this compound is deposited in crystals on the surface of a calcium fluoride crystal exposed to the vapour[327]; similar spectra have been observed with strontium and barium.[328-9]

The normal fluorides MF_2 are slightly soluble salts, whose solubility increases with the atomic number of the metal.

Calcium fluoride, CaF_2, occurs as the mineral fluor spar, the name of which is derived from its use as a flux, and has itself given rise to the name of fluorine and the term 'fluorescence', although the mineral is, in fact, not fluorescent but phosphorescent; it is the most widely distributed compound of fluorine. It is transparent to ultra-violet rays, and melts at 1,330°. Its solubility in water is 25·3 mg. per litre at 18°[330-1]; it is more soluble on addition of hydrofluoric acid, with which it forms a solid of the composition $CaF_2, 2\,HF, 6\,H_2O$, which should no doubt be written $Ca[F_2H]_2, 6\,H_2O$.

Strontium fluoride also has the fluorite lattice; it melts above 1,450°, and boils at 2.489°.[332] It is stable in air up to 1,000°, but above this temperature it is oxidized to strontium oxide. Sol^y 11·7 mg./18°.[333]

Barium fluoride, BaF_2. This can be made by treating barium chloride with potassium hydrogen fluoride. It is better to use barium nitrate, to avoid the co-precipitation of chloride.[334] It has a fluorite lattice; it melts at 1,285°[335] and boils at 2,137°[335]; it is stable in air to 1,000°, and is oxidized at higher temperatures. Sol^y 0·209/25°.

Radium fluoride, RaF_2, is little known, but X-ray analysis of its crystal structure has shown[336] that like the other difluorides of this subgroup it has the fluorite lattice, the radius of the Ra^{++} ion being 1·43 A, corresponding to 1·52 A for the crystallographically 6-co-ordinated state.

[327] K. H. Hellwege, *Z. physikal. Chem.* 1938, B **39**, 465.

[328] R. Mecke, *Naturwiss.* 1925, **13**, 755: 1928, **16**, 521; *Z. Phys.* 1925, **32**, 823: 1927, **42**, 390; R. Mecke and M. Guillery, *Phys. Z.* 1927, **28**, 479, 514.

[329] O. H. Walters and S. Barratt, *Proc. Roy. Soc.* 1928, **118**, 120.

[330] F. Kohlrausch and F. Rose, *Z. physikal. Chem.* 1893, **12**, 234.

[331] F. Kohlrausch, ib. 1904, **50**, 356.

[332] O. Ruff, *Z. angew. Chem.* 1928, **41**, 807.

[333] F. Kohlrausch, *Z. physikal. Chem.* 1905, **50**, 355; 1908, **64**, 168.

[334] J. H. de Boer, ib. 1931, B **14**, 156.

[335] O. Ruff and W. Plato, *Ber.* 1903, **36**, 2358.

[336] G. E. R. Schultze, *Z. physikal. Chem.* 1936, B **32**, 430.

Chlorides

Calcium chloride is remarkable for its strong affinity for water. The system $CaCl_2$—water has been worked out in great detail (for the solid, liquid, and vapour phases) by Roozeboom.[337] It forms a hexahydrate, two monotropic tetrahydrates, a di- and a monohydrate. The hexahydrate is isomorphous with all the other hexahydrates of the alkaline earth chlorides and bromides (they are formed by all except barium chloride and bromide), and the X-ray analysis shows that the six water molecules are arranged octahedrally round the cation.[338] The two tetrahydrates are remarkable for the fact that the unstable one has a congruent and the stable one an incongruent melting-point. The solubility in water is very great. The cryohydric point is at $-55°$, this solution containing 42·5 g. $CaCl_2$ to 100 of water; the sol^y (of the hexahydrate) is 81·5/25°. The use of the anhydrous salt and of the lower hydrates for drying is familiar. The salt is also easily soluble in alcohols (even amyl), and in organic acids such as acetic, with most of which it forms solvates (see later under complexes).

Calcium chloride is made commercially on an enormous scale as a by-product in the ammonia-soda process, which consists essentially in the reaction:

$$2\,NaCl + CaCO_3 = Na_2CO_3 + CaCl_2$$

Strontium chloride is similar but less soluble. It melts at 870°, and forms hydrates with 6, 2, and 1 H_2O; the hexahydrate is stable in contact with the solution up to 66·5°.[339] Sol^y (of the hexahydrate) 55·5/25°. Its solubility in alcohols is also much less than that of calcium chloride.

Barium chloride melts at 955°, and has a transition point at 925°.[340] It is the least soluble of the three chlorides, though more soluble than radium chloride. It forms no hexahydrate, but a dihydrate which is stable in contact with the solution from the cryohydric point of $-7·8°$ up to 60° at least; the nature of the solid phase above this temperature is uncertain.[341] Sol^y 37·2/25°; in presence of other chlorides the solubility is less, and in 9 per cent. sodium chloride solution it is only 23·1/20°.

Barium chloride is slightly soluble in methyl alcohol (2·20/16°), but it is practically insoluble in ethyl alcohol.

Radium chloride only forms a dihydrate, isomorphous with barium chloride dihydrate; this loses its water between 150° and 200°, and the anhydrous salt melts about 900°.

Radium chloride is markedly less soluble in water than barium chloride: sol^y 24·5/20°.[342]

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[337] H. W. Bakhuis Roozeboom, *Z. physikal. Chem.* 1889, **4**, 31.

[338] Z. Herrmann, *Z. anorg. Chem.* 1931, **197**, 339.

[339] W. A. Tilden, *J.C.S.* 1884, **45**, 269.

[340] C. Lieber, *Z. physikal. Chem.* 1939, B **42**, 240.

[341] See E. Jänecke, ib. 1915, **90**, 267.

[342] O. Erbacher, *Ber.* 1930, **63**, 141.

Bromides

Calcium bromide, m. pt. 760°,[343] forms a hexahydrate with sol^{y} 140·0/25°, but no other hydrate.

Strontium bromide melts at 643°; it forms a hexahydrate of sol^{y} 99·7/25°, which goes to a dihydrate at 88·6°. It is also soluble in alcohol.

Barium bromide like the chloride gives no hexahydrate, but a di- which goes at 75° to a mono-; sol^{y} 104·1/20°.[342] It is also soluble in methyl alcohol (41·9/20°), ethyl alcohol (4·13/20°), and acetone (0·026/20°).

Radium bromide also forms a dihydrate, with sol^{y} 70·6/20°.[342]

Iodides

Calcium iodide melts at 740°[343] and forms a hexahydrate of m. pt. 42°; sol^{y} 204/20°.

Strontium iodide forms a hexahydrate stable up to 84°, and then a di- and monohydrate.[344] Sol^{y} 179·6/20°; in ethyl alcohol about 3·6/20°.

Barium iodide is similar; m. pt. 740°[345]; cryohydric point—33·5°; forms a hexahydrate,* which goes to a dihydrate at 25·7°, and this to a mono- at 98·9°.[345] Solubilities are: water 205·3/20°; ethyl alcohol 77/20°; propyl alcohol *ca.* 3/15°; formic acid 75/20°; methyl acetate 4·3/58°.

Oxy-salts of Carbon: Carbonates

The stability of the carbonates, like that of the peroxides, increases steadily with the atomic number throughout the whole series from beryllium to barium. Neutral beryllium carbonate can only be precipitated from a solution of a beryllium salt in an atmosphere of carbon dioxide; otherwise a basic carbonate is formed. The other metals form stable carbonates, but their readiness to dissociate diminishes as the atomic number of the metal increases, the temperature at which the dissociation pressure of the carbon dioxide is one atmosphere being approximately:

$BeCO_3$	$MgCO_3$[346]	$CaCO_3$[347]	$SrCO_3$[348]	$BaCO_3$[349]
(25°)	540°	900°	1,289°	1,360°

Calcium carbonate. This occurs in nature in two forms, as calcite, hexagonal and isomorphous with sodium nitrate, and aragonite, rhombohedral and isomorphous with strontianite. All alkaline earth carbonates seem to crystallize in these two forms. The solubility of calcite in water (0·62 mg./39°) is less than that of aragonite, which therefore must be the

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* This was supposed to contain 7·5 H_2O, but really contains 6: see Herrmann.[338]

[343] O. Ruff and W. Plato, ib. 1902, **35**, 3616; 1903, **36**, 2357.

[344] G. F. Hüttig and C. Slonim, *Z. anorg. Chem.* 1929, **181**, 76.

[345] J. Packer and A. C. D. Rivett, *J.C.S.* 1926, 1061.

[346] W. Manchot and L. Lorenz, *Z. anorg. Chem.* 1924, **134**, 316.

[347] H. Remy, *Lehrb.* i. 225 (1931).

[348] W. Dutoit, *J. Chim. Phys.* 1927, **24**, 110.

[349] G. Tammann and W. Pape, *Z. anorg. Chem.* 1923, **127**, 50.

stable form at this temperature, though it is possible that there is a transition temperature below 0°. By the action of carbon dioxide on lime water, especially in the presence of sucrose, a hexahydrate $CaCO_3, 6\ H_2O$ can be obtained; this loses its water very easily, and may be a metastable form.[350–2] Calcium carbonate is more soluble in water containing carbon dioxide, which converts it into the more soluble acid salt $Ca(CO_3H)_2$ ('temporary hardness').

Strontium carbonate occurs in nature as strontianite (rhombohedral). Like calcium carbonate it is dimorphic, the rhombic form being stable below 926° and the hexagonal above[353]; this last has the crystal structure of calcite. M. pt. 1,497°; sol^y 0·59 mg./18°.

Barium carbonate occurs as the mineral witherite, isomorphous with aragonite and strontianite; if this is heated in carbon dioxide under pressure (to repress dissociation) it changes at 811° from this γ-form to a hexagonal β-, and this at 982° into a regular α-form. Under a high pressure of carbon dioxide it melts at 1,740°; in the absence of carbon dioxide the melting-point is much lower, owing to partial dissociation. Sol^y 0·86 mg./18°; carbon dioxide raises this, the value being 150 mg./16° with half an atmosphere, no doubt through the formation of an acid carbonate, though no such salt has been isolated. The dissociation on heating (which is less than with any other carbonate of the series) has already been mentioned.

Formates

Calcium formate, $Ca(OCHO)_2$: anhydrous. Sol^y 17/25° and 18/80°; slightly soluble in alcohol.

Strontium formate forms a dihydrate which goes over at 65° into the anhydrous salt. Sol^y 9·47/20°; insoluble in alcohol and ether.

Barium formate forms no hydrates. Sol^y 31·3/20° 6·3 mg./ord. temp. in alcohol.

Acetates

Calcium acetate: the dihydrate goes to a monohydrate at 84°; sol^y 34·7/20° and 29·65/100°. It is insoluble in alcohol.

Strontium acetate: crystallizes with 4 H_2O, going to 0·5 H_2O at 9·5°. Sol^y 40·81/20°.[354]

Barium acetate forms a trihydrate which goes to a monohydrate at 25°, and this at 40° into the anhydrous salt. Sol^y 72·8/21·6; in cold alcohol 38 mg./100 g.

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[350] J. E. MacKenzie, *J.C.S.* 1923, **123**, 2409.

[351] J. Hume, ib. 1925, **127**, 1036.

[352] J. Hume and B. Topley, ib. 1926, 2932; *Proc. Leeds Lit. Phil. Soc.* 1927, 1, 169.

[353] W. Eitel, *Z. Krist.* 1925, **61**, 596.

[354] Y Osaka and R. Abe, *Mem. Sci. Kyoto Univ.* 1919, 3, 51.

Oxalates

Calcium oxalate. This is very insoluble in water, and is used for the quantitative determination of calcium and of oxalate. It forms a tri- and a monohydrate; the latter can be obtained by drying at 130°; at 200° it goes to the anhydrous salt, which on further heating begins to decompose at 430°.[355] Sol^y 0·58 mg./25°.[356]

Strontium oxalate forms hydrates with 2·5 and with 1 H_2O; sol^y (of 1 H_2O) 4·16 mg./18°.

Barium oxalate. The 3·5-hydrate goes over at about 0° to the dihydrate, which changes to a hemihydrate at 40°. Sol^y 11·2 mg./18°.

An acid oxalate $Ba(OCO \cdot COOH)_2$ with 2, 1, and 0 H_2O also exists, and is more soluble.

The conductivities of solutions of calcium, strontium, and barium oxalates give no indications of auto-complex formation.[357]

Oxy-salts of Nitrogen: Nitrites

Calcium nitrite can be made by the usual double decompositions. It forms a monohydrate, which is isomorphous with the strontium and barium salts. Sol^y 98·2/20°; in alcohol 0·97/20°.

Strontium nitrite. The monohydrate loses its water over phosphorus pentoxide *in vacuo*. Sol^y 68·6/20[358]; in alcohol 0·04/20°.

Barium nitrite is made by double decomposition from barium chloride and sodium nitrite.[359] It loses its water *in vacuo* over phosphorus pentoxide, and the anhydrous salt melts with decomposition at 217°. Sol^y 67·5/20°.

Nitrates

Calcium nitrate. Deposits of this salt are found where animal matter has decayed. It forms a tetrahydrate, and probably a tri- and dihydrate also. It is hygroscopic; sol^y 121/18°. Owing to the formation of ammines, the solution will absorb more ammonia than pure water.[360] The salt is also readily soluble in organic solvents, as the following values of the sol^y/25° show[361-2]:

Methyl alcohol	190	Amyl alcohol	15·6
Propyl ,,	57·5	Acetone	141
Isobutyl ,,	33·3	Methyl acetate	69·5[a]

a = [362]

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[355] J. Krustinsons, *Z. anal. Chem.* 1939, **117**, 330.

[356] W. H. McComas and W. Rieman (*J.A.C.S.* 1942, **64**, 2946).

[357] R. Scholder, *Ber.* 1927, **60**, 1510.

[358] M. Oswald, *Ann. Chim.* 1914, [ix] **1**, 64.

[359] J. Matuschek, *Ber.* 1907, **40**, 991.

[360] F. M. Raoult, *Ann. Chim. Phys.* 1874, [v] **1**, 270.

[361] J. D'Ans and R. Siegler, *Z. physikal. Chem.* 1913, **82**, 35.

[362] A. Naumann, *Ber.* 1909, **42**, 3789.

Strontium nitrate forms a tetrahydrate going to the anhydrous salt at 31·3°. Sol^y 70·8/20°; in other solvents[361] at 25°:

Methyl alcohol	1·26	Amyl alcohol	0·003
Ethyl ,,	0·02	Acetone	0·02
Propyl ,,	0·02	Pyridine	0·71[a]
Isobutyl ,,	0·01		

a = [363]

Barium nitrate is always anhydrous; m. pt. 595°. Sol^y 9·1/20°; methyl alcohol 0·057/25°; ethyl alcohol 0·0033/25°.[361] Unlike barium chloride it gives a transport number independent of concentration, so that complex nitrates are not formed.[364]

Radium nitrate. Also anhydrous. Sol^y 13·9/20.[365]

Oxy-salts of Sulphur: Sulphites

Calcium sulphite: 2 H_2O. Sol^y 0·167/15°.

Strontium sulphite: anhydrous. Sol^y 3 mg. 18.[366]

Barium sulphite: anhydrous. Sol^y 2·2 mg. 16°.[366]

Sulphates

Calcium sulphate. This occurs in a variety of forms, several of which are found as minerals. Anhydrous calcium sulphate is known in at least two modifications, β- and γ-, the last being the minerals anhydrite and alabaster: there is a hemihydrate $CaSO_4$, 1/2 H_2O, the chief constituent of plaster of Paris, and a dihydrate which is gypsum. The setting of plaster of Paris is due to its conversion into the dihydrate. The relations and the vapour pressures of these forms were examined by van 't Hoff and his co-workers,[367] but owing to the small solubility and the slowness of change from one form to another, the relations are still somewhat uncertain. The hemihydrate has been said to be zeolitic (i.e. a phase with continuous variable water content), but the vapour pressures and the X-ray patterns show that this is not so, and that it has a fixed composition.[368] The most probable conclusion[369] are these: the only solid phases from 0° to 200° are β-$CaSO_4$, γ-$CaSO_4$ (anhydrite), the hemihydrate, and the dihydrate. β-$CaSO_4$ is always metastable to γ-. On heating, the dihydrate goes to the β- at 420°, or if the β- is not formed, to the hemihydrate at 97°; between 42° and 97° the dihydrate is metastable; at some higher temperature the hemihydrate loses its water and changes into γ-$CaSO_4$.[371]

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[363] R. Müller, *Z. anorg. Chem.* 1924, **142**, 130.

[364] A. A. Noyes, *Z. physikal. Chem.* 1910, **36**, 75.

[365] O. Erbacher, *Ber.* 1930, **63**, 141.

[366] W. Autenrieth and A. Windaus, *Z. anal. Chem.* 1898, **37**, 293.

[367] For a summary see J. H. van 't Hoff, E. F. Armstrong, W. Hinrichsen, and F. Weigert, *Z. physikal. Chem.* 1903, **45**, 257.

[368] H. B. Weiser, W. O. Milligan, and W. C. Ekholm, *J.A.C.S.* 1936, **58**, 1261.

[369] E. Posnjak, *Amer. J. Sci.* 1938, [v] **35**, A 247.

[370] G. A. Hulett, *Z. physikal. Chem.* 1901, **37**, 385.

A saturated solution of the dihydrate at 25° contains 0·107 g. $CaSO_4$ to 100 g. water. With this substance (and with barium sulphate) Hulett[370] demonstrated the influence of particle size on solubility. He showed that the solubility is not affected so long as the particles are more than $1·9 \times 10^{-3}$ mm. (1·9 μ) across, but that below this point it increases, and with the smallest particles he prepared (0·2 μ) it was 22 per cent. greater than with the large ones.

Strontium sulphate. This is known only in the anhydrous state[372]; it occurs in nature as celestine. It melts at 1,605°.[373] Sol^y^ 11·4 mg. at 18°.[374]

Barium sulphate occurs as Heavy Spar, the most important source of barium. It is more stable to heat than the calcium or strontium compounds, and does not decompose below 1,400°, where it begins to give off sulphur trioxide. It melts with considerable decomposition at 1,580°.[375] The solubility depends on the particle size even more than with calcium sulphate; the sol^y of ordinary precipitated barium sulphate is 0·22 mg./20°,[370,376] but that of the finest particles obtainable (0·1 μ) was found to be 80 per cent. greater than this.[370,377]

Radium sulphate is isomorphous with the barium salt: it is the least soluble of all the sulphates, having the sol^y $2·1 \times 10^{-6}$ g./25°.[378]

Oxy-salts of the Halogens

[Calcium hypochlorite $Ca(OCl)_2$ is a constituent of bleaching powder: see further under 'Chlorine', vii. 1201.]

Chlorates

Calcium chlorate, $Ca(ClO_3)_2$. This is usually made by passing chlorine into heated milk of lime. It forms a hexahydrate from the cryohydric point of −41° to −27°; a tetrahydrate to −8°; and a dihydrate which goes to the anhydrous salt at 76°; sol^y 194·5/25°.[379,380]

Strontium chlorate is similar; it begins to evolve oxygen at 290°, and then melts. It is said to form a trihydrate.[381] Sol^y 174·9/18°.[380] Insoluble in alcohol.

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[371] K. K. Kelley, J. C. Southard, and C. T. Anderson (U.S. Bureau of Mines 1941, paper 625) gives a very full account of the system $CsSO_4$, H_2O and its heat properties. The authors get these solid phases: (I) $CaSO_4$, 2 H_2O; (II*a* and II*b*) two forms of $CaSO_4$, 1/2 H_2O; and three forms III*a*, III*b*, IV of anhydrous $CaSO_4$. The form II*b* is metastable to II*a*.

[372] The transient formation of a hydrated sulphate when it is precipitated from solution has been observed by B. Lambert and W. Hume-Rothery, *J.C.S.* 1926, 2637.

[373] W. Grahmann, *Z. anorg. Chem.* 1913, **81**, 257.

[374] F. Kohlrausch, *Z. physikal. Chem.* 1905, **50**, 355; 1908, **64**, 152.

[375] F. O. Doeltz and W. Mostowitsch, *Z. anorg. Chem.* 1907, **54**, 148.

[376] F. Kohlrausch and F. Rose, *Z. physikal. Chem.* 1893, **12**, 243.

[377] M. L. Dundon, *J.A.C.S.* 1923, **45**, 2662.

[378] S. C. Lind, J. E. Underwood, and C. F. Whittemore, ib. 1918, **40**, 467.

[379] W. S. Jegorow, *Chem. J.* (*Russ.*), 1931, **1**, 1266 (Landolt-Börnstein Erg. iii, p. 488).

[380] W. F. Ehret, *J.A.C.S.* 1932, **54**, 3131.

[381] A. Potylizyn, *Z. Krist.* 1892, **20**, 183.

Barium chlorate, $Ba(ClO_3)_2$. This forms a monohydrate which loses its water at 120° and begins to give off oxygen at 300°; sol^y 33·8/20°.[382] It is very slightly soluble in alcohol, and practically insoluble in all other organic solvents. The monohydrate has been shown to give a continuous series of solid solutions with the bromate.[383]

Perchlorates

The perchlorates of the alkaline earths are all very soluble, not only in water but in many organic solvents as well. The values have been determined by Willard and Smith,[384] and are given, in g. of anhydrous salt to 100 g. of solvent at 25°, in the following table:

Solvent	$Ca(ClO_4)_2$	$Sr(ClO_4)_2$	$Ba(ClO_4)_2$
Water	188·6	309·7	198·3
Methyl alcohol	237·2	212·0	217·0
Ethyl ,,	166·2	180·7	124·6
n-Propyl ,,	144·9	140·4	75·6
n-Butyl ,,	113·6	113·5	58·2
Iso-Butyl ,,	56·9	77·9	56·2
Acetone	61·8	150·1	124·7
Ethyl acetate	75·4	136·9	113·0
Ethyl ether	0·26	. .	. .

Calcium perchlorate seems to be always anhydrous.

Strontium perchlorate forms a tetrahydrate which goes to a dihydrate at 25°, and this at 37° to the hydrate $Sr(ClO_4)_2$, 2/3 H_2O.

Barium perchlorate is the most stable perchlorate of the series; the loss of oxygen on heating is very slow and very small below 450°. It forms hydrates with 3 and 1 H_2O; if the trihydrate is dried *in vacuo* at 100–140° it goes straight to the anhydrous salt without melting, and forms a porous mass of this which is as effective a drying agent as concentrated sulphuric acid.[385] To obtain it perfectly free from water it must be dried for 5–6 hours at 260°.[386] The saturated aqueous solution boils at 140°.

Bromates

Calcium bromate crystallizes with 1 H_2O, this being isomorphous with the strontium and barium salts; sol^y 90/ord. temp.

Strontium bromate is formed by the direct action of bromine on the hydroxide[387]; sol^y 31/15°.

Barium bromate: the monohydrate loses its water on heating, but not over sulphuric acid. It begins to lose oxygen at 265°, and does so almost

[382] C. di Capua and A. Bertoni, *Gaz.* 1928, **58**, 250.

[383] J. E. Ricci and S. H. Smiley, *J.A.C.S.* 1944, **66**, 1011.

[384] H. H. Willard and G. F. Smith, ib. 1923, **45**, 286.

[385] G. F. Smith, *J. Ind. Eng. Chem.* 1927, **19**, 411.

[386] O. Hönigschmid and R. Sachtleben, *Z. anorg. Chem.* 1929, **178**, 16.

[387] H. B. Dunnicliff, H. D. Suri, and K. L. Malhotra, *J.C.S.* 1928, 3106.

explosively at 300°[388]; sol^y 0·652/20°[389] a remarkable drop from the strontium salt.

Iodates

Calcium iodate.[390] There is a hexahydrate up to 35°; then a dihydrate to 57·5°, and then the anhydrous salt. Sol^y 0·307/25°. The transitions are slow, and the solutions readily supersaturate.

Strontium iodate has 6 and 1 H_2O; sol^y 0·026/15°.

Barium iodate only occurs with 1 and 0 H_2O; the monohydrate is stable from 0° to at least 99°. It loses its water at about 180°; sol^y 0·022/20°.

Alkaline Earth Complexes

These elements behave like magnesium in the formation of complexes, but owing to the larger size of the atoms the tendency to co-ordinate is less, and it falls off as the atomic number of the metal rises. The complexes resemble those of magnesium in many ways; they are mainly complexes of the divalent cation, and the affinity is greatest for oxygen and less for nitrogen; other elements, even the halogens, scarcely co-ordinate at all, though there is evidence of the formation of auto-complexes in solutions of the chlorides.

Nitrogen Complexes

These are practically confined to the ammines, though one or two compounds of hydroxylamine and of hydrazine have been prepared. The ammines are formed almost exclusively by the chlorides, bromides, and iodides. Hüttig and his colleagues[391-3] have prepared these ammines by the action of gaseous ammonia on the dry halides, and have determined their dissociation tension. The tendency to co-ordinate falls off from calcium to barium; the mean values of the temperatures at which the dissociation pressure is 100 mm. are Ca 105·4°; Sr 71·9°; Ba 12·5°.

Oxygen Complexes

This is by far the largest group, as the ions of these elements, like those of magnesium, will take up a number of oxygenated organic molecules by co-ordination with the oxygen. There are clear indications that this power falls off from calcium to barium: thus the halides (and sometimes the hydroxide and nitrate as well) of barium will combine with glycerol, sugar-alcohols, sugars, carboxylic acids, and aminoacids; strontium halides will also combine with alcohol and acetone: calcium salts in addition to all these

[388] L. Hackspill and Winterer, *C.R.* 1930, **191**, 663.
[389] M. Trautz and A. Anschütz, *Z. physikal. Chem.* 1906, **56**, 240.
[390] A. E. Hill and S. F. Brown, *J.A.C.S.* 1931, **53**, 4319.
[391] Calcium: G. F. Hüttig, *Z. anorg. Chem.* 1922, **123**, 31.
[392] Strontium: id., ib. **124**, 322.
[393] Barium: G. F. Hüttig and W. Martin, ib. **125**, 269.

classes of compounds will co-ordinate with phenol catechol, acetals, aldehydes, esters, urea, and di- and tripeptides. The still greater co-ordinating power of beryllium has already been discussed.

This fall in the tendency to co-ordinate with oxygen as we go from calcium to barium is very clearly shown by the degree of hydration of the salt (see Table III, p. 221).

Chelate Oxygen Complexes

Practically the only neutral co-ordination compounds of these elements that are known are a small number of chelate derivatives of β-diketones, β-keto-esters, and α-dicarboxylic esters.

The acetylacetonates of all three elements can be made by the action of acetylacetone on the hydroxide,[394–5] or on an aqueous solution of the cyanide.[396] Unlike the magnesium compound they crystallize from solvents containing water with two molecules of water of crystallization, which are readily removed by warming *in vacuo*. These compounds are insoluble in water and only slightly soluble in alcohol, and are no doubt chelate compounds, with co-ordination numbers of 4 in the anhydrous and 6 in the hydrated state.

Derivatives of acetoacetic ester and of malonic ester[397] can be made from the cyanides in the same way. They are of the same MA_2 type; they do not seem to form hydrates.

These elements may form chelate oxygen-linked complexes also in the double oxalates, the only double salts of the alkaline earths that have any claim to be regarded as complex: but the evidence for their complexity is not strong.[398–400] The behaviour of the calcium derivatives of hydroxy-acids (lactic, citric, etc.) in giving solutions of low Ca^{++} content ('free' and 'bound' calcium) is of importance both chemically and physiologically.[401]

Complex Halides

No double halides of the alkaline earths have been isolated, but Noyes[402] has shown that the change with concentration of the transport number of barium chloride (and the calcium and strontium salts behave in the same way) indicates a certain amount of auto-complex formation in the solution; it is particularly noticeable that the nitrate does not show this effect, the NO_3 group having, in general, less tendency to complex formation than any other anion except ClO_4. In the following table the transport numbers (multiplied by 100) for barium chloride and barium nitrate are

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[394] S. Tanatar and E. Kurowski, *J. Russ. Phys. Chem. Ges.* 1908, **40**, 580 (*Chem. Centr.* 08. ii. 1096).

[395] H. Franzen and W. Ryser, *J. prakt. Chem.* 1913, [2] **88**, 297.

[396] G. T. Morgan and H. W. Moss, *J.C.S.* 1914, **105**, 195.

[397] H. Erdmann and E. van der Smissen, *Ann.* 1908, **361**, 66.

[398] R. Scholder, E. Gadenne, and H. Niemann, *Ber.* 1927, **60**, 1489.

[399] Id., ib. 1510.

[400] R. Scholder, ib. 1525.

[401] See *Recent Advances in Protein Chemistry*, 1945, vol. i.

[402] A. A. Noyes, *Z. physikal. Chem.* 1901, **36**, 63.

given, and for comparison those for potassium sulphate, as a uni-divalent salt which cannot be supposed to form a complex.

	K_2SO_4	$Ba(NO_3)_2$	$BaCl_2$
0·1 molar	49·31	45·50	41·47
0·02 molar	49·62	45·99	44·22
Difference	0·31	0·49	2·75

GROUP II B

GENERAL

As we have seen, the resemblance between the two divisions of Group II is much closer than that between those of Group I. While monovalent copper, silver, and gold scarcely resemble the alkali metals in anything except the valency, there is considerable resemblance between II A and II B, and in particular between zinc and cadmium in one subgroup and magnesium in the other, zinc being in a way intermediate between magnesium and cadmium. This is shown, for example, in the solubility of the sulphates, and also in the relatively low melting-points of the metals, zinc melting at 419° and cadmium at 321°, while magnesium, the most fusible of the A elements, melts at 649°.

In Group II, as in Group I, the B elements form covalent compounds much more readily than the A; thus of the 'calcides'* (binary compounds of elements of the oxygen group), all those of zinc, cadmium, and mercury have covalent lattices, with the unexplained exception of cadmium oxide, which has an NaCl structure[403]; so do the beryllium calcides, but those of magnesium and the alkaline earths all form ionic lattices except the one compound most likely to be covalent, magnesium telluride. Again, the B elements as usual show much more individuality than the A. Zinc and cadmium resemble one another fairly closely, though cadmium has a stronger tendency to co-ordination; the increase of this with atomic number is a normal characteristic of B elements, in contrast to A, where the change is in the opposite direction. But mercury differs greatly from the other two, and is in some ways the most peculiar of all the elements, especially in its tendency to be satisfied with a valency group of 4 shared electrons. Thus, while the rather low conductivity of $CdCl_2$ is due to auto-complex formation, giving $Cd[CdCl_3]_2$ and $Cd[CdCl_4]$, the much smaller conductivity of $HgCl_2$ in solution is not due to the formation of $Hg[HgCl_4]$, of which there is little evidence, but to the $HgCl_2$ molecules remaining in the covalent state. This stability of the shared quartet is a factor in the inertness of the alkyl compounds: while those of zinc and cadmium are spontaneously inflammable in air and at once decomposed by water, the mercury dialkyls are stable to both. Signs of a similar though smaller stability of a shared quartet are found in the aurous (I. 148), thallic (III. 464), plumbic compounds (IV. 592), and perhaps in those of bismuth (IV. 592).

Hence we can treat zinc and cadmium together, but mercury requires to be dealt with separately.

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* It is convenient to have general terms, corresponding to 'halogen', 'halide' for the elements of the oxygen–tellurium subgroup and their binary compounds, and the words 'chalkogen', 'chalkogenide' are often used. But it is obvious that they are derived from *calx*, lime, and not from χαλκός, copper, and so should be spelt calc-; also the compounds should be called calcides on the analogy of halides.

[403] V. M. Goldschmidt, *Geochem. Vert.* viii, 1927.

ZINC AND CADMIUM

THESE elements give cations of considerable deforming power (power of covalency formation), that of cadmium being much the stronger. Here again, as in Subgp. I B, the simple relation between size of ion and deforming power, so important among the A elements, no longer holds; the radii of the divalent ions are

Mg″	Ca″	Zn″	Cd″	Hg″
0·78	1·06	0·83	1·03	1·12

Magnesium and zinc are nearly the same size, and so are calcium, cadmium, and mercury; but the tendency to covalency formation is definitely stronger with zinc than with magnesium, and with cadmium and mercury than with calcium; moreover, it is much stronger with cadmium than with zinc, though the latter is smaller.

These are among the less common metals, especially cadmium, which is as rare as mercury; the amounts in g. per ton in the earth's crust according to Goldschmidt are

Zn	Cd	Hg
40	0·5	0·5

Cadmium is scarcely ever found except in zinc ores; blende usually contains from 0·1 to 0·2 per cent., and calamine 0·2–0·3 per cent.; it is separated from the zinc by means of its greater volatility.

The solubilities of the salts in water are usually similar to those of Group II A, and especially to those of magnesium. The chlorides, bromides, iodides, chlorates, and nitrates are all very soluble, and the hydroxides, sulphides, carbonates, and oxalates very insoluble. The solubilities of the chlorides, bromides, and iodides of zinc in water are enormous, and they are very large in organic solvents also, a characteristic of salts with highly deformable anions; those of cadmium are less soluble, owing no doubt to their much greater complex formation; in the chlorates, nitrates, and sulphates, where there is much less complex formation owing to the smaller deformability of these anions, the zinc and cadmium salts are about equally soluble. The values for the fluorides and sulphates in moles of salt to 100,000 moles water at 25° are:

Fluorides

Be	Mg	Ca	Sr	Ba	Zn	Cd
ca. 10,000	4	0·4	6	12	280	520

Sulphates

7,200	5,400	28	1	0·017	6,300	6,700

Metals

The melting-points, boiling-points, Trouton constants (heat of evapn./b. pt. °K.), and densities of these metals, together with those of magnesium and barium, are given in the table below:

	Zn	Cd	Hg	Mg	Ba
M. pt.	419°	321°	−38·9°	649°	850°
B. pt.	906°	764°	357°	1,100°	1,540°
Trouton	23·2	23·0	22·2	. .	. .
Density	7·14	8·64	13·59	1·74	3·6

The metals are practically entirely monatomic in the vapour above 1,000°, and also presumably in the liquid, since they give normal values of the Trouton constant. But enough diatomic molecules are present in the vapours of all three to give characteristic bands in the absorption spectra: and new bands of this kind are found with mixed vapours such as Zn—Hg and Cd—Hg,[404] and mixtures of Zn, Cd, and Hg with alkali metals[405]; it is, however, possible that the bands of cadmium are due to impurities.[406]

Hydrides

Zinc and cadmium have a small power of absorbing hydrogen, but there is no evidence that either of them can form a definite hydride.[407]

Carbides

Neither zinc nor cadmium seems to form a carbide M_2C. Zinc gives an acetylide ZnC_2 as a white powder when acetylene is passed into a solution of zinc ethyl in ligroin[408]; it is decomposed by water to give $Zn(OH)_2$, whereas the acetylides of beryllium, copper, and silver are hydrolysed only by acids or alkalies.

Similar acetylides of cadmium, such as CdC_2,C_2H_2 (or $Cd(C_2H)_2$, have also been made,[409] but these are stable to water and are not explosive.

ALKYL AND ARYL COMPOUNDS

The zinc alkyls were the first of the metallic alkyls to be discovered (E. Frankland, 1849); but they are less well known than those of magnesium, though better than those of cadmium. They may be divided into the alkyl and aryl metallic halides, the dialkyls, and the diaryls; the first of these classes is known with zinc but not with cadmium.

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[404] J. G. Winans, *Phys. Rev.* 1928, **32**, 427; *Phil. Mag.* 1929, **7**, 565.

[405] S. Barratt, *Trans. Far. Soc.* 1929, **25**, 759.

[406] J. M. Walter and S. Barratt, *Proc. Roy. Soc.* 1929, **122**, 201.

[407] For zinc see F. Paneth, M. Mathies, and E. Schmidt-Hebel, *Ber.* 1922, **55**, 787.

[408] J. F. Durand, *C.R.* 1923, **176**, 992.

[409] K. Gebauer, *Z. anorg. Chem.* 1928, **176**, 283.

Zinc Alkyl and Aryl Halides[410]

These compounds have a much smaller practical importance than the Grignard reagents. As zinc has less affinity for oxygen and the halogens than magnesium, they are less reactive, but they can sometimes be used when the Grignard reagents would go too far, as, for example, in preparing a ketone from an acyl chloride, which with a magnesium compound would react further to produce a tertiary alcohol. Their use in syntheses is largely due to Blaise.[411,412] Their reactions are interfered with by ether, and as a solvent Blaise uses a mixture of ethyl acetate and toluene.

The solution of the alkyl zinc iodide is a rather viscous colourless liquid which fumes strongly in air and is very easily oxidized.

In the absence of a solvent the compound can be made, as Frankland showed,[413] as a white crystalline solid stable in carbon dioxide but at once decomposed by air or water. The corresponding chlorides, bromides, and cyanides are even more readily oxidized than the iodides.[414]

With secondary iodides, petroleum ether must be used instead of aromatic hydrocarbons, which would be alkylated if present while the alkyl zinc halide was being formed, though not afterwards. Zinc reacts with a secondary iodide very readily, but the yield is not more than 60 per cent.; tertiary iodides cannot be made to give satisfactory yields at all.

Aryl zinc halides are made by treating the Grignard reagent with a solution of zinc chloride in ether, adding toluene, and evaporating off the ether, when a toluene solution is obtained.

In general, an alkyl zinc halide will not react in the cold with a simple organic halide, ether, ketone, or ester, or with a double carbon link, but it will often do so if these groups have an electronegative group attached to the same atom: for example, with chlorine in an acid chloride, and with the carbonyl group in ethyl oxalate or chloracetyl chloride.[411]

Zinc Dialkyls and Diaryls

Zinc ethyl was first prepared by Frankland in 1849[415] by heating zinc with ethyl iodide to 150° in an autoclave; it was of great theoretical importance for determining (through its vapour density) the atomic weight of zinc, and also for leading to a number of organic syntheses, of the kinds now carried out more easily by means of the Grignard reagents.

The zinc alkyls can be made under ordinary pressure by heating zinc with alkyl iodide (not bromide) at the boiling-point of the latter, when the whole is converted into the alkyl zinc iodide. The temperature is then raised, and the zinc dialkyl distils over:

$$2\ \text{Alk—Zn—I} = \text{Zn(Alk)}_2 + \text{ZnI}_2.$$

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[410] See Krause and v. Grosse, pp. 61–8.

[411] See his summary: E. Blaise, *Bull. Soc. Chim.* 1911, [4] 9, i–xxvi (*Chem. Centr.* 1911, i. 1807–9).

[412] C. R. Noller, *J.A.C.S.* 1929, **51**, 594.

[413] E. Frankland, *Ann.* 1855, **95**, 36.

[414] A. Job and R. Reich, *Bull. Soc. Chim.* 1923, [4] **33**, 1414.

[415] *Ann.* 1849, **71**, 171; see also *Phil. Trans.* 1852, **142**, 417; *Ann.* 1853, **85**, 329.

The reactions must be carried out in complete absence of air, usually in a stream of carbon dioxide.

The reaction goes more slowly than with magnesium, but it can be hastened by a variety of catalysts: zinc–copper couple (essentially zinc superficially alloyed with copper) is more reactive than pure zinc, and an alloy of zinc with 5–8 per cent. copper is found to be equally effective; zinc which has previously been etched with sulphuric acid can also be used. Iodine and ethyl acetate also have a catalytic effect; but it is to be noticed that ether has no effect whatever. The dialkyls can also be made by the action of metallic zinc on the mercury dialkyls or, better, by heating the Grignard reagents with zinc chloride.

The zinc alkyls are colourless volatile liquids.

Compound	*B. pt.*	*F. pt.*	*Trouton*
$ZnMe_2$[a]	44°	−29·2°	22·5
$ZnEt_2$	117·6°	−30·0°	24·6
Zn—a—Pr_2	139·4°	−83°	23·3
Zn—a—Bu_2	201·1°	−57·7°	21·7

(Primary propyl and primary normal butyl)

a = [417]

The infra-red and Raman spectra indicate that the dimethyl has a linear C—Zn—C group, with an eclipsed arrangement of the methyls.[416] They are very stable by themselves; they can be kept indefinitely even in the light, and can be distilled up to over 200° without decomposition: in this stability they differ from their cadmium analogues. They have been shown to be monomolecular both in the vapour state[416,418] and in benzene at the freezing-point.[419] Zinc ethyl has the low dielectric constant of 2·55[419] (compare benzene 2·29, carbon disulphide 2·63: the group C—Zn—C like C—Mg—C is no doubt linear); it is a non-conductor in the pure state, but has a specific conductivity of 10^{-4} in ether.[420]

These alkyls are extremely readily attacked by oxygen and by many compounds containing oxygen or other electronegative elements. The lower members catch fire in air very easily; the higher members (i.e. those with a smaller zinc content) from the diamyl compound upwards fume violently in air, but do not always catch fire. On more gradual oxidation zinc methyl at low temperatures gives the methyl-methylate

$$CH_3—Zn—O—CN_3,$$

and zinc ethyl at rather higher temperatures a compound $Zn(C_2H_5)_2O_2$

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[416] H. W. Thompson, J. W. Linnett, and F. J. Wagstaffe, *Trans. Far. Soc.* 1940, **36**, 797.

[417] C. H. Bamford, D. L. Levi, and D. M. Newitt, *J.C.S.* 1946, 468.

[418] A. W. Laubengayer and R. H. Fleckenstein, *Z. anorg. Chem.* 1930, **191**, 283.

[419] F. Hein and H. Schramm, *Z. physikal. Chem.* 1930, **149**, 408.

which has oxidizing properties, and seems to be a peroxide.[421-2] They react with water, alcohols, ammonia, etc., in the same way as the Grignard reagents, but differ from the latter in not reacting with carbon dioxide, in which they can be prepared. Many of the synthetic reactions of the Grignard reagents had previously been worked out with the zinc dialkyls.

Zinc Diaryls

These are white crystalline solids, which can be made from metallic zinc and the mercury diaryls.[423] Their melting-points are: zinc diphenyl b. pt. 283°, m. pt. 107°; di-*p*-fluorophenyl m. pt. 135°; di-*o*-tolyl 208°; di-β-naphthyl 185°. They are not spontaneously inflammable, but are very readily oxidized.

All attempts to prepare zinc dibenzyl by the action of zinc on mercury dibenzyl were failures, the only product being dibenzyl.

Cadmium Alkyls and Aryls

The alkyl and aryl cadmium halides are unknown.

Cadmium diethyl was first made in an impure state by Wanklyn in 1856[424] by the action of cadmium on ethyl iodide; some sixty years later Hilpert and Grüttner[425] made cadmium diphenyl from mercury diphenyl, and soon after this Krause[426] showed that the dialkyls can be made much more easily from the Grignard reagents and cadmium bromide. They can also be made in solution by adding cadmium chloride to the Grignard reagent in ether.[427]

The boiling- and melting-points of some of the cadmium dialkyls are given in the following table:

	B. pt.	*at mm.*	*M. pt.*
Cadmium Dimethyl	105·5°	760	−4·5°
Diethyl	64°	19·5	−21°
Di-*n*-propyl	84°	21·5	−83°
Di-*n*-butyl	103·5°	12·5	—48°
Di-*iso*-butyl	90·5°	20	—37°
Di-*iso*-amyl	121·5°	15	*ca.*—115°

The cadmium dialkyls are markedly less stable in themselves than those of the other metals. Only the dimethyl compound (like mercury and boron methyls, but unlike those of lithium and beryllium) can be kept without decomposition. The rest, especially in the light, soon deposit a black precipitate of metallic cadmium; if they are heated to 150° or above they decompose, often with violence. Though they show this tendency to

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[421] H. W. Thompson and N. S. Kelland, *J.C.S.* 1933, 746, 756.

[422] C. H. Bamford and D. M. Newitt, ib. 1946, 688.

[423] K. A. Kozeschkow, A. N. Nesmejanov and W. I. Potrosov, *Ber.* 1934, **67**, 1138.

[424] J. Wanklyn, *J.C.S.* 1857, **9**, 193.

[425] S. Hilpert and G. Grüttner, *Ber.* 1913, **46**, 1682.

[426] E. Krause, ib. 1917, **50**, 1813.

[427] P. L. de Bennoville, *J. Org. Chem.* 1941, **6**, 462.

dissociate, in most of their reactions they are less active than the zinc alkyls, though more so than those of mercury.[428] In the air they evolve clouds of cadmium oxide smoke, but they only catch fire under special circumstances, as when dropped on filter-paper. When put into water they sink to the bottom in large drops, which decompose in a series of sudden explosive jerks, with a crackling sound, which may go on for hours. Their boiling-points are much higher than those of their zinc and even sometimes of the mercury analogues: for example, $ZnMe_2$ 46°; $CdMe_2$ 105·5°; $HgMe_2$ 92°.

Cadmium diphenyl[425] can also be made[429] by the action of cadmium bromide on a solution of lithium phenyl in ether in an atmosphere of nitrogen. It melts at 173-4°; it behaves like the dialkyl with oxygen, water, and most other reagents; it will exchange its phenyl groups with mercuric chloride, stannic chloride, and antimony trichloride.

Cyanides

Zinc cyanide, $Zn(CN)_2$, can be made by the action of cyanogen gas on the metal at 300° (Berthelot); by dissolving zinc oxide in prussic acid, or by precipitating a solution of a zinc salt with potassium cyanide; it is a white powder practically insoluble in water and alcohols. It is one of the most stable of cyanides to heat; it only loses (by volatilization) 1 per cent. of its weight on ignition for half an hour.[430] It dissolves readily in solutions of alkaline cyanides to give complexes.

Cadmium cyanide, $Cd(CN)_2$, is similar, but is more soluble in water (1·71/15°) and slightly soluble in alcohol. It also readily forms complex cyanides.

Nitrides

Zinc nitride, Zn_3N_2, is very difficult to prepare in the pure state. It can be made[431] (1) by heating zinc amide $Zn(NH_2)_2$ to 330°; (2) by heating zinc dust to 600° in a stream of ammonia. It is a blackish-grey, definitely crystalline substance, and gives clear X-ray lines. The heat of formation of the solid from the metal and nitrogen gas is 5·3 k.cals.

Zinc amide, $Zn(NH_2)_2$, was first obtained by Frankland[432] by the action of ammonia on zinc ethyl. Juza and his colleagues[433] made it by Frankland's method, using an ethereal solution of zinc ethyl; after 5 hours in ammonia at 150° it contains a small amount of carbon, probably as $Zn(NH_2)Et$. It is a white powder, which is decomposed by water and acids. At 200° it begins to lose ammonia and forms the nitride Zn_2N_2.

Cadmium nitride, Cd_3N_2, is said to occur[434–5] but has never been analysed.

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[428] H. Gilman and J. F. Nelson, *Rec. Trav.* 1936, **55**, 518.

[429] A. N. Nesmejanov and L. G. Makarova, *J. Gen. Chem. Russ.* 1937, **7**, 2649.

[430] W. Truthe, *Z. anorg. Chem.* 1912, **76**, 154.

[431] R. Juza, A. Neuber, and H. Hahn, ib. 1938, **239**, 273.

[432] E. Frankland, *J. prakt. Chem.* 1858, **73**, 35.

[433] R. Juza, K. Fasold, and W. Kuhn, *Z. anorg. Chem.* 1937, **234**, 86.

[434] F. Fischer and F. Schröter, *Ber.* 1910, **43**, 1465.

[435] H. B. Baker and R. J. Strutt, ib. 1914, **47**, 1049.

Cadmium amide, $Cd(NH_2)_2$, can be made by the action of potassamide KNH_2 on cadmium cyanide or thiocyanate in liquid ammonia. It is a white substance which reacts violently with water to give cadmium hydroxide and ammonia, and explodes on rapid heating with separation of metallic cadmium.

Oxides

The supposed suboxides Zn_2O and Cd_2O are only mixtures of the normal oxides with the metal.[436-7]

The normal oxides ZnO and CdO are easily made by burning the metal in air; zinc oxide from its flocculent appearance was known as flowers of zinc or philosophical wool. These oxides have a large heat of formation, and so are very stable.

Zinc oxide melts at 2,000°, or above, and sublimes under 1 atmosphere pressure at about 1,720°[438]; it has a covalent (wurtzite) lattice.[439,440]

In the pure state it is colourless when cold, but yellow above 250°. Its properties depend largely on its method of preparation: a specimen made by dehydrating the hydroxide at 100° had nearly 1,000 cals. more energy per ZnO than one dehydrated at 600°.[441-2]

Cadmium oxide at the ordinary temperature has any colour from brownish-yellow to black, according to the way it is made; when cooled in liquid air it is similar to zinc oxide, but it has a sodium chloride (ionic) lattice[443]; it sublimes at 1,930°.[444]

Hydroxides

The hydroxides $Zn(OH)_2$ and $Cd(OH)_2$ are definite crystalline compounds: $Cd(OH)_2$ has a cadmium iodide (brucite) lattice, like magnesium hydroxide[445]; the crystal structure of zinc hydroxide is different[446]; with cadmium the X-ray results show that no other solids are formed than CdO and $Cd(OH)_2$.[447] They are, however, stable only over a limited range. Hüttig has shown[441] that below +39° zinc oxide and water react with fall in free energy to give the hydroxide $Zn(OH)_2$; above this temperature the oxide alone is stable. With cadmium[447] the relations seem to be very similar. (Mercuric hydroxide $Hg(OH)_2$ does not occur as a solid phase at all.)

Both the hydroxides are nearly insoluble in water, but are soluble in ammonia owing to the formation of amines; zinc oxide dissolves in excess

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[436] W. R. A. Hollens and J. F. Spencer, *J.C.S.* 1934, 1062.

[437] R. E. Hedger and H. Terrey, *Trans. Far. Soc.* 1936, **32**, 1614.

[438] G. F. Hüttig and K. Toischer, *Z. anorg. Chem.* 1932, **207**, 273.

[439] W. H. Zachariasen, *Z. Phys.* 1927, **40**, 637.

[440] S. Tolksdorf, *Z. physikal. Chem.* 1928, **132**, 161.

[441] G. F. Hüttig and H. Möldner, *Z. anorg. Chem.* 1933, **211**, 368.

[442] R. Fricke and F. Blaschke, *Z. Elektrochem.* 1940, **46**, 46.

[443] V. M. Goldschmidt, *Geochem. Vert.* viii, Oslo, 1927.

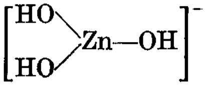
[444] E. J. Kohlmeyer, *Metall. Erz.* 1929, **26**, 62.

[445] G. Natta, *Gaz.* 1928, **58**, 344.

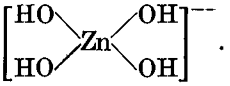
[446] C. Gottfried and H. Mark, *Z. Krist.* 1927, **65**, 416.

[447] G. F. Hüttig and R. Mytyzek, *Z. anorg. Chem.* 1930, **190**, 353.

of alkali, but cadmium oxide does not. Cadmium has less acidic character (less power of forming the anions $[HO—M—O]^-$ and $[O—M—O]^{--}$) than zinc; this power always diminishes (even in B subgroups) with rise of atomic number. From a solution of zinc oxide in very concentrated alkali a series of readily soluble and highly hydrolysed zincates can be prepared,[448] such as $Na[HO—Zn—O]$, 4 and 1 H_2O, and $Na_2[ZnO_2]$, 4 and 2 H_2O; the anions should perhaps be written



and



The corresponding cadmiates, such as Na_2, $Cd(OH)_4$, and $Ba_2Cd(OH)_6$, have recently[449] been made, though less easily, from very concentrated alkali. No mercurates could be made in this way, the product being crystalline mercuric oxide.

Peroxides

Indefinite hydrated peroxides can be obtained from zinc and cadmium hydroxides by treatment with hydrogen peroxide[450-1]; but neither element forms a definite peroxide by direct combination with oxygen. Zinc oxide will not take up any more oxygen even under 12 atmospheres pressure. Cadmium, however, seems to have a slight tendency to form a peroxide directly: the oxide formed by burning cadmium in air contains a small amount of peroxide. (Among the alkaline earth metals, which give peroxides much more readily, the tendency increases with the atomic number.)

Sulphides, Selenides, and Tellurides

These compounds are all insoluble crystalline substances with covalent 4:1 lattices (zinc blende or wurtzite or both); the colour darkens as the atomic weight of either constituent increases, being white for zinc sulphide, yellow for cadmium sulphide, zinc selenide, and cadmium selenide, red for zinc telluride, and black for cadmium telluride.

Zinc sulphide, ZnS, occurs in nature as zinc blende, the chief ore of zinc; 'Sidot's blende', containing traces of manganese and copper, is very sensitive to radium and X-rays, and hence is often used for X-ray screens. It is dimorphic, the low-temperature zinc-blende form changing at 1,020°.

From their heats of solution in hydrochloric acid it appears that the heat of transformation of sphalerite into wurtzite is 3·19 k.cals/mol.[452] It begins to sublime at 1,200°, and melts under pressure at 1,800–1,900°. When ignited in the air it burns to zinc oxide. *Zinc selenide* and *telluride* are similar, and have zinc blende lattices.[453-4]

[448] R. Scholder and H. Weber, *Z. anorg. Chem.* 1933, **215**, 355.

[449] R. Scholder and E. Staufenbiel, ib. 1941, **247**, 259.

[450] Zinc: G. Cogné, *C.R.* 1938, **206**, 1119.

[451] Cadmium: T. R. Perkins, *J.C.S.* 1929, 1687.

[452] A. F. Kapustinski and L. G. Tschentzova, *C. R. Acad. Sci. U.R.S.S.* 1941, **30**, 489.

[453] W. H. Zachariasen, *Z. physikal. Chem.* 1926, **124**, 436.

[454] Id., ib. 277.

Cadmium sulphide, CdS, occurs as the mineral Greenockite. It has a wurtzite lattice[455]; its colour varies from lemon-yellow to brown according to the method of preparation. It begins to sublime about 1,000°, and melts at 1,750°; 0·13 mg. will dissolve in 100 g. water at 18°.

The *selenide* (wurtzite lattice[453]) melts at 1,350° and the *telluride* (zinc blende lattice[454]) at about 1,050°, but at this temperature is already dissociating with volatilization of metallic cadmium.[456]

Halides

The following table gives some of the properties of the compounds.

	ZnF_2	$ZnCl_2$	$ZnBr_2$	ZnI_2	CdF_2	$CdCl_2$	$CdBr_2$	CdI_2
M. pt.	872°	275°	390°	446°	1,110°	568°	585°	381°
B. pt.	..	720°	670°	..	1,200°	964°	863°	..
*G./100 g. water	$1{\cdot}62_{20}$	420_{25}	488_{25}	730_{25}	$4{\cdot}34_{25}$	115_{20}	115_{20}	$85{\cdot}5_{25}$
Hydration	4, 0	4, 3, 2·5, 1·5, 1, 0	3, 2, 0	4, 2, 0	0	4, 2·5, 1, 0	4, 1, 0	0
Hydrn: Hg″	2	0	0	0				

* Subscript numbers give the temperature.

Hydration of other Salts of Zn, Cd, Hg

	Zinc	*Cadmium*	*Mercuric*
Nitrate	9, 6, 3, 2	9, 4, 2	8, 1/2
Sulphate	7, 6, 5, 3 2, 1	7, 8/3, 1	2, 1
Carbonate	1, 1/2	1/2	..
Oxalate	2	3, 2	0
Acetate	3, 2	3	0
Chlorate	6, 4, 2	2	..
Bromate	6	2, 1	2
Iodate	2	1	0
Average highest	4·7 (9)	3·7 (9)	2·6 (7)

Fluorides

Zinc fluoride ZnF_2. This forms a tetrahydrate and an anhydrous salt; sol^y 1·62/20°; it forms no 'acid' fluorides.[457-8]

Cadmium fluoride, CdF_2, is similar; it melts at 1,110°[459] and unlike the zinc salt is not volatile even at 1,200°. It can be made[457,460] by adding ammonium fluoride to a cadmium chloride solution; its solubility in water is 4·34/25° and only 2·30/61°.

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[455] W. L. Bragg, *Phil. Mag.* 1920, **39**, 647.

[456] M. Kobayashi, *Z. anorg. Chem.* 1911, **69**, 1.

[457] A. Kurtenacker, W. Finger, and F. Hey, ib. 1933, **211**, 89.

[458] For the basic fluorides, their stability relations and X-ray structures see W. Feitknecht and H. Bucher, *Helv. Chim. Acta*, 1943, **26**, 2177 (cadmium); 2196 (zinc).

[459] N. A. Puschin and A. V. Baskow, *Z. anorg. Chem.* 1913, **81**, 358.

[460] P. Nuka, ib. 1929, **180**, 235.

Chlorides, Bromides, and Iodides

All the other halides of these two metals are extremely soluble in water and tend more or less to form auto-complexes. It is generally assumed that this tendency is much stronger with cadmium than with zinc, but recent work makes this very uncertain, and suggests that the greater abnormality of the cadmium halides in solution is due in part to their having something of the tendency which is so marked in mercury to go into the non-complex dicovalent form hal-M-hal.

Zinc Chloride

This melts at 275° and is very readily super-cooled; it boils without decomposition at 720°. Its vapour density at 900° corresponds to $ZnCl_2$.[461] It is very difficult to remove the last traces of water from the solid, which is said to be as hygroscopic as phosphorus pentoxide. It is one of the most soluble of solids; it forms several hydrates: the compositions and transition-points of the various solid phases in the system $ZnCl_2—H_2O$ are as follows:

$$\text{Ice} \underset{-62^\circ}{\rightleftharpoons} 4\,\text{aq.} \underset{-30^\circ}{\rightleftharpoons} 3\,\text{aq.} \underset{+6}{\rightleftharpoons} 2\,1/2\,\text{aq.} \underset{+11{\cdot}5^\circ}{\rightleftharpoons} 1\,1/2\,\text{aq.} \underset{26^\circ}{\rightleftharpoons} 1\,\text{aq.} \underset{28^\circ}{\rightleftharpoons} 0$$

It is very soluble not only in water (420/25°) but also in many organic solvents containing oxygen or nitrogen, such as alcohols, ethers, esters, ketones (43·5/18° in acetone), furfurol, as well as amines and nitriles.

The hydrolysis of the aqueous solution is remarkably small; a value of 0·0006 per cent. (6 parts per million) in 0·25 molar solution at 18° was found by E.M.F. measurements,[462] and 0·1 per cent. in 0·06 molar solution at 100° by the inversion of cane sugar.[463]

Various basic halides such as $Zn(hal)_2, 4\,Zn(OH)_2$, and $Zn(hal)_2, 3\,Zn(OH)_2$ are known, and their X-ray analysis shows that they have layer lattices with the normal salt and the hydroxide in alternate layers, and cannot have the 'hexol' structures suggested by Werner.[464]

Zinc Bromide

This is very similar to the chloride. It forms hydrates with 3 and 2 H_2O, the latter going to the anhydrous salt at 37°. It is even more soluble in water (488/25°).[465] It is easily soluble in alcohol, but less so in ether. There is evidence of complex formation in solution: Hittorf showed[466] that in 4-molar solution the transport number of the zinc is negative, and Parton and Mitchell,[467] determining by E.M.F. the activity coefficients of the zinc halide, showed that these indicated that the dissociation of the chloride is less complete than that of the bromide and iodide.

[461] V. Meyer and C. Meyer, *Ber.* 1879, **12**, 1195.
[462] K. Drucker, *Z. Elektrochem.* 1912, **18**, 244.
[463] H. Ley, *Z. physikal. Chem.* 1899, **30**, 226; C. F. Kullgren, ib. 1913, **85**, 473.
[464] W. Feitknecht, *Helv. Chim. Acta*, 1930, **13**, 22; 1933, **16**, 427.
[465] R. Dietz, *Z. anorg. Chem.* 1899, **20**, 247.
[466] W. Hittorf, *Z. physikal. Chem.* 1903, **43**, 249.
[467] H. N. Parton and J. W. Mitchell, *Trans. Far. Soc.* 1939, **35**, 758.

Zinc Iodide

This salt melts at 446°. It is the most soluble of these halides; sol^y 730/25° (26·4 mols. per cent.). Like the bromide it is easily soluble in alcohol, but less in ether.

The E.M.F. measurements of Bates[468] indicate that zinc iodide behaves in water as a normal electrolyte so long as the concentration does not exceed 0·8-molar; but Hittorf[469] has shown that in concentrated solution the transport number of the zinc becomes negative and van Rysselberghe, Grinnell, and Carlson[470] that a mixture of zinc and potassium iodides at a total concentration of 4-normal has a molecular conductivity some 10 per cent. less than that calculated from the values for its components.

Cadmium Chloride

Cadmium chloride melts at 568° and boils at 964°.[471] It forms a series of hydrates with the following transition points:

$$\text{Ice} \underset{-9^\circ}{\rightleftharpoons} 4\text{ aq.} \underset{-5^\circ}{\rightleftharpoons} 2\,1/2\text{ aq.} \underset{+34^\circ}{\rightleftharpoons} 1\text{ aq.} \underset{ca.\ 100}{\rightleftharpoons} 0\text{ aq.}$$

Solubilities are water 115/20°; CH_4OH 1·71/15°; C_2H_5OH 1·52/15°; benzonitrile 0·063/15°. It is also slightly soluble in acetone but not in dry ether.

Basic chlorides with layer lattices like those of zinc chloride are known.[472]

Cadmium Bromide

M. pt. 585°, b. pt. 863°; vapour density at 920° normal[473]; its hydrates and their transition points are:

$$4\text{ aq.} \underset{+36^\circ}{\rightleftharpoons} 1\text{ aq.} \underset{ca.\ 100^\circ}{\rightleftharpoons} 0\text{ aq.}$$

The solubilities are: water 115/20°[474]; acetone 1·56/18°[475]; benzonitrile 0·857/18°; ethyl alcohol 26·5 g. $CdBr_2$, 4 aq./15°; ether 0·4 g. $CdBr_2$, 4 aq./15°.

Cadmium iodide melts at 381°.[476] It forms no hydrates. Its solubility in water is: 85·5/25°,[477] in organic solvents:

Methyl alcohol	153, 7/20°	Acetone	25/18°
Ethyl ,,	74·3/20°	$C_6H_5\cdot CN$	1·63/18°
Propyl ..	40·7/20°	Benzene	0·047/16°
Ether ,,	0·143/20°		

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[468] R. G. Bates, *J.A.C.S.* 1938, **60**, 2983.

[469] W. Hittorf, *Pogg. Ann.* 1859, **106**, 513.

[470] P. van Rysselberghe, S. W. Grinnell, and J. M. Carlson, *J.A.C.S.* 1937, **59**, 336.

[471] K. Hachmeister, *Z. anorg. Chem.* 1920, **109**, 153.

[472] W. Feitknecht and W. Gerber, *Z. Krist.* 1937, **98**, 168.

[473] V. and C. Meyer, *Ber.* 1879, **12**, 1284.

[474] O. H. Weber, *Z. anorg. Chem.* 1899, **21**, 359.

[475] A. Naumann, *Ber.* 1904, **37**, 4337.

[476] G. C. Schmidt and R. Walter, *Ann. Phys.* 1923, [4] **72**, 575.

[477] E. Cohen, C. W. G. Hetterschij, and A. L. T. Moesveld, *Z. physikal. Chem.* 1920, **94**, 224.

Behaviour of the Cadmium Halides in Water

There is abundant evidence that these halides of cadmium do not behave as normal electrolytes in aqueous solution. This is most clearly shown by the fall in the molecular conductivity with increasing concentration, as compared with that of a normal di-univalent salt such as magnesium chloride. The relative values of the molecular conductivity ($\Lambda_\infty = 1$) are as follows (the value for mercuric chloride would be *ca.* 0·01):

Dilution	$CdCl_2$	$CdBr_2$	CdI_2	$MgCl_2$	$Cd(NO_3)_2$	$ZnCl_2$
$V = 100$	0·72	0·66	0·55	0·84	0·86	0·87
10	0·43	0·39	0·26	0·75	0·72	0·73
1	0·19	0·16	0·13	0·50	0·48	0·49

The same conclusion follows from E.M.F. measurements.[478] It will be seen that the abnormality is very great with the cadmium halides and increases with the atomic number of the halogen, while it is barely perceptible with zinc chloride. Cadmium nitrate (the nitrate ion is very slightly deformable) shows it to the same minute extent as zinc chloride.

This may be due (1) to the imperfect dissociation of the simple halide—to the presence of undissociated molecules of hal-Cd-hal and undissociated cations $[\text{Cd-hal}]^+$; or (2) to the formation of complex anions $[Cd(hal)_3]^-$ and $[Cd(hal)_4]^{--}$. The evidence shows that both these phenomena occur, so that the problem is very complicated. From E.M.F. measurements with cadmium electrodes Riley and Gallafent[479] have got concordant values for the concentrations of the various molecular species, which are confirmed by the freezing-points. In a solution containing 0·01 molar cadmium in all its forms they find the following percentages:

	$CdCl_2$	$CdBr_2$	CdI_2
Cd^{++}	41·0	32·8	23·1
$Cd(hal)^+$ . . .	56·3	60·6	66·4
$Cd(hal)_2$ . . .	3·9	6·5	6·9
$\left.\begin{array}{l}[Cd(hal)_3]^- \\ [Cd(hal)_4]^{--}\end{array}\right\}$ . .	0·05	0·17	0·47

The $[Cd(hal)_3]^-$ ions are found to be about 25 times as many as the $[Cd(hal_4)]^{--}$; but the values for the complex ions are scarcely more than orders of magnitude.

The results are confirmed by the conductivity measurements of Righellato and Davies,[480] and the E.M.F. values of Bates and Vosburgh.[481-3]

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[478] G. Soatchard and F. R. Tefft, *J.A.C.S.* 1930, **52**, 2270.

[479] H. L. Riley and V. Gallafent, *J.C.S.* 1932, 514.

[480] E. L. Righellato and C. W. Davies, *Trans. Faraday Soc.* 1930, **26**, 592.

[481] R. G. Bates and W. C. Vosburgh, *J.A.C.S.* 1937, **59**, 1583.

[482] Id., ib. 1938, **60**, 137.

[483] R. G. Bates, ib. 1939, **61**, 308.

OXY-SALTS OF ZINC AND CADMIUM

O—C Salts: I. *Carbonates*

The carbonates of zinc and cadmium are much less stable than those of the alkaline earths. $CdCO_3$ has a dissociation pressure of 1 atmosphere at 350°, and $ZnCO_3$ at about the same temperature.[484-5] Here again we find a similarity to magnesium, for which the pressure is 1 atmosphere at 540°, compared with 900° for calcium and 1,330° for barium.

Acetates

Zinc acetate crystallizes with 2 H_2O. The anhydrous salt melts at 244,[486] and under 150 mm. pressure sublimes undecomposed at 200°.[487] It is very soluble in water (41·6/100 at 150°), and in organic compounds of oxygen (methyl (not ethyl) alcohol, acetone, acetyl chloride, acetic anhydride, ethyl acetate, methyl sulphate, epichlorhydrin) and of nitrogen (aniline, pyridine, benzonitrile). For its conversion into the 'basic' acetate, and the structure of the latter, see p. 283.

Cadmium acetate can be made by boiling the nitrate with acetic anhydride[488]; it melts at 255°. It forms a very soluble trihydrate.

Oxalates

Zinc oxalate crystallizes with 2 H_2O which it loses at 140°. It is only very slightly soluble in water (2·09 mg./18°).[489]

Cadmium oxalate is very similar; it forms a trihydrate, sol^y 5·0 mg./18°.[489] The supposed cadmous oxide Cd_2O left on igniting the oxalate is really a mixture of the metal with the oxide CdO.

Scholder[489] has examined the conductivity of saturated solutions of the oxalates of divalent metals in water; the fall with rise of concentration shows clearly that there is considerable auto-complex formation with cadmium oxalate, and even more with zinc oxalate. Other evidence that cadmium co-ordinates less readily with oxygen than zinc does will be given later (p. 281).

O—N Salts: Nitrites

Zinc nitrite, $Zn(NO_2)_2$, is so easily hydrolysed that it cannot be prepared from water, from which only basic salts will separate; but it can be got in a fairly pure state by treating sodium nitrite with zinc sulphate in alcoholic solution, filtering, and evaporating.[490]

Cadmium nitrite, though it is very unstable and readily hydrolysed, can be obtained from aqueous solutions of cadmium chloride and silver nitrite or cadmium sulphate and barium nitrite. It is very soluble in water. The

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[484] G. F. Hüttig, A. Zörner, and O. Hnevkovsky, *Mon.* 1938, **72**, 31.

[485] A. Rose, *C.R.* 1939, **208**, 905.

[486] J. Peterson, *Z. Elektrochem.* 1914, **20**, 328.

[487] A. P. N. Franchimont, *Ber.* 1879, **12**, 13.

[488] E. Späth, *Mon.* 1912, **33**, 235.

[489] R. Scholder, *Ber.* 1927, **60**, 1510.

[490] F. Ephraim and E. Bolle, *Ber.* 1915, **48**, 643.

dry salt decomposes at 150° to cadmium nitrate and oxide and nitric oxide.

Nitrates

Zinc nitrate, sol^y 127/25°, forms a series of hydrates with the following transition points:[491]

$$\text{Ice} \underset{-25^\circ}{\rightleftharpoons} 9\text{ aq.} \underset{-18^\circ}{\rightleftharpoons} 6\text{ aq.} \underset{+35^\circ}{\rightleftharpoons} 3\text{ aq.}$$

Cadmium nitrate is very similar. It forms the hydrates:

$$\text{Ice} \underset{-13^\circ}{\rightleftharpoons} 9\text{ aq.} \underset{0^\circ}{\rightleftharpoons} 4\text{ aq.} \underset{65^\circ}{\rightleftharpoons} 2\text{ aq.}$$

Sol^y 134·4/25°.[492] The anhydrous salt melts at about 360°; it is soluble in ethyl acetate, but not in pyridine or benzonitrile.

O—S Salts: Sulphites

Zinc sulphite[493] crystallizes with 2·5 H_2O. Sol^y 0·13/ord. temp. It is very readily oxidized in air to the sulphate.

Cadmium sulphite crystallizes with 2 H_2O; it is slightly soluble in water.[494]

Sulphates

Zinc sulphate forms hydrates with 7, 6, ? 5, ? 4, ? 3, 2 and 1 H_2O.[495] The heptahydrate is a vitriol, and forms the usual double salts of the type of K_2SO_4, $ZnSO_4$, 6 H_2O; it goes over into the hexahydrate at 38°.[496] The solubilities are: 57·5/25°[497]; methyl alcohol 0·65/18°.[498]

Cadmium sulphate in the anhydrous form melts at 1,000°.[499] It is rather more soluble in water than the zinc salt (77·2/25°); the crystalline hydrates include a peculiar form of the composition $CdSO_4$, 8/3 H_2O, which has a large stability range, from −18° to +75°[500]; its crystal structure has been worked out in detail by Lipson.[501] The normal heptahydrate vitriol can be prepared but it is always metastable to the 8/3 hydrate; the only other is the monohydrate, whose solubility (like that of many other sulphates) falls rapidly with a rise of temperature, being 86·9/75° and 60·8/100°.[500] The salt is very slightly soluble in methyl and ethyl alcohols, and in ethyl acetate.

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[491] R. Funk *et al.*, *Z. anorg. Chem.* 1899, **20**, 398; *Ber.* 1899, **32**, 99.

[492] Id. *Wiss. Abh. Reichsanst.* 1900, **3**, 440.

[493] W. E. Henderson and H. B. Weiser, *J.A.C.S.* 1913, **35**, 239.

[494] K. Seubert and M. Elten, *Z. anorg. Chem.* 1893, **4**, 62.

[495] P. Vallet and M. Bassière, *Bull. Soc. Chim.* 1938, [v] **5**, 546.

[496] E. Cohen and L. R. Sinnige, *Z. physikal. Chem.* 1909, **67**, 432, 513: E. Cohen, *Z. Elektrochem*, 1909, **15**, 600.

[497] E. Cohen and A. L. T. Moesvold, *Proc. Akad. Amst.* 1925, **28**, 461.

[498] C. A. Lobry de Bruyn, *Z. physikal. Chem.* 1892, **10**, 784.

[499] O. Ruff and W. Plato, *Ber.* 1903, **36**, 2363.

[500] F. Mylius and R. Funk, *Ber.* 1897, **30**, 825.

[501] H. Lipson, *Proc. Roy. Soc.* 1936, **156**, 462.

The conductivities and the transport numbers indicate a certain amount of auto-complex formation with both these sulphates in concentrated solution.

O-halogen Salts: Chlorates

Zinc chlorate forms a hexahydrate, which goes at 15° to a tetrahydrate, and this at about 50° to a dihydrate; sol^y 205/25°, 307/55°.[502] The hexahydrate is isomorphous with the calcium salt.[503]

Cadmium chlorate crystallizes with 2 H_2O[490]; sol^y 323/18°. It is easily soluble in ethyl alcohol, and slightly in acetone.

Bromates

Zinc bromate forms a hexahydrate, which is very soluble in water (about 50/15°; Rammelsberg, 1851). The crystal structure of the hexahydrate was determined with X-rays by Wyckoff in 1922[504]; this was the first proof that a hexahydrate had its 6 water molecules arranged octahedrally round the cation; later and more detailed examination of the structure[505] has entirely confirmed his results.

Cadium bromate forms a di- and monohydrate.

Iodates

Zinc iodate[506] forms a dihydrate; sol^y only 0·88/15°.

Cadmium iodate forms a monohydrate which loses its water below 200°.

Perchlorates

Zinc perchlorate forms a hexahydrate melting at 106°[507] and a tetrahydrate. It is very soluble in water, and soluble in alcohol.

Cadmium perchlorate is a deliquescent salt, which is very soluble in alcohol. Hering and Leray[508] find that from the cryohydric point of −66·5° to 247° the only solid phases are a hexahydrate (m. pt. 129·4°), two dihydrates, and the anhydrous salt; there is no sign of a tetrahydrate.

COMPLEX COMPOUNDS OF ZINC AND CADMIUM

These may be classified according to the atoms directly attached to the metal, the open-chain complexes being first discussed, and then the chelate compounds.

I. *Carbon Complexes*

These include the very peculiar complex alkyl compounds, a few addition compounds to unsaturated hydrocarbons, and the complex cyanides.

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[502] A. Meusser, *Ber.* 1902, **35**, 1416.

[503] M. Hasselblatt, *Z. anorg. Chem.* 1914, **89**, 69.

[504] R. W. G. Wyckoff, *Amer. J. Sci.* 1922, 4, 188.

[505] S. H. Yü and C. A. Beevers, *Z. Krist.* 1937, **95**, 426.

[506] F. Ephraim and A. Jahnsen, *Ber.* 1915, **48**, 53.

[507] R. Salvadori, *Gaz.* 1912, **42**, i. 482.

[508] H. Hering and A. Leray, *Bull. Soc. Chim.* 1939, [v] **6**, 1034.

Complex Alkyl Compounds of Zinc

These contain a group of complex ions of an unusual kind, which are not usually recognized as such.

As we have seen, it was discovered by Wanklyn in 1858[509] that sodium will dissolve in zinc ethyl with precipitation of metallic zinc, and that the solution on evaporation leaves a colourless product melting at 27°, which has the composition $NaZn(C_2H_5)_3$. A similar caesium salt $CsZnEt_3$ has been isolated.[509a] It was shown by Hein[510–11] that although lithium ethyl in the fused state is a non-conductor, and so also is zinc ethyl, a solution of lithium or sodium ethyl in zinc ethyl conducts quite well, the concentrated solution as well as decinormal potassium chloride. The coloured ionized alkaline compounds, such as lithium benzyl, which were already known to conduct in ether, form similar solutions in zinc ethyl, with a rather higher conductivity. Hein ascribes this to ionization of the alkaline alkyl by the solvent, but the dielectric constant of zinc ethyl is so low (2·55, between those of benzene and carbon disulphide) that it could hardly cause this by a purely physical effect. It is far more likely that a complex salt $Li[ZnEt_3]$ or $Li_2[ZnEt_4]$ corresponding to $Li_2[ZnCl_4]$ is formed. Lithium ethyl evolves heat on solution in zinc ethyl, which suggests a chemical reaction; also sodium and potassium alkyls only form the conducting solution after heating, showing that there is a heat of activation, which is never observed in the ionization of a covalent link. Aluminium ethyl behaves like zinc ethyl. It is remarkable that (with aluminium as well as zinc ethyl) the molecular conductivities calculated on the amount of alkali metal present diminish instead of increasing as the concentration diminishes. This seems to show that the number of lithium atoms is greater in a molecule of the complex salt than in a molecule of the lithium alkyl in equilibrium with it in the solution, and hence that the association of the lithium alkyl is not so great in zinc ethyl as it is in benzene, possibly owing to the formation in the former solvent of covalent solvate molecules Li—Et, $(ZnEt_2)_x$.

The solutions in zinc ethyl behave on electrolysis as such a salt should. They give zinc at the cathode in the proportions required by Faraday's law; this is obviously a secondary product from the lithium first produced; it is known that lithium will displace zinc from zinc ethyl. At the anode a gas is evolved containing about 40 per cent. ethylene, 40 per cent. ethane, 17 per cent. butane, and about 3 per cent. propane. It is clear that the primary process at the anode is

$$[ZnEt_4]^{--} \longrightarrow ZnEt_2 + 2\,C_2H_5.$$

The liberated ethyl radicals partly redistribute to ethylene+ethane, and partly polymerize to butane. This is supported by the observation that if

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[509] J. A. Wanklyn, *Ann.* 1858, **108**, 67; 1859, **111**, 234; 1866, **140**, 211.

[509a] J. de Postis, *C.R.* 1946, 223, 1006.

[510] F. Hein, *Z. Elektrochem.* 1922, **28**, 469.

[511] F. Hein, E. Petzchner, K. Wagler, and F. A. Segitz, *Z. anorg. Chem.* 1924, **141**, 161–227.

a lead anode is used no gas is evolved, and lead tetraethyl $PbEt_4$ is formed: the loss of weight of the lead anode was within 6 per cent. of that required by the theory.

Other alkaline derivatives found to act in the same way were LiMe, LiΦ, Li·CH_2·Φ, NaEt, and KEt. Zinc propyl can be used as solvent but not zinc methyl or aluminium trimethyl, owing to the higher melting-points and smaller solubilities of the methyl compounds.

An unexplained observation was that lithium or sodium ethyl dissolved in cadmium ethyl does not conduct: possibly cadmium has less tendency than zinc to combine with carbon.

Addition Compound of C=C

A zinc compound of this type with trimethyl ethylene

$$(CH_3)_2C{=}CH{\cdot}CH_3(Bu)$$

has been prepared[512]; it has the composition 2 $ZnCl_2$,Bu; it can be made by the direct combination of the unsaturated hydrocarbon with zinc chloride, or by heating the amyl alochol compound $ZnCl_2$, 2 $C_5H_{11}OH$.

Complex Cyanides

The complex cyanides of zinc are of two types, $MZn(CN)_3$ and $M_2Zn(CN)_4$. Of the first type the sodium, potassium, and ammonium salts are known[513]; the sodium salt is easily soluble in water, more so than the potassium salt (characteristic of the salts of strong acids). The second type is better known; the potassium salt[514] has been shown[515] to have the dissociation constant for the complex anion $1{\cdot}3\times10^{-17}$, about the same as for the cadmium salt, but considerably greater than for the cupric salt

$$M_2[Cu(CN)_4].$$

The tetrahedral structure of the zinc in this anion was established by Dickinson.[516]

The cadmium salt $K_2[Cd(CN)_4]$ is exactly like the zinc compound; it has the same crystal structure[516]; according to Euler [515] it has the almost identical dissociation constant of $1{\cdot}4\times10^{-17}$. It can be used in analysis for the separation of cadmium from nickel and cobalt.[517]

Ammines

Both zinc and cadmium form complexes with ammonia, most of which contain the anions $[M(NH_3)_x]^{--}$. The maximum value of x is 6, if we exclude a few solid compounds such as $ZnCl_2$,10 NH_3 which have an ammonia tension little less than that of liquid ammonia at the same

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[512] I. L. Kondakov, F. Balas, and L. Vit, *Chem. Listy*, 1930, **24**, 1.

[513] W. J. Sharwood, *J.A.C.S.* 1903, **25**, 570.

[514] N. Herz, ib. 1914, **36**, 912.

[515] H. v. Euler, *Ber.* 1903, **36**, 3404.

[516] R. G. Dickinson, *J.A.C.S.* 1922, **44**, 774, 2404.

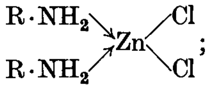
[517] E. Ebler, *Z. anorg. Chem.* 1906, **48**, 83.

temperature, and are obviously van der Waals compounds. Those which are formed from aqueous solution, where the ammonia has to compete as a solvating molecule with the water, usually contain 2 NH_3, but occasionally 4. The stabilities of the solid anhydrous ammines of the two metals do not differ greatly. For example, with the hexammines the temperatures at which the dissociation tension of ammonia is 100 mm. are:[518-19]

	MCl_2	MBr_2	MI_2
ZnX_2, 6 NH_3 . .	23°	31°	28°
CdX_2, 6 NH_3 . .	24°	45°	65°

Organic Ammines

The anhydrous salts of zinc and cadmium also form complexes with many organic amines[520]: the chlorides, bromides, and iodides most readily,[521] but many other salts as well. Of resulting ammines over 70 per cent. are diammines, such as $ZnCl_2$, 2 $C_2H_5 \cdot NH_2$; these are presumably covalent, with the structure

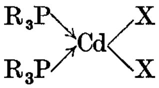


Werner[522] has shown by the boiling-point in pyridine that in this solvent cadmium iodide has the molecular weight 348·3 (calculated for undissociated form 364·7). Accordingly these diammines are often more soluble in alcohol than in water. The hexammines of cadmium salts are nearly all compounds either of methylamine (small size), or chelate compounds of ethylene diamine (greater stability of chelate groups): while the zinc salts form hexammines only with ethylene diamine, and form pentammines with methylamine alone.

Phosphine and Arsine Compounds

Mann *et al.*[523-4] discuss the co-ordination compounds formed by tertiary phosphines and arsines with the halides of cadmium. The cadmium compounds are of three types (P stands for phosphorus or arsenic);

I. $(R_3P)_2CdX_2$ =



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[518] W. Biltz, *Z. anorg. Chem.* 1923, **130**, 98.

[519] F. Ephraim, *Z. physikal Chem.* 1913, **81**, 513.

[520] See Gmelin, *Zinc*, 1924, pp. 262–71; *Cadmium*, 1925, pp. 140–53.

[521] For the heats of formation of the cadmium ammines see W. Hieber and E. Reindl, *Z. Elektrochem.* 1940, **46**, 556.

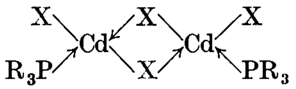
[522] A. Werner and W. Schmijlow, *Z. anorg. Chem.* 1897, **15**, 23.

[523] R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J.C.S.* 1940, 1209.

[524] F. G. Mann and D. Purdie, ib. 1230.

This is tetrahedral.

II. $(R_3P)_2(CdX_2)_2$ =



III. $(R_3P)_3(CdX_2)_2$

The structure of this is uncertain.

Nitrile Compounds

A few of these have been described; they are all of the type $M(hal)_2$, $2\,R\cdot CN$.[525-6]. They are more readily formed and more stable with zinc than with cadmium.

Complex Nitrites (Nitro-compounds)

A few of these have been described: they seem to be less unstable with cadmium than with zinc.

The zinc salts are of the types $K_2[Zn(NO_2)_4]$, $2\,H_2O$[527] and $K_3[Zn(NO_2)_5]$, $3\,H_2O$[528]; these are hygroscopic and easily soluble in water, in which they soon decompose. The recurrence of the type $[M(NO_2)_5]$ is noticeable.

The cadmium salts are rather better known. Potassium salts of two types have been prepared,[529-30] $K[Cd(NO_2)_3]$ and $K_2[Cd(NO_2)_4]$; it is remarkable that the cadmium salts, unlike the zinc salts, are anhydrous, and that they do not include the pentanitro-type.

$K[Cd(NO_2)_3]$ is very soluble in water, but almost insoluble in alcohol. It is stable in air, and even on boiling the solution.[531] The tetranitro-compound $K_2[Cd(NO_2)_4]$ forms pale yellow crystals which are also very soluble in water: here again the solution does not decompose on boiling.

Oxygen-complexes

A large number of these are known with zinc, but relatively few with cadmium. This may be accidental, but it is one of the facts that suggest that the question of the relative tendency of zinc and cadmium to form complexes is not easily answered (see p. 275).

Open-chain Complexes

The zinc salts, especially the halides, but also the sulphate, will form solid compounds with variety of organic substances containing oxygen. Thus with alcohols we have $ZnBr_2$, $2\ CH_3OH$, and $2\ C_2K_5OH$[532]; zinc sulphate will also take up glycerol to form $ZnSO_4$, $3\ C_3H_8O_3$; this last compound, though not very stable, is more so than the corresponding

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[525] A. Naumann and A. Schier, *Ber.* 1914, **47**, 250.

[526] A. Naumann and A. Bertges, ib. 1370.

[527] J. Lang, *J. prakt. Chem.* 1862, **86**, 295.

[528] A. Rosenheim and K. Oppenheim, *Z. anorg. Chem.* 1901, **28**, 171.

[529] A. Fock, *Z. Krist.* 1889, **17**, 177.

[530] V. Kohlschütter, *Ber.* 1902, **35**, 488.

[531] W. Hampe, *Ann.* 1863, **125**, 348.

[532] B. N. Menschutkin, *Z. anorg. Chem.* 1909, **62**, 43.

alcoholates, which suggests that it is chelate.[533] They will also combine with ethers: zinc bromide forms two etherates, $ZnBr_2, 2\ Et_2O$ (stable below +4°) and $ZnBr_2, Et_2O$ (stable below +16°): a saturated solution of the bromide in ether at 25° contains 223 g. of the salt to 100 of ether[534]; in the same way the iodide combines with two molecules of ether, of acetal, and of various esters; these compounds are less stable than the corresponding magnesium complexes.[535–6] Zinc chloride will also combine with various ketones such as acetophenone,[537] benzophenone,[538] and quinones.[539]

Of the corresponding cadmium compounds surprisingly few are known. The iodide like zinc iodide will form an etherate with 2 molecules of cineol[540]: there is a compound of cadmium chloride with 2 molecules of acetamide, which may be co-ordinated through oxygen,[541] and a double and perhaps complex formate.[542]

Chelate Oxygen Complexes

These include complex salts (ato-complexes) and neutral derivatives like the acetylacetonates and the basic carboxylates.

Among the ato-compounds of zinc the double oxalates are important; their complexity is shown by their solubility, those of Zn and Cd oxalates at 25° being respectively 42 and 100 mg. per litre.[546] The potassium salt is $K_2[Zn(C_2O_4)_2]$, with 5[543] or according to later work 7 and 0 H_2O[544]; no other salt could be isolated, but measurements of E.M.F.[543] and solubility suggest that at higher concentrations the trichelate ion $[Zn(C_2O_4)_3]''''$ is formed. The existence of a double ammonium oxalate is doubtful.[545]

With cadmium the sodium[547] and potassium[548] double oxalates of the type $M_2[Cd(C_2O_4)_2]$ have been prepared. The sodium salt is slightly soluble in water; the potassium salt is 'decomposed' by water, i.e. is incongruent.

A series of fairly stable catechol derivatives of the type $M_2[Zn(C_6H_4O_2)_2]$ (M = pyridinium, Na, K, NH_4) have been prepared.[549–50]

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[533] A. Grun and F. Bockisch, *Ber.* 1908, **41**, 3465.
[534] H. H. Rowley and F. V. Olsen, *J.A.C.S.* 1939, **61**, 1949.
[535] H. H. Rowley and R. B. Anderson, ib. 1941, **63**, 1908.
[536] E. Blaise, *C.R.* 1905, **140**, 661.
[537] $ZnCl_2, C_6H_5{\cdot}CO{\cdot}CH_3$: P. Pfeiffer, *Org. Molekülvbdgn.* Ed. ii, p. 92.
[538] G. Reddelien, *Ann.* 1912, **388**, 191.
[539] $ZnCl_2$, 1 phenanthraquinone: K. H. Meyer, *Ber.* 1908, **41**, 2574.
[540] R. H. Pickard and J. Kenyon, *J.C.S.* 1907, **91**, 900.
[541] G. André, *C.R.* 1886, **102**, 115.
[542] W. Lossen and G. Voss, *Ann.* 1891, **266**, 49.
[543] F. Kunschert, *Z. anorg. Chem.* 1904, **41**, 338.
[544] V. Mettler and W. C. Vosburgh, *J.A.C.S.* 1933, **55**, 2625.
[545] H. W. Foote and I. A. Andrew, *Amer. Chem. J.* 1905, **34**, 164.
[546] R. Scholder, *Ber.* 1927, **60**, 1510.
[547] A. Souchay and E. Lenssen, *Ann.* 1857, **103**, 317.
[548] V. Kohlschütter, *Ber.* 1902, **35**, 485.
[549] R. Weinland and H. Sperl, *Z. anorg. Chem.* 1925, **150**, 69.
[550] E. Sellés, *Anal. Fis. Quim.* 1941, **37**, 114.

Acetylacetone Derivatives

The zinc and cadmium compounds, ZnA_2 and CdA_2 ($A = C_5H_7O$), are both known; they differ from those of the alkaline earths in not being hydrated even when crystallized from water. The zinc compound[551-3] is very like its beryllium analogue. It melts at 138° and can be distilled under 350 mm. (temperature not stated)[553]; the vapour density indicates a simple molecular weight. It is easily soluble in benzene and also in water, which does not hydrolyse it except on boiling (BeA_2 (II. 64) has m. pt. 108°, b. pt. 270°: it is almost insoluble in water, and hydrolysed by it on boiling; the insolubility in water is no doubt due to the beryllium being covalently saturated).

The cadmium compound[553] is similar, but is less soluble in water.

Zinc 'Basic' Acetate

This compound, $Zn_4O(O \cdot CO \cdot CH_3)_6$, is made by distilling zinc acetate in a high vacuum.[554] It is crystalline and melts at 249–50°. Its composition, stability, and volatility show that it must be of the same type as the analogous beryllium compound (p. 213), with the unique oxygen at the centre of a tetrahedron, the 4 Zinc atoms at the 4 corners, and the 6 acetate groups bridging the 6 edges.[555] It differs, however, from the beryllium compound, which is stable to water, in being at once hydrolysed by water or alcohol. This is obviously due to the 4-covalent zinc being able to increase its covalency to 6 by taking up water or alcohol, which the 4-covalent beryllium cannot do.

No analogous cadmium compound is known (a further indication that the Cd—O link is weaker than Zn—O).

Sulphato-compounds

The following double sulphates have been made, but there is no good evidence of their complexity. They nearly all give the vitriols M'_2SO_4, $M''SO_4$, 6 H_2O, which are probably not true complexes.

Zinc. Na_2, 4 aq.[556]; K_2, 6 and 0 aq.[557]; $(NH_4)_2$, 6 aq.[558,563]; (N_2H_5), anh.[559-60]; Cs_2, 6 aq.[561]

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[551] F. Gach, *Mon.* 1900, **21**, 116.

[552] S. Tanatar and E. Kurowski, *J. Russ. Phys. Chem. Ges.* 1908, **40**, 580 (*Chem. Centr.* 1908, ii. 1096).

[553] G. T. Morgan and H. W. Moss, *J.C.S.* 1914, **105**, 195.

[554] V. Auger and I. Robin, *C.R.* 1924, **178**, 1546.

[555] J. W. Wyart, *Bull. Soc. Fr. Min.* 1926, **49**, 148.

[556] J. Koppel and A. Gumpertz, *Z. physikal. Chem.* 1905, **52**, 408.

[557] G. F. Lipscomb and G. A. Hulett, *J. Phys. Chem.* 1916, **20**, 75.

[558] A. E. Tutton, *J.C.S.* 1905, **87**, 1140.

[559] T. Curtius and F. Schrader, *J. prakt. Chem.* 1894, [2] **50**, 329.

[560] F. Sommer and K. Weise, *Z. anorg. Chem.* 1916, **94**, 51.

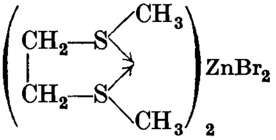
[561] A. E. Tutton, *J.C.S.* 1893, **63**, 361.

Cadmium. Na_2, 2 aq.[556]; K_2, 6, 4, 2 and 1·5 aq.[557]; $(NH_4)_2$ 6 aq.[562-3]; Rb_2, 6 aq.[564]; Cs_2, 6 aq.[564]

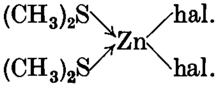
The double selenates are very similar.

Sulphur Complexes

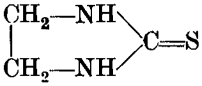
Dimethyl sulphide forms complexes of the composition $Zn(hal)_2, (CH_3)_2S$ with zinc bromide[565] and iodide[566]; thiourea forms a similar complex $ZnCl_2$, 2 Thi.[567] A chelate sulphur compound $ZnBr_2$,



was isolated by Werner and Maiborn.[566] These last authors found from the boiling-points that the zinc halides were not dissociated in methyl sulphide solution, the values obtained for the molecular weights being (theoretical values in brackets) $ZnCl_2$ 128 (136); $ZnBr_2$ 218 (225); ZnI_2 313 (319); CdI_2 369 (365). The complex, no doubt, is



Of the cadmium salts, the iodide behaves in dimethyl sulphide solution like the zinc halides. A series of complexes of cadmium salts with ethylene thiocarbamide (etu)



have been prepared by Morgan and Burstall.[568] These all have the composition $[Cd(etu)_4]X_2$; they are insoluble in organic solvents but easily soluble in water, and are clearly salts, at least in water; the aqueous solution of the nitrate is a good conductor. The halides may well be covalent when pure: their melting-points are chloride 220°, bromide 208°, iodide 165°.

Complex Halides

These are numerous with both metals and with all four halogens. They are, as a rule, not very stable, but some at least must be complex, especially as the binary halides of zinc and cadmium undoubtedly form complexes. Details and references will be found in the usual handbooks, especially in the volumes of Gmelin on Zinc (1924) and Cadmium (1925). The double salts contain from 3 halogen atoms per Zn or Cd to 5 with zinc and 6 with

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[562] J. Locke, *Amer. Chem. J.* 1902, **27**, 455.

[563] A. E. H. Tutton, *Phil. Trans.* 1916, **216**, 1.

[564] Id., *J.C.S.* 1893, **63**, 407.

[565] G. Patein, *Bull. Soc. Chim.* 1890, [3], **3**, 168.

[566] A. Werner and A. Maiborn, *Z. anorg. Chem.* 1897, **15**, 13.

[567] R. Maly, *Ber.* 1876, **9**, 172.

[568] G. T. Morgan and F. H. Burstall, *J.C.S.* 1928, 143.

cadmium; this difference may be due to the greater size of the cadmium atom (radii Zn 1·31, Cd 1·48) or to the greater affinity of cadmium for halogen. The pentahalides seem to be crystal aggregates of the tetrahalides with the simple halides. X-ray analysis has shown[569] that in the salt $(NH_4)_3ZnCl_5$ the zinc is surrounded tetrahedrally by 4 Cl atoms at 2·25 A (theory 2·30), and the fifth is farther off. The formation of complex cadmium halide anions in solution has been studied potentiometrically by Leden,[570] who finds CdX_3^- and CdX_4^{--} ions, but none higher.

The following list gives the numbers of known salts of each type.

Zinc	$MZnX_3$	M_2ZnX_4	M_3ZnX_5
X = F	3	2	..
Cl	5	9	3
Br	3	4	2
I	3	7	1
Total	14	22	6

Cadmium	$MCdX_3$	M_2CdX_4	M_3CdX_5	M_4CdX_8
X = F	1	1	..	..
Cl	5	6	..	6
Br	4	3	1	4
I	5	6	1	..
Total	15	16	2	10

MERCURY

MERCURY has so many peculiarities of its own that it stands quite apart from the other metallic elements. The most important of these, though by no means the only ones, are:

(1) Its very high ionization potential in the gaseous state; the values for the first and second ionizations of these elements are:

	First	*Second*
Zinc . . .	9·36	17·89 volts
Cadmium . .	8·96	16·84
Mercury . .	10·38	18·67

The value of 10·38 is higher than that for any cation-forming element except hydrogen (13·53); in fact the only elements with potentials above 10 v. are Hg, H, C, the inert gases, and the electronegative elements of groups V B, VI B, and VII B.

(2) The volatility of the metal.

(3) Its abnormal valency in the mercurous salts.

(4) Its strong tendency to form covalent rather than ionized links, as is shown, for example, in the minute ionization of mercuric chloride, bromide, and iodide.

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[569] H. P. Klug and L. Alexander, *J.A.C.S.* 1944, **66**, 1056.

[570] I. Leden, *Z. physikal. Chem.* 1941, **188**, 160.

(5) This is the most singular: its power of being satisfied with a shared quartet of valency electrons, and its small tendency to increase this to an octet by complex formation; thus the slightly ionized chloride shows little signs of polymerization or of forming complexes in water like $Hg[HgCl_4]$, such as are formed by cadmium.

(6) The remarkable stability, especially to air and water, of its covalent link to carbon. The alkyl compounds are unassociated, like those of zinc and cadmium, and unlike those of beryllium and magnesium; further, they are not acted on by air or water, in which they differ from all neutral metallic alkyls that have less than a complete octet. This stability is not due to any exceptional strength of the Hg-C link, which, on the contrary, can be shown to be unusually weak. It is probably due partly to the small affinity of mercury for oxygen, and partly to its slight tendency in these compounds to co-ordination. It results in the formation of a great variety of organic derivatives.

Mercury has a strong tendency to form covalent links with nitrogen, and next to this with chlorine, bromine, and iodine, but not with fluorine, and with sulphur but not with oxygen,* for which its affinity is very small; for hydrogen it is almost nil.

Metallic Mercury

Mercury is the most fusible and the most volatile of metals: the following comparison is of interest:

	Hg	Cs	Ga
M. pt. . . .	−38·8°	+28·5°	+29·8° C.
B. pt. . . .	357°	670°	2,300°

The structure of the liquid has been examined by X-rays from the melting-point to 200° C.[571] Each atom has 6 nearest neighbours 3·0 A away.

The volatility of mercury is without parallel among the metals: the only others boiling below 1,000° C. are the alkali metals from Cs (670°) to Na (890°), cadmium (764°), and zinc (906°). The position is clearer if we compare the vapour pressures at 200° and 600°:

Vap. press.	Mg	Zn	Cd	Hg
At 200°	*ca.* 10^{-5}mm.	2×10^{-5}mm.	3×10^{-4}mm.	18 mm.
At 600°	7 mm.	12 mm.	80 mm.	16,500 mm. = 22 atm.

One cubic metre (1.3 kg.) of air saturated at 20° contains 14 mg., and at 100° 2·4 g. of mercury. The vapour is practically wholly monatomic,[572]

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* It is possible that the ion Hg^{++} may be capable of hydration. Nearly all mercuric 'salts' are anhydrous, but the few that form hydrates are highly ionized [see p. 325].

[571] J. A. Campbell and J. H. Hildebrand, *J. Chem. Phys.* 1943, **11**, 330.

[572] See R. W. Ditchburn and J. C. Gilmour, *Rev. Mod. Phys.* 1941, **13**, 310.

and thus mercury is the only element other than the inert gases which can give a measurable concentration of a monatomic vapour at moderate temperatures. The resemblance to the inert gases does not stop here. The solubility of mercury in water has recently[573-4] been found to be about 0·02 mg. per litre at 20°, and 0·6 at 100°; this is just about the value calculated for a heavy inert gas.*

This resemblance of mercury to the inert gases is the first sign we have met of the 'inert pair' of valency electrons. Many of the heavier elements of the B subgroups behave in some of their compounds as if two of their valency electrons were absent or formed part of the core, and so resemble the elements two places before them in the table: thus we have Tl′ like Au′, Pb″ like Hg″, and ICl_3 and IF_5 corresponding to $SbCl_3$ and SbF_5. The theoretical reason for this has been pointed out by Grimm and Sommerfeld.[575] The maximum size of the quantum groups is given by $2n^2$ (2, 8, 18, 32), where n is the principal quantum number. Now a group of 8, the maximum for the quantum number 2, can behave as practically complete, showing little tendency to take up more electrons, even when its quantum number is 3, 4, 5, or 6, as in argon, krypton, xenon, and emanation, and in the cations of the typical and A metals; the same occurs with 18 in xenon and emanation, where its quantum number is 4 and 5. For some reason this is not true in general for the group of 2: a closed group of 2 electrons is only found where the quantum number is 1. These examples of the 'inertness' of the first pair of valency electrons occur where this group of 2 can show something of the inertness which it has in helium or lithium, though its quantum number is greater than 1.

We have no theoretical guidance as to when this will occur, but experimentally we find that (1) it never occurs with the A elements but only with the B. (2) In every group it becomes more marked as the atomic number increases. (3) As we pass from the earlier to the later groups it spreads in an increasing degree to the lighter elements. The evidence will be considered in detail under the later groups, but the results are summed up in the following table, in which the elements exhibiting the 'inert pair' are those below the line

Be	B	C	N	O	F
Mg	Al	Si	P	S	Cl
Zn	Ga	Ge	As	Se	Br
Cd	In	Sn	Sb	Te	I
Hg	Tl	Pb	Bi	..	..

In this second periodic group there are only two valency electrons; so if these become inert the valency should vanish, and the element acquire

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* For some reason the solubility in hexane is much greater, 7·0 mg./litre at 65°; it can be measured gravimetrically with gold foil.[573]

[573] H. Reichardt and K. F. Bonhoeffer, *Z. Elektrochem.* 1930, **36**, 753.

[574] A. Stock, *Z. anorg. Chem.* 1934, **217**, 241.

[575] H. G. Grimm and A. Sommerfeld, *Z. Physik*, 1920, **36**, 30.

in some degree the properties (or absence of properties) of an inert gas. As we have seen, this does occur with mercury, though not with zinc or cadmium.

The use of the strong resonance line of mercury vapour at 2,537 A for the atomization of hydrogen has been mentioned (I. 16); it depends on the fact that the energy of this radiation per g.-atom is 112 k.cals., while that required to disrupt the hydrogen molecule is 103 k.cals. (see further Cline and Forbes).[576]

Mercury vapour gives absorption and emission bands which show that it contains diatomic molecules, though the amount of them is so small that it cannot be detected by the ordinary methods, such as vapour densities[577] or specific heats. The heat of dissociation is not more than a few k.cals. (3·5[578] or 1·6[579]: see also refs. [580–1]).

Amalgams

Another peculiarity of mercury is its power of forming liquid metallic solutions or amalgams.[582] This property, which is common to metals in general above their melting-points, is of particular interest with mercury because the melting-point is so low. It is clear that the principles of molecular structure which hold in a metal may be very different from those in a liquid or solid which has no metallic conductivity. There can, however, be little doubt that some of the metallic compounds of mercury contain definite polyatomic molecules, since their melting-points are much higher than those of their components: for example:

	Hg	Na	Hg_2Na	K	Hg_2K
M. pt.	—39°	+98°	346°	64°	270°

Many metals, even some which amalgamate very readily, have only a minute solubility in mercury. This is difficult to measure, because one cannot see whether there is a homogeneous solution or a suspension of finely divided metal; it is usually determined by measuring the E.M.F. of the solution against pure mercury; as long as that changes on electrolysing more metal into the mercury, this must have gone into true solution. The following table gives the weight percentage of metal in mercury saturated at 20° or thereabouts; it is taken mainly from Tammann,[583–4] but partly from later papers.[585–93]

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[576] J. E. Cline and G. S. Forbes, *J.A.C.S.* 1941, **63**, 2152.

[577] W. Klemm and H. Kilian, *Z. physikal. Chem.* 1942, B **51**, 306 [this corrects a previous paper].

[578] J. G. Winans, *Phys. Rev.* 1931, ii. **37**, 897.

[579] H. Kuhn and K. Freudenberg, *Z. Phys.* 1932, **76**, 38.

[580] S. Mrozowski, ib. 1929, **55**, 338.

[581] F. L. Arnot and J. C. Milligan, *Proc. Roy. Soc.* 1936, **153**, 359.

[582] Traces of oxidizable metals cause the 'tailing' of mercury, the formation of a surface film. This will detect one part of base metal in ten million (E. Wickers, *Ind. Eng. Chem., News Edn.* 1942, **20**, 1111).

[583] G. Tammann and K. Kollmann, *Z. anorg. Chem.* 1927, **160**, 242.

[584] G. Tammann and J. Hinnüber, ib. 240.

TABLE

Li 0·09	Mg 0·24	Al 0·003	Sn 0·62
K 0·80	Ca 0·3	La 0·0090	Pb 1·3
Cu 0·0032	Ba 0·33		
Ag 0·040	Zn 2·15	In 0·0073	
Au 0·13	Cd 4·92	Tl 42·8	Th 0·0154

V *ca.* 0	Cr $3{\cdot}1 \times 10^{-11}$	Mn $2{\cdot}5 \times 10^{-4}$
As *ca.* 0	Mo *ca.* 0	Fe $1{\cdot}0 \times 10^{-17}$
Sb $2{\cdot}9 \times 10^{-5}$	W *ca.* 0	Co $1{\cdot}7 \times 10^{-7}$
Bi 1·4	U $1{\cdot}4 \times 10^{-4}$	Ni $5{\cdot}9 \times 10^{-4}$
		Pt. 0·02

Thus 1 cubic mm. of iron amalgam contains 15 individual atoms of iron.

Mercury Hydride

The spectrum of hydrogen containing mercury vapour includes bands which indicate[594] the presence of a hydride HgH with a heat of dissociation of 8·50 k.cals.

Geib and Harteck[595] mixed hydrogen containing mercury at low pressure with atomic hydrogen, and froze out with liquid air a black solid. This began at −125° to decompose into mercury and hydrogen, the reaction being almost complete at −100°; in the absence of atomic hydrogen no such product was formed. Analysis showed that the black product (about 200 mg. were formed per hour) could contain up to 70 per cent. HgH.

MERCUROUS COMPOUNDS

BEFORE we deal with the normal mercuric compounds we may consider the mercurous derivatives, practically all of which are salts of the mercurous ion. This ion has been shown, unlike the cuprous ion, not to be Hg^+ but Hg_2^{++}, and this fact is so important for the general theory that we have to consider the evidence in some detail. The chief arguments are five.

(1) Ogg[596] treated silver nitrate solution with liquid mercury. This causes a partial replacement of the silver ions in the water by mercurous ions, while the expelled silver dissolves in the mercury. If the mercurous ion is monatomic we have

$$(1)\ Hg + Ag^+ = Hg^+ + Ag$$

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[585] Ag: R. J. Maurer, *J. Phys. Chem.* 1938, **42**, 515.

[586] Ag: A. A. Sunier and C. B. Hess, *J.A.C.S.* 1928, **50**, 662.

[587] Au: A. A. Sunier and C. M. White, ib. 1930, **52**, 1842.

[588] Au: A. A. Sunier and B. E. Gramkee, ib. 1929, **51**, 1703.

[589] Au: G. Mees, *J.A.C.S.* 1938, **60**, 870.

[590] La: W. G. Parks and J. L. Campanella, *J. Phys. Chem.* 1936, **40**, 333.

[591] In: W. G. Parks and W. G. Moran, ib. 1937, **41**, 343.

[592] Th: W. G. Parks and G. E. Prime, *J.A.C.S.* 1936, **58**, 1413.

[593] Pt: I. N. Plaskin and N. A. Suvarovskaja, *Acta Phys.-Chem. U.R.S.S.* 1940, **13**, 83.

[594] E. Hulthén, *Z. Phys.* 1925, **32**, 32; 1928, **50**, 319.

[595] K. H. Geib and P. Harteck, *Ber.* 1932, **65**, 1550.

[596] A. Ogg, *Z. physikal. Chem.* 1898, **27**, 285.

Hence
$$\frac{[Hg^+]\cdot[Ag]}{[Ag^+]} = k_2\cdot[Hg] = K_1,$$
and if it is diatomic
$$(2)\ 2\,Hg + 2\,Ag^+ = Hg_2^{++} + 2\,Ag$$
whence
$$\frac{[Hg_2^{++}]\cdot[Ag]^2}{[Ag^+]^2} = k_2\cdot[Hg]^2 = K_2.$$

The concentration of the neutral mercury [Hg] does not vary (the silver solution being less than 0·05 per cent.) and so becomes part of the final constant; [Ag] is of course the varying concentration of silver in the amalgam. The concentrations of the mercurous and silver ions in the solution, and of the silver in the mercury, were determined; these of course depend on the strength of the silver nitrate solution originally taken, and on the amount of liquid mercury. It was found that for a variation of the final Hg^+ concentration in the ratio 8:1, K_1 varies in the ratio 3:1, while K_2 remains constant within 20 per cent.

(2) Ogg[596] and also E. Abel[597] treated mercuric nitrate solution with metallic mercury, which dissolves to some extent with the formation of mercurous nitrate; they then determined the concentrations of mercurous and mercuric ions in the solution. Here we have

$$(1)\quad Hg + Hg^{++} \rightleftharpoons 2\,Hg^+$$
$$\frac{[Hg^{++}]}{[Hg^+]^2} = k_1\cdot[Hg] = K_1.$$
$$(2)\quad Hg + Hg^{++} \rightleftharpoons Hg_2^{++}$$
$$\frac{[Hg^{++}]}{[Hg_2^{++}]} = k_2\cdot[Hg] = K_2.$$

Here again it was found that K_2 was constant and not K_1, a further proof that the mercurous ion is diatomic. The value of the ratio of mercurous to mercuric ions in presence of liquid mercury, that is $1/K_2$, expressed in molar concentrations, was found by Ogg to be at 18° 112, and by Abel to be 120. We may take the mean 116 as the probable value. This constant is of great importance in determining the conditions under which a mercurous salt goes into a mercuric and mercury, as in the parallel instances of the cuprous and aurous ions.

(3) Ogg[596] also determined the change in the molecular conductivity of mercurous nitrate in solution, in presence of a slight excess of nitric acid to repress hydrolysis, and showed that it is that required for a uni-divalent and not for a uni-univalent salt, as the following figures indicate:

Equivalent Conductivity at 10°

	$Hg_2(NO_3)_2$	$Pb(NO_3)_2$	$AgNO_3$
$V = 250$	69·58	102·16	84·04
$V = 5$	51·85	76·82	63·55
Ratio	0·66	0·67	0·73

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[597] *Z. anorg. Chem.* 1901, 26, 376.

(4) The X-ray analysis of the crystal structure of mercurous chloride[598] shows that it is built up of linear units Cl—Hg—Hg—Cl: while all compounds MCl have a succession of M and Cl atoms in the crystal, as in Cu—Cl—Cu—Cl—.

(5) Woodward[599] has examined the Raman spectrum of mercuric nitrate in water, at an equivalent concentration of 0·6 normal, in presence of excess of nitric acid. A monatomic ion such as Hg^+ can of course give no Raman lines, and accordingly solutions of all other metallic nitrates (including thallous) give only the lines of the NO_3 ion. But mercurous nitrate gives in addition a strong line which must be due to the Hg—Hg link.

It is thus proved that the mercurous ion is diatomic, in striking contrast to the monatomic cuprous ion. It must have the structure $^+Hg—Hg^+$, one of the two valency electrons of each atom being shared with the other atom, and the other electron removed. This behaviour of mercury is quite unique (the suggestion that the thallous ion is partly diatomic was disproved by Woodward); in all other polymerized molecules of metallic compounds, as in Al_2Cl_6 and Fe_2Cl_6, it has been shown that the metallic atoms are not united directly but through atoms of the other component.* The formation of the diatomic mercurous ion is a remarkable sign of the tendency of mercury to use its valency electrons for covalencies rather than for electrovalencies. The structure is also remarkable in that the mercury is satisfied not as elsewhere with a quartet, but with a duet of electrons. It is indeed rather unstable; this Hg—Hg link seems to be able to exist almost only when the atoms have a positive charge; covalent mercurous compounds are very rare, and even the salts are readily converted into mercuric compounds and mercury. But in the ionic form this group with two shared electrons has a singular stability. The tendency to go over into mercuric salt+mercury is greatly promoted by the minute solubility of the latter. In presence of metallic mercury

$$[Hg_2^{++}]/[Hg^{++}] = 116.$$

Now the true equilibrium constant K is given by

$$\frac{[Hg_2^{++}]}{[Hg^{++}]\cdot[Hg]} = K\text{: hence } \frac{[Hg_2^{++}]}{[Hg^{++}]} = K\cdot[Hg]$$

or

$$K\cdot[Hg] = 116, \text{ or } K = \frac{116}{[Hg]}.$$

From Stock's results 1 litre of water at 18° contains about 0·02 mg. of mercury, or 10^7 litres one g.-atom. Hence $[Hg] = 10^{-7}$, and K, the true equilibrium constant for the formation of the mercurous ion, is $1{\cdot}16\times10^9$.

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* Probable exceptions are iron enneacarbonyl [p. 1369] and some similar molecules.

[598] R. T. Havighurst, *Am. J. Sci.* 1925, **10**, 15; *J.A.C.S.* 1926, **48**, 2113.

[599] L. A. Woodward, *Phil. Mag.* 1934, [7] **18**, 823.

Properties of the Mercurous Ion

The chemistry of the mercurous compounds is practically that of the ion. The hydroxide $Hg_2(OH)_2$ is not nearly so weak as mercuric hydroxide $Hg(OH)_2$, and accordingly the salts, though considerably hydrolysed in solution, are much less so than their mercuric analogues. This difference is to be expected since the two positive charges which cause deformation and so can form a covalent link with hydroxyl are spread over two atoms instead of being concentrated on one. The salts are in general less soluble than the mercuric, especially the sulphate, chloride, bromide, iodide, and the salts of organic acids such as acetic. The only more soluble salts are those of the strong monobasic oxy-acids such as nitric, chloric, and perchloric.

In solution the mercurous salts are all highly ionized; the abnormally low dissociation so characteristic of many mercuric compounds is not found among the mercurous at all. Indeed the mercurous salts are devoid of nearly all the peculiarities of mercuric mercury, since the latter depend primarily on the tendency of the single mercury atom to form covalencies, which is almost completely absent from the mercurous ion; it forms practically no complexes, and in striking contrast to the mercuric ion it cannot form stable covalent links with carbon or nitrogen.

The tendency of mercurous salts to go into mercuric depends, as we have seen, on the limiting value of 116 for the ratio $[Hg_2^{++}]/[Hg^{++}]$ in presence of metallic mercury. Accordingly, anything which diminishes the concentration of the mercuric ion will promote the change.[600]

Hence mercurous cyanide cannot be prepared, since mercuric cyanide is almost wholly undissociated, and in the presence of CN ions the mercuric ions are all removed. So, too, acetylacetone acts on mercurous chloride to give mercuric acetylacetonate and metallic mercury.[601] In the same way ammonia, amines, and alkyl sulphides, which form stable co-ordination compounds with the mercuric ion, at once decompose mercurous salts in solution with the separation of metallic mercury. (See further, under mercurous complexes, p. 295.)

There are some mercurous compounds which are of special interest.

Oxide and Hydroxide

The black 'mercurous oxide Hg_2O' of the text-books, formed on treating a mercurous solution with alkali, has been proved by X-ray examination to be an intimate mixture of mercuric oxide and metallic mercury.[602]

This is supported by the molecular heats of formation (from liquid metal+oxygen gas) which are 21·6 k.cals. both for mercurous and mercuric oxides.[603] The hydroxide $Hg_2(OH)_2$ has never been isolated, but it may be present in the yellow precipitate first formed on addition of alkali

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[600] W. Lang, *Ber.* 1888, **21**, 1587.

[601] G. T. Morgan and H. W. Moss, *J.C.S.* 1914, **105**, 195.

[602] R. Fricke and P. Ackermann, *Z. anorg. Chem.* 1933, **211**, 233.

[603] Bichowsky and Rossini, *Thermochemistry*, p. 69.

to a mercurous solution, which rapidly loses water to give the black mixture of mercuric oxide and mercury.

Mercurous Sulphide, Hg_2S

This is precipitated by the action of hydrogen sulphide or alkaline sulphide on a mercurous solution, but it at once changes over into a mixture of mercuric sulphide and mercury. It is obvious that we have in the solution at equilibrium the following relations:

$$\frac{[\text{Sol}^{\text{y}} \text{ of } Hg_2S]^2}{[\text{Sol}^{\text{y}} \text{ of } HgS]^2} = \frac{\text{Sol}^{\text{y}} \text{ prod. } Hg_2S}{\text{Sol}^{\text{y}} \text{ prod. } HgS} = \frac{[Hg_2^{++}]\cdot[S^{--}]}{[Hg^{++}]\cdot[S^{--}]} = \frac{[Hg_2^{++}]}{[Hg^{++}]} = 116.$$

Hence if mercurous sulphide has more than $\sqrt{116} = 11$ times the solubility of mercuric sulphide (of which the solubility is only $1{\cdot}25 \times 10^{-24}$ g. per litre at 25°), the stable state must be $HgS+Hg$.

Mercurous Halides

The *fluoride* is quite unlike the other halides in behaviour (as occurs also with the mercuric halides), though its tetragonal crystals have the same lattice as mercurous chloride[604]; it is very soluble in water but at once hydrolysed by it (owing to the weak acidity of hydrogen fluoride) to hydrogen fluoride and the black 'oxide'.

The *chloride bromide* and *iodide* are very similar to one another. They are all very insoluble in water, the solubility falling off as the atomic weight of the halogen rises. The solubilities[605] are given below, in gram-molecules per litre at 25°, with those of the mercuric halides:

	Hg_2Cl_2	Hg_2Br_2	Hg_2I_2
	103×10^{-8}	$3{\cdot}7 \times 10^{-8}$	$0{\cdot}037 \times 10^{-8}$
	$HgCl_2$	$HgBr_2$	HgI_2
	0·269	0·0171	0·00013
Ratio Hg″/Hg′	$2{\cdot}6 \times 10^5$	$4{\cdot}6 \times 10^5$	$3{\cdot}5 \times 10^5$.

The mercuric salt is always 300,000 or 400,000 times more soluble.

Mercurous chloride, Hg_2Cl_2, is known as calomel, from the late Greek word καλομέλας, 'beautiful black', owing to the colour of the precipitates which it forms with alkalies or ammonia (see below, p. 295). It melts at 54·3°, and sublimes even below this temperature. Its vapour density is only half that required for Hg_2Cl_2, suggesting that the molecule in the vapour is HgCl; this is, however, really due to the decomposition into free mercury and mercuric chloride, as was established by measuring the absorption of the mercury resonance line at 2,537 A.[606] and by the diamagnetism of the vapour,[607] since HgCl must be paramagnetic. Gucker

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[604] F. Ebert and H. Woitinek, *Z. anorg. Chem.* 1933, **210**, 269.

[606] A. E. Brodsky and J. M. Scherschewer, *Z. Elektrochem*, 1926, **32**, 3.

[605] F. T. Gucker and R. H. Munch, *J.A.C.S.* 1937, **59**, 1275.

[607] P. W. Selwood and R. Preckel, ib. 1940, **62**, 3055.

and Munch[606] found that drying had some effect in stopping the dissociation; moist calomel was wholly dissociated to $Hg+HgCl_2$ at 100°, while if it was dried, free mercury did not appear below 250°; but the vapour density at 375–425° was that of HgCl or $Hg+HgCl_2$; Baker[608] had found the vapour density of dried calomel to be that of Hg_2Cl_2 at 440°. The reactivity of mercurous halides is certainly much diminished by careful drying; thus their reaction with alkyl sulphides to form mercury and co-ordinated mercuric halides only takes place in the presence of water.

$$Hg_2Cl_2 + Alk_2S = Alk_2S \rightarrow HgCl_2 + Hg.$$

Beckmann[609] has found, from the freezing-points of solutions in the mercuric halides, that the molecules of these compounds are Hg_2Cl_2, Hg_2Br_2, and Hg_2I_2. Mercurous bromide has also been found to have in the vapour a density corresponding to HgBr (or $Hg+HgBr_2$).[610]

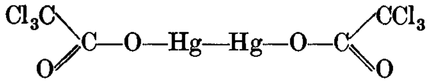
Mercurous iodide varies in colour from yellow to green according to the method of preparation and the amount of finely divided mercury present. The *iodide* is relatively unstable, and if warmed with water is slowly converted into mercury and mercuric iodide.

The *cyanide* $Hg_2(CN)_2$ cannot be prepared: the ionization of mercuric cyanide is so minute that the conversion of the mercurous salt into the mercuric and free mercury is complete.

Mercurous salts of Oxy-acids

The *carbonate* is a yellow powder slightly soluble in water and losing carbon dioxide when heated with it. The *formate* (sol^y 0·4/17°) is readily converted into mercury and carbon dioxide on boiling with water; the *acetate* (sol^y 8·1/15°) is more stable.

The *trichloracetate* appears to give a covalent form, as it is soluble in benzene. The dipole moment is 2·65 D, while that of the hydroquinone ester $Cl_3C\cdot CO\cdot O$$O\cdot CO\cdot CCl_3$ is 1·50.[611] This excludes any chelate structure for the mercurous compound, which must be



$$\begin{matrix}Cl_3C & & & & & & CCl_3\\ & C—O—Hg—Hg—O—C & & \\ O & & & & & & O\end{matrix}$$

with free rotation round the line O—Hg—Hg—O. The oxalate is insoluble. All these carboxylic salts are anhydrous.

The nitrate, one of the best known of the mercurous salts, is very soluble in water (sol^y *ca.* 30/25°) and forms various basic salts; the only normal salt is $Hg_2(NO_3)_2$, $2\,H_2O$, which is dimorphic.[612] Various double nitrates have been described, mostly of the type $M''(NO_3)_2$, $2\,Hg_2(NO_3)_2$,

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[608] H. B. Baker, *J.C.S.* 1900, **77**, 646.
[609] E. Beckmann, *Z. anorg. Chem.* 1907, **55**, 175.
[610] G. Jung and W. Ziegler, *Z. physikal. Chem.* 1930, **150**, 139.
[611] N. R. Davidson and L. E. Sutton, *J.C.S.* 1942, 565.
[612] H. G. Denham and C. V. Fife, ib. 1933, 1416.

but there is no reason to think they are complex, especially as complex mercurous salts are not otherwise known.

The mercurous salts of the oxy-acids of the sulphur subgroup are all nearly insoluble in water, and decomposed by it with more or less ease according to the strength of the acid. The sulphate Hg_2SO_4, the only well-known member of the class, can be made by grinding $HgSO_4$ with mercury; sol^y 0·06/20°. It is colourless: it darkens in light (especially ultraviolet), and gives a basic salt with water.

The salts of the chlorate series are fairly soluble, but the solubility falls off in the order $ClO_3 > BrO_3 > IO_3$, the last being almost insoluble. The perchlorate forms a tetrahydrate at low temperatures, going to a dihydrate at 36°, which is stable above 100°.[613]

Ammonia Compounds

The nature of the black solids which are formed when mercurous salts are treated with ammonia has been much disputed. The 'black precipitate' which gives its name to calomel has been known since the Middle Ages, and has the composition $Hg_2 \cdot Cl \cdot NH_2$; but it was variously regarded as a true mercurous amide $H_2N \cdot Hg \cdot Hg \cdot Cl$ or a mixture of the mercuric amide and free mercury $H_2N \cdot Hg \cdot Cl + Hg$. It was first suggested by Feigl[614] that a reversible reaction took place between these two systems, and the detailed work of Gleditsch and Egidius[615] has shown that this is true.

They find that the first effect of ammonia on mercurous chloride is to replace one chlorine, and give $H_2N \cdot Hg \cdot Hg \cdot Cl$. This is the 'black precipitate' as first produced. If it is filtered off and dried it can be kept indefinitely without change, but in contact with the mother liquor, or with any solution containing ammonia, it undergoes a slow change (some weeks in the cold) into free mercury and the mercuric amidochloride $H_2N \cdot Hg \cdot Cl$, which can be detected by its giving red mercuric iodide with potassium iodide. The corresponding nitrate $H_2N \cdot Hg \cdot Hg \cdot NO_3$ is formed in the same way, and undergoes the corresponding change in presence of ammonia, but much more rapidly (in about an hour).

Mercurous Complexes

The great majority of the complexes formed by mercuric mercury have no mercurous analogues. There is no evidence that the double nitrates are true complexes. No complexes of the mercurous ion with ammonia, diethyl sulphide, or the halogens have been prepared. If an attempt is made to prepare them from a mercurous salt, the mercuric complex is formed with separation of metallic mercury. This occurs with pyridine,[616]

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[613] E. Newbury, *J. Electrochem. Soc.* 1936, **69**, 57.

[614] F. Feigl and A. Sucharipa, *Z. anal. Chem.* 1925, **67**, 134.

[615] E. Gleditsch and T. F. Egidius, *Z. anorg. Chem.* 1936, **226**, 265; **228**, 249.

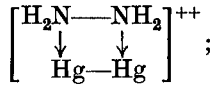
[616] W. Lang, *Ber.* 1888, **21**, 1587.

with ammonia, and with dialky lsulphides.[617] The reason, as Lang[616] pointed out, is that the equilibrium in the reaction

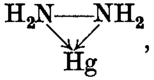
$$[Hg{-}Hg]^{++} \rightleftharpoons [Hg]^{++} + Hg$$

is disturbed by anything present that combines with either the mercuric or the mercurous ion. Now nearly all donors will co-ordinate with a doubly rather than a singly charged ion; hence they usually remove the mercuric ion as such and the mercurous salt is decomposed.

The only donors which might be expected to combine with the mercurous ion by preference would be chelate groups, if they were too small to complete a stable ring through a single metallic atom, but could do so through two; and it is interesting that the only certain mercurous complex is of this kind. Hofmann and Marburg[618] obtained an addition compound with hydrazine of the composition $N_2H_4 \cdot Hg_2(NO_3)_2$. It was formed from the components, but they give no details. Now this is a case where a mercurous complex is possible. The hydrazine molecule (like ethylene diamine) might co-ordinate through both its nitrogen atoms giving the complex



such a structure with only a 4-ring would usually be unstable, but this ring is peculiar, because the mercury atoms are more than twice as large as the nitrogens (radii of atoms Hg 1·48:N 0·70 A). With these radii the angles in the ring are 68° 40′ at the mercury and 111° 20′ at the nitrogen. The mercury has its usual shared quartet, in which the natural angle is 180°; but there is evidence that with a quartet the valency angle does not exert much resistance to compression; the nitrogen, on the other hand, has a full octet, which strongly resists deformation, but here the valency angle is 111° 20′, which is very near the normal tetrahedral angle of 109° 28′. With the mercuric ion the hydrazine must either form a 3-ring



in which the angles would be 72° at the nitrogen and 36° at the mercury, and the strain impossibly great, or an open-chain complex

$$[H_2N{-}NH_2{\rightarrow}Hg],$$

which would lack the stability of the chelate ring. So we can see why in this particlar case a mercurous complex is possible.

MERCURIC COMPOUNDS

These are far more numerous and important than the mercurous. The hydroxide $Hg(OH)_2$, from which the salts are derived, is a very weak base, at least as regards its second dissociation constant (i.e. has a strong tendency to assume the covalent state), and accordingly the salts when they are highly ionized are also highly hydrolysed.

[617] W. F. Faragher, J. C. Morell, and S. Comay, *J.A.C.S.* 1929, **51**, 2774.

[618] K. A. Hofmann and E. C. Marburg, *Ann.* 1899, **305**, 215.

The mercuric salts are unique in the extent to which their degree of ionization varies with the nature of the anion: no other element behaves in this way except hydrogen, which mercury resembles closely in some respects, especially in the fact that the group of shared electrons that the ion acquires when it goes over to the covalent state is a stable number for that element (4 for mercury, 2 for hydrogen). From this point of view the mercuric derivatives can be divided into four classes.

A. The salts of the strongest inorganic oxyacids, such as nitric, sulphuric, chloric, and perchloric. These are highly ionized (they are strong electrolytes), and considerably hydrolysed, so that their solutions have a strong acid reaction. The fluoride seems to belong to this group; it is highly ionized in water, and so highly hydrolysed (owing to the weak acidity of hydrofluoric acid) that it is almost completely decomposed by cold water into mercuric oxide and hydrogen fluoride.

B. The chloride, bromide, iodide, and thiocyanate. These are only slightly ionized in water (of the order of 1 per cent. or less, in *n*/20 solution) but enough to give a precipitate of the hydroxide with alkalies. They are accordingly only slightly hydrolysed, and their solutions have only a weak acid reaction.

C. Mercuric derivatives of the 'half-strong' organic acids, carboxylic and the like. These are partially ionized like the acids from which they are derived, and to about the same extent (see below p. 325).

D. Derivatives of compounds which have acidic hydrogen attached to carbon or nitrogen, such as hydrogen cyanide, acetamide, and imides. These are scarcely ionized (or hydrolysed) at all. They give no precipitates with alkalies. From these compounds we can go on to derivatives of non-acidic compounds like amines and hydrocarbons (e.g. to the mercury alkyls and aryls), in which the mercury, like the hydrogen it replaces, is not ionized at all. Thus with the sole exceptions of the chloride, bromide, and iodide, and perhaps the thiocyanate and fluoride (Class B), all the mercuric derivatives obey a peculiar but very simple rule: they are ionized to about the same extent as the hydrogen compounds from which they are derived. Where the acid is strong—that is, a strong mineral acid—the salt is a strong electrolyte (NO_3, SO_4, etc.) (Class A). Where the acid is 'half strong', i.e. with the carboxylic acids, the salt is also a 'half-strong' electrolyte, and is dissociated to about the same extent as the acid (Class C). When the hydrogen compound has its hydrogen attached to nitrogen, it is never a real acid of any strength: when it is attached to carbon it is practically not acidic at all. Mercury behaves in the same way. When it is linked to nitrogen the ionization is very small (Class D), and when to carbon the compounds are purely covalent.

Solubilities of Mercuric Salts

The solubilities of the mercuric salts, as compared with those of zinc and cadmium, are largely affected by their peculiarities of ionization. The mercuric salts of strong oxy-acids, such as the nitrate, chlorate, perchlorate, and sulphate, are readily soluble, like the zinc and cadmium salts. The oxides, sulphides, and carbonates of all three metals (only a basic mercuric carbonate is known) are all insoluble, and so are the oxalates. On the other hand, the slightly ionized chloride, bromide, and iodide, though much more soluble than their mercurous analogues (mercuric chloride dissolves to more than 7 per cent. in water at 25°), are far below the enormous solubilities of the zinc halides, and the very considerable solubilities of those of cadmium; while the almost un-ionized mercuric cyanide is very soluble—nearly 500 times as much as cadmium cyanide, and 10,000 times as much as zinc cyanide.

A general peculiarity of the mercuric salts is that they are rarely, if ever, hydrated, unless the anion can take up water; the mercuric cation scarcely hydrates at all. This is to be expected for two reasons: (1) the reluctance of mercury to combine with oxygen, and (2) its willingness to be content without a complete octet.

Compounds with Mercury-Carbon Links

Mercury stands quite alone among metals in its power of forming compounds with organic radicals. The replacement of hydrogen atoms in organic compounds by mercury is almost as easy as bromination or nitration, and the number of compounds which can be formed in this way is so large that mercury may almost be said to have an organic chemistry of its own.[619] This work has been stimulated by the hope, so far not fulfilled, of finding new and valuable drugs.

The organo-mercury compounds are also remarkable for the fact that unlike all other (neutral) alkyl or aryl derivatives of elements of any of the first three periodic groups, they are not acted on by air or water. These well-known facts have led to the natural belief that the Hg—C link is very strong, and is formed with a large emission of energy.

This, however, is not so. We can calculate the heat-value of the link in the following ways.

I. The heats of combustion of liquid mercury dimethyl and diethyl, and solid mercury diphenyl, have been determined[620]; from the results the heats of formation from the elements in their standard states can be got. For the heats of evaporation we may assume a Trouton constant of 21, giving 8, 9, and 19 k.cals. respectively (mercury diphenyl has an extrapolated b. pt. of 350° C.); to the last must be added the heat of fusion, which from the melting-point can be calculated to be 4 k.cals. From the resulting H_f values (see table, p. 299) we get H_a, the heat of

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[619] A very complete account of the work done on this subject up to 1921 is given in F. C. Whitmore's *Organic Compounds of Mercury*, Chem. Catalog Co., New York, 1921. This is quoted in what follows as 'Whitmore, p. x'. A more recent summary, which is less complete, but gives a very clear description of the more important facts, is contained in E. Krause and A. v. Grosse, *Met.-Org. Vbdgn.*, *Borntraeger*, Berlin, 1937, pp. 127–90.

[620] M. Berthelot, *C.R.* 1899, **129**, 918.

[621] P. Walden, *Z. Elektrochem.* 1908, **14**, 715.

formation from the atoms, using the heats of atomization C 170·4, H 51·7, Hg 14·6.[623] From these must be subtracted the heats of all the links except C—Hg—C (assuming C—H 98·8, C—C 81·6, C═C 146·1: heat of resonance of benzene nucleus 39 k.cals., we thus get:

	$HgMe_2$	$HgEt_2$	$Hg(C_6H_5)_2$
H_f (from elements in standard states)	—37·8 liq.	—15·4 liq.	—90 solid k.cals.
H_f for compounds as gases	—45·5	—24·5	—113
H_a (from atoms)	619·5	1,187·7	2,462
Energies of bonds other than Hg—C	593·5	1,152·7	2,432
H_a for C—Hg—C	26	35	30
H_a for Hg—C	13	17·5	15

Considering that these last are small differences of large numbers, they agree fairly well; the mean value for Hg—C is 15 k.cals. This is an almost unprecedentedly low value for a chemical bond,* and is more of the order to be expected for a van der Waals attraction.

There are, however, other reasons for thinking that the link of mercury to carbon is exceptionally weak.

II. All mercury dialkyls and diaryls except the dimethyl decompose spontaneously in the cold to mercury and the hydrocarbon (see below, p. 311). We may therefore assume that this reaction, which involves the change of linkage

$$\text{C—Hg—C} \longrightarrow \text{Hg} + \text{C—C}$$

is exothermic. Hence $2(\text{Hg—C}) < \text{C—C}\ (= 81{\cdot}6)$ so that $(\text{Hg—C}) < 40{\cdot}8$.

III. The same change of linkage occurs as we go from $Hg(CN)_2$ to $Hg+(CN)_2$. Their H_f values are $61{\cdot}8_{\text{sol.}}$: +14·6: and 72; giving the heat of reaction as 4·4.

For gaseous $Hg(CN)_2$ we must add S, the unknown heat of sublimation, which may well amount to between 10 and 20 k.cals. Thus

$$2(\text{Hg—C}) = \text{C—C} - S - 4{\cdot}4 = 77{\cdot}2 - S$$

or

$$\text{Hg—C} = 38{\cdot}7 - S/2.$$

IV. Krishnamurti[624] finds in the Raman spectrum of mercuric cyanide two lines, one at 2,192 cm.$^{-1}$ due to C≡N, and another at 276 cm.$^{-1}$ due to Hg—C. If these lines are accurately assigned, which there is no reason to doubt, the force constants accurately calculated,† are for $f_{\text{C≡N}}$ $17{\cdot}8 \times 10^5$, a normal value for this link, and for $f_{\text{Hg—C}}$ $1{\cdot}16 \times 10^5$, the latter probably the lowest value for a force constant that has yet been found. On the

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* A similar calculation from the heat of combustion of zinc ethyl gives for Zn—C 37·5 k.cals.

† I am indebted for the calculation to Dr. L. A. Woodward.

[623] Bichowsky and Rossini, *Thermochemistry*, p. 69.

[624] P. Krishnamurti, *Ind. J. Phys.* 1930, 5, 651.

rough assumption that the force constant is proportional to the heat of rupture, that of the Hg—C link, taking Pauling's value of 212 k.cals. for C≡N, is

$$212 \times \frac{1\cdot16}{17\cdot8} = 13\cdot8 \text{ k.cals.}$$

We have assumed that the mercury in the cyanide is attached to carbon; if it is not, then it is the Hg—N link that is so weak; but the Hg—C link must then be weaker still, or the mercury would be attached to the carbon. Conversely, if the mercury is joined to the carbon, the Hg—N link (though it is so stable) must be even weaker than the Hg—C.

The values obtained for Hg—C may be summed up thus:

I.	From heat of combustion of $HgMe_2$	13
	,, ,, ,, $HgEt_2$	17·5
	,, ,, ,, $Hg\Phi_2$	15
II.	Spontaneous decomposition of $HgAlk_2$	< 41
III.	,, ,, ,, $Hg(CN)_2$	$< 38\cdot7$
IV.	Raman spectrum of $Hg(CN)_2$	*ca.* 14
[Zn—C	from combustion of $ZnEt_2$	37]

It is thus clear that the energy of the Hg—C link is very small, much smaller than that of the Zn—C link in the highly reactive and spontaneously inflammable zinc ethyl. The chemistry of the mercury alkyls entirely supports this conclusion; almost any metal (Li, Na, Be, Mg, Zn, Cd, Al, Sn, Sb, Bi, Te) will remove the hydrocarbon radical from the mercury (for references, see p. 311).

The stability of the mercury organic compounds in spite of the small energy value of this link may be ascribed to two causes.

(1) The common belief in the great stability of the mercury alkyls is largely founded on their indifference to air and water, which attack all other non-ionized alkyl derivatives of elements of the first three periodic groups. But mercury has a peculiarly small affinity for oxygen; this is shown in the exceptionally high ionization of the salts of oxy-acids—mercury is reluctant to ionize, but even more reluctant to form covalent links with oxygen—and in the almost complete absence of covalent Hg—O compounds, even the normally stable chelate derivatives of β-diketones. The heat of formation of the oxide is abnormally small. The values for the formation of the solid oxides (*a*) H_f from the elements in their ordinary states, and (*b*) H_a from the atoms are:

	H_f	H_a
ZnO	83·5	170·0
CdO	65·2	152·1
HgO	21·6	95·3

The instability of the oxide to heat is familiar. Thus the indifference to air and water is no real proof of the strength of the link of mercury to alkyls and aryls.

(2) But even when full allowance is made for this there is still much to explain in the multiplicity and the stability of these Hg—C compounds, if it is true that the energy of the Hg—C link is so minute.

Now the position of mercury in these compounds is in a minor degree not unlike that of carbon itself in organic compounds, the remarkable multiplicity of which is not fully accounted for by the energy values of the links (see IV. 490). In other words, the stability of the organic compounds of mercury is largely not thermodynamic at all, but what we may call for want of a better name mechanical, depending on the heat of activation and not that of reaction. The explanation is probably the same with both elements. The ordinary saturated carbon atom has a valency octet which is fully shared, and also cannot expand farther, so that it cannot co-ordinate either as donor or as acceptor, and it is therefore precluded from undergoing any change through co-ordination, and consequently its rates of reaction are very much diminished. Mercury in its organic derivatives has a quartet of valency electrons, which is fully shared, so that it cannot act as a donor. But, as we have seen, its chief peculiarity is the small tendency that this quartet has to expand, or in other words the small tendency that di-covalent mercury has to co-ordinate as acceptor. This tendency is likely, as with other elements, to be exceptionally small in the alkyl and aryl compounds.

The organo-metallic compounds of mercury are of two kinds, according as one or both of the valencies of the mercury are attached to carbon. The first kind R—Hg—X are more easily made, and they can be converted by special reactions into the second kind HgR_2, which also can sometimes be made directly. The radicals attached to the mercury can be derived from paraffins, olefines, acetylenes, aromatic hydrocarbons, heterocyclic compounds like pyridine and thiophene, and their substitution products.

The various methods used for the replacement of other atoms attached to carbon by mercury may be classified according to the nature of the atoms replaced, which can be (1) hydrogen, (2) another metal, (3) nitrogen, (4) a halogen; it is also possible (5) to form these compounds by addition to doubly linked C=C groups.

1. *Replacement of Hydrogen*

This is the process known as 'mercuration'; it is highly characteristic of mercury, and scarcely if at all known in this direct form with other metals. Our knowledge of it is largely due on the aromatic side to O. Dimroth, and on the aliphatic to K. A. Hofmann, both of whom began their work on it in 1898. The process can be carried very far, and with many aliphatic compounds such as alcohol all the hydrogen on the carbon can be replaced by mercury; such fully mercurated products are known as mercarbides.[625]

Mercuration, like other replacements of hydrogen attached to carbon,

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[625] See Whitmore, pp. 125–31.

occurs more readily with the aromatic hydrocarbons than with the paraffins, and much more readily with many of the substitution products of the hydrocarbons than with the hydrocarbons themselves. The saturated paraffins cannot be mercurated directly, though many of the olefines can, and acetylene and its mono-derivatives with great ease. The aromatic hydrocarbons are mercurated by heating with mercury acetate: thus benzene when heated with it under pressure at 100-110° gives phenyl mercuric acetate, $C_6H_5\cdot Hg\cdot O\cdot CO\cdot CH_3$.[626] Heterocyclic compounds of the aromatic type, such as furane and thiophene, react more readily still.

The substitution products of both classes of hydrocarbons are more readily mercurated. On the aliphatic side this is especially true of the oxygenated derivatives, such as the alcohols and ketones. Ethyl alcohol when treated with mercuric oxide and alkali is converted into ethane hexamercarbide, $C_2Hg_6O_2(OH)_2$ (see further below, p. 314), in which all the hydrogen on the carbon has been replaced by mercury. Ketones containing the group $—CO—CH_2—$ mercurate easily, no doubt through the intermediate formation of the enol. Thus acetophenone is readily substituted in the methyl group, giving $C_6H_5—CO—CH_2—HgOAc$, while benzophenone, which cannot form an enol, does not mercurate below 150°, where it forms the ortho-mercury compound.

Among the aromatic compounds, substitution products, especially phenols and amines, mercurate (as they brominate) with great ease; there is some reason to think that the mercury may attach itself first to the oxygen or the nitrogen. Mercury is unlike practically all other aromatic substituents[627] in always taking up the ortho- or para-position whatever the previous substituent may be. Thus if benzoic acid is fused with mercuric acetate, or mercury benzoate is heated to 170°, the mercury goes to the ortho- (not as was thought the para-) position. Even with nitrobenzene the product is mainly ortho- and para-[628-9] substituted, the proportions being ortho:meta:para = 53:38:9[630]; napthalene derivatives behave in the same way.[631]

In nearly all these mercurations the mercury compound used must have the metal attached to oxygen and not to halogen; in the aliphatic series mercuric oxide or a salt in an alkaline solution is used, and in the aromatic mercuric acetate. The reason obviously is that the affinity of mercury for oxygen is almost as small as for carbon, while it is much higher for the halogens.*

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* The heats of formation of the links of mercury to the halogens are only about 22 k.cals. less than for carbon, the values being:

		Hg—hal.	C—hal.
Hal. =	Cl	52·9	78·0
	Br	45·0	65·5
	I	35·4	57·0

[626] O. Dimroth, *Ber*. 1898, **31**, 2154.

[627] When free aryls displace hydrogen from aromatic hydrocarbons to give diaryls, they always do so in the ortho- or para-positions to any substituents present: W. S. Rapson and R. G. Shuttleworth, *Nature*, 1941, **147**, 675.

The only exception to this is in the replacement of hydrogen attached to triply linked carbon, in acetylene and its monosubstitution products. These can not only be mercurated with great ease by compounds in which the mercury is attached to oxygen or to carbon (cyanide), but even by the halides[632-3]; the reaction

$$\text{Alk—Hg—Cl} + \text{H—C}\equiv\text{C—R} = \text{Alk—Hg—C}\equiv\text{C—R} + \text{HCl}$$

takes place very readily.

Hydrogen is of course very weakly held by triply linked carbon (for a reason, see IV. 508). If the heat value for C—H were normal, this reaction would be highly endothermic:

$$\begin{array}{lcccccc} & \text{C—H} & + \ \text{Hg—Cl} & = & \text{C—Hg} & + \ \text{H—Cl} & + \ \text{Q} \\ & 98{\cdot}8 & 52{\cdot}9 & & 15 & 102{\cdot}7 & \\ \text{Total} & & 151{\cdot}7 & = & 117{\cdot}7 & & + \ \text{Q} \\ & & \text{Hence Q} & = & 34{\cdot}0. & & \end{array}$$

2. *Replacement of Other Metals*

The energy of the Hg—C link is so small that the replacement of any other metal attached to carbon by mercury must involve expenditure of energy, and so can only occur if there is a counterbalancing gain in some other part of the reaction. Thus alkyl and aryl radicals can be introduced by means of the Grignard reagent[634-6]; for example:

$$2\,\text{CH}_3\cdot\text{Mg}\cdot\text{Br} + \text{HgBr}_2 = \text{Hg(CH}_3)_2 + 2\,\text{MgBr}_2.$$

Similarly, mercury can exchange a halogen for an alkyl with other elements such as boron,[637] tin, and antimony.[638] Mercury diphenyl can also be made by heating phenyl arsenic oxide $C_6H_5\cdot AsO$ with mercuric chloride in alkaline solution.[639] If mercury diethyl is heated with lead tetramethyl an equilibrium is established.[640]

Another example of a very peculiar kind is the reaction of mercuric chloride with aluminium carbide Al_4C_3 in presence of water and hydrochloric acid (as it were with nascent methane); this occurs in the cold, with separation of drops of mercury dimethyl[641]:

$$2\,\text{Al}_4\text{C}_3 + 3\,\text{HgCl}_2 + 18\,\text{HCl} = 3\,\text{Hg(CH}_3)_2 + 8\,\text{AlCl}_3.$$

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[628] O. Dimroth, *Ber.* 1902, **35**, 2036.

[629] Id., *Ann.* 1925, **446**, 148.

[630] J. Jürgens, *Rec. Trav.* 1926, **45**, 61.

[631] J. Krynski, *Rocz. Chem.* 1928, **8**, 71.

[632] R. J. Spahr, R. R. Voigt, and J. A. Nieuwland, *J.A.C.S.* 1933, **55**, 2465, 3728.

[633] T. H. Vaughan, ib. 3453.

[634] P. Borgstrom and M. M. Dewar, ib. 1929, **51**, 3387.

[635] H. Gilman and R. E. Brown, ib. 928.

[636] Id., ib. 1930, **52**, 3314.

[637] A. Michaelis and P. Becker, *Ber.* 1882, **15**, 180.

[638] R. C. Freidlina, A. A. Kotscheschkov, and A. A. Nesmejanov, *Ber.* 1935, **68**, 565.

[639] D. R. Patent, *Chem. Centr.* 1914, i. 1469.

[640] G. Calingaert, H. Soroos, and H. Shapiro, *J.A.C.S.* 1941, **63**, 947.

[641] S. Hilpert and M. Ditmar, *Ber.* 1913, **46**, 3738.

3. *Replacement of Nitrogen*

The nitrogen atom of an aromatic amine can be replaced by mercury through the diazo-compound. The double salt of the diazonium chloride with mercuric chloride can be decomposed by copper powder, as in the Gattermann reaction[642-3]:

$$\mathrm{Ar\cdot N_2[HgCl_3] + 2\,Cu = Ar\cdot Hg\cdot Cl + 2\,CuCl + N_2.}$$

In place of copper powder we can use silver, gold, iron, zinc, or magnesium as metallic powders, or stannous chloride,[644] or the diazonium salt may be treated directly with mercury finely divided by vigorous stirring[645]:

$$\mathrm{Ar\cdot N_2Cl + Hg = Ar\cdot Hg\cdot Cl + N_2.}$$

Another modification of this is to treat the diazonium borofluoride with mercuric chloride and stannous chloride, stirring rapidly as before.[646]

A further method is by the action of mercuric oxide on phenyl hydrazine.[647-8]

4. *Replacement of Oxygen*

This may be done with mercury amalgam. Thus the mercury dialkyls have been prepared by treating the dialkyl sulphate with $\frac{1}{2}$ per cent. sodium amalgam in presence of a little ethyl acetate as catalyst.[649-50]

5. *Replacement of Halogens*

The simple reaction of the type

$$\mathrm{Alk{-}hal + M = Alk{-}M{-}hal}$$

which goes so readily, for example, with zinc and with magnesium, occurs with mercury only in a few cases, as would be expected from the energy values, which show that it should be slightly endothermic:

$$\begin{array}{lcl} \mathrm{C{-}Br + Hg} & = & \mathrm{C{-}Hg{-}Br} \\ 65{\cdot}5 & - & 15 + 45{\cdot}0 \\ 65{\cdot}5 & & \quad 60 \end{array}$$

It takes place with methyl iodide (in the cold in sunlight), with methylene iodide (giving $\mathrm{I{-}Hg{-}CH_2{-}Hg{-}I}$), with benzyl iodide, and with some unsaturated iodides such as alkyl iodide. With other halides it can be effected by sodium amalgam in presence of ethyl acetate, the original method of Frankland and Duppa[651]; a weak amalgam must be used, or

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[642] A. A. Nesmejanov, *Ber.* 1929, **62**, 1010.
[643] A. A. Nesmejanov and E. J. Kahn, ib. 1018.
[644] A. A. Nesmejanov, *Sci. Rep. Mosc. State Univ.*, 1934, **3**, 291.
[645] R. E. McClure and E. Lowy, *J.A.C.S.* 1931, **53**, 319.
[646] M. F. W. Dunker, E. B. Starkey, and G. L. Jenkins, ib. 1936, **58**, 2308.
[647] E. Fischer and W. Ehrhard, *Ann.* 1879, **199**, 332.
[648] M. O. Forster, *J.C.S.* 1898, **73**, 791.
[649] K. Fuchs, *J. prakt. Chem.* 1928, ii. **119**, 209.
[650] H. F. Lewis and E. Chamberlin, *J.A.C.S.* 1929, **51**, 291.
[651] E. Frankland and B. F. Duppa, *J.C.S.* 1863, **16**, 415; *Ann.* 1864, **130**, 104.

the olefine is formed. Thus mercury diphenyl can be made from bromobenzene and a 2·7 per cent. sodium amalgam at about 120°, or by the action of sodium on a benzene solution of bromobenzene and mercuric chloride.[652]

6. *Addition to Double Carbon Bonds*

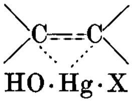
Mercuric salts, especially the acetate (particularly in methyl alcohol solution, where it is probably present in the basic form

$$CH_3 \cdot CO \cdot O \cdot Hg \cdot OH)^{653}$$

add on the ethylene and other unsaturated carbon compounds. The products, according to the conditions, have the composition either of a 1:1 addition compound, or of a molecule derived from two of these by removing a molecule of water. Hofmann, to whom the discovery is due,[654] assumed that the products had the structures of a mercurated alcohol and ether: for example, from ethylene $HO \cdot CH_2 \cdot CH_2 \cdot Hg \cdot X$ and

$$X \cdot Hg \cdot CH_2 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot Hg \cdot X,$$

but the compounds on treatment with mineral acids, instead of forming the alcohol or ether, regenerate the original ethylene or other unsaturated hydrocarbon. Hence Manchot[655] concluded that they are really 'molecular compounds' (whatever that may mean) and he wrote the structure



and in similar improbable ways.[653,656-8]

Hofmann's structure is supported by the great stability of the compounds not only to heat but to any reagent that is not acidic; thus hydrogen sulphide merely forms a sulphide of the organo-mercury derivative; the 'alcohol' product can be benzoylated without decomposition[659]; more recently[660] Hofmann has supported his theory by a series of chemical reactions, especially the conversion of the substance by iodine into iodohydrin

$$HO \cdot CH_2 \cdot CH_2 \cdot Hg \cdot Br + I_2 = HO \cdot CH_2 \cdot CH_2 \cdot I + HgBrI.$$

Moreover, the separation of ethylene on treatment with acids occurs with other metals as well. Thus ethyl magnesium bromide reacts[661] with

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[652] A. Michaelis and A. Reese, *Ber.* 1882, **15**, 2877.

[653] G. F. Wright, *J.A.C.S.* 1935, **57**, 1993.

[654] K. A. Hofmann and J. Sand, *Ber.* 1900, **33**, 1340, 1353, 2692; J. Sand, ib. 1901, **34**, 1385, 2906; 1902, **35**, 3170; J. Sand and O. Genssler, 1903, **36**, 3704.

[655] W. Manchot, ib. 1920, **53**, 984; *Ann.* 1920, **420**, 170.

[656] A. A. Nesmejanov and R. C. Freidlina, *Ber.* 1926, **69**, 1631.

[657] L. T. Sandborn and C. S. Marvel, *J.A.C.S.* 1926, **48**, 1413.

[658] E. Griffith and C. S. Marvel, ib. 1931, **53**, 789.

[659] J. Sand, *Ber.* 1901, **34**, 1390.

[660] K. A. Hofmann and K. Leschewski, ib. 1923, **56**, 123.

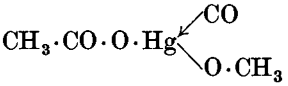
[661] E. Krause and B. Wendt, quoted by Hofmann and Leschewski, loc. cit.

manganous chloride to give a mixture of equal volumes of ethylene and ethane, along with metallic manganese and magnesium halide.

Addition compounds of these kinds are formed by many unsaturated molecules, such as *cis* and *trans* cinnamic ester,[656, 662] *cis* and *trans* stilbene,[663] and *cis* and *trans* styryl cyanide.[664] In these reactions each steric form gives its own addition product. The addition is much more rapid to *cis* than to *trans* stilbene, and it is also more rapid to the low-melting form of styryl cyanide, which may, therefore, be assumed to be the *cis* cyanide. It is much quicker in presence of ordinary nitric acid, owing to the peroxide which it contains; the effect is not produced by nitric acid which has been freed from peroxide, while it is produced by benzoyl peroxide.

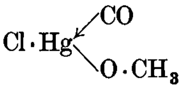
6. A. *Addition to Carbon Monoxide*

A methyl alcoholic solution of mercuric acetate absorbs carbon monoxide, though much more slowly than ethylene, and will finally take up 1 CO per Hg at 1 atm. in the cold.[665] The product, which, as Manchot showed,[666] should be written



$$\mathrm{CH_3\cdot CO\cdot O\cdot Hg}\begin{matrix}\swarrow\mathrm{CO}\\ \diagdown\mathrm{O\cdot CH_3}\end{matrix}$$

melts at 110° with loss of CO. Potassium chloride converts it into the chloride



$$\mathrm{Cl\cdot Hg}\begin{matrix}\swarrow\mathrm{CO}\\ \diagdown\mathrm{O\cdot CH_3}\end{matrix}$$

and hydrochloric acid very readily expels the CO, with the formation of the complex mercuric halide. This makes it certain that the carbon monoxide is co-ordinated to the mercury.

Heterocyclic Derivatives

The hydrogen atoms of heterocyclic compounds of aromatic character, such as furane,[667] thiophene,[668–70] selenophene,[671–2] pyrrol,[673–4] indol,

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[662] G. F. Wright, *J.A.C.S.* 1935, **57**, 1993.

[663] A. M. Birks and G. F. Wright, ib. 1940, **62**, 2412.

[664] W. H. Brown and G. F. Wright, ib. 1991.

[665] W. Schoeller, W. Schrauth, and W. Essers, *Ber.* 1913, **46**, 2864.

[666] W. Manchot, ib. 1920, **53**, 984.

[667] H. Gilman and G. F. Wright, *J.A.C.S.* 1933, **55**, 3302.

[668] O. Dimroth, *Ber.* 1899, **32**, 759.

[669] W. Steinkopf and M. Bauermeister, *Ann.* 1914, **403**, 55.

[670] W. Steinkopf, ib. 1917, **413**, 318.

[671] H. V. A. Briscoe, J. B. Peel, and G. W. Young, *J.C.S.* 1929, 2589.

[672] M. T. Bogert and C. N. Andersen, *J.A.C.S.* 1926, **48**, 223.

[673] H. Fischer and R. Müller, *Z. physiol. Chem.* 1925, **148**, 155.

[674] G. Plancher and G. Rossi, *Gaz.* 1925, **55**, 61.

thionaphthene,[675] pyridine,[676] quinoline, etc., are even more readily replaced by mercury, as they are also by other substituents, than those of the carbocyclic hydrocarbons. Dimroth has shown that we can free benzene from thiophene by boiling it with mercuric oxide in aqueous acetic acid; the thiophene has all gone into the water as the mercury compound $C_4H_3S\cdot Hg\cdot O\cdot CO\cdot CH_3$ within an hour, while the benzene only reacts under pressure at temperatures of 100° and above.

In the 5-ring compounds the substitution, like halogenation and nitration, always takes place by preference in the α- or 2 and 5 positions. We can replace the β-hydrogen atoms as well; both furane and pyrrol can be made to react with mercuric acetate so as to replace the whole of the hydrogen, giving tetra-mercury derivatives, such as $C_4O(Hg\cdot OAc)_4$.[677]

Hydrogen attached to triply linked carbon is peculiarly easily replaced by mercury; the preparation as well as the properties of these mercury derivatives of acetylene is described later (p. 315).

Catalytic Action of Mercury in Organic Reactions

It is no doubt owing to the readiness with which mercury will replace hydrogen linked to carbon, or attach itself to the carbon double link, that it can act as a catalyst in so many organic reactions.[678-86] Thus mercury promotes the hydration of acetylene to aldehyde and of nitriles to amides[685]: the nitration[683] and the sulphonation[648-50,681,684] of aromatic compounds; and the oxidation by concentrated sulphuric acid of organic substances in the Kjeldahl reaction, and of naphthalene to phthalic acid,[686] and by nitric acid of benzene to dinitrophenol.[682] It is clear that in most if not all of these reactions the first stage is the attachment of the mercury to carbon; we know that this occurs with acetylene (p. 315), and in sulphonation it has been shown[684] that where this normally occurs in the meta-position (as with nitrobenzene and with benzene sulphonic acid) the extra sulphonation in presence of mercury is mainly in the ortho- and para-positions.

Conversion of Mono- into Di-derivatives

$$R\cdot Hg\cdot X \longrightarrow HgR_2$$

The simpler mercury dialkyls and diaryls can be made directly, for example, by the action of mercuric halides on zinc or magnesium alkyls and aryls. Occasionally, too, organic compounds can be mercurated straight

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[675] F. Challenger and S. A. Miller, *J.C.S.* 1939, 1005.
[676] G. Sachs and R. Eberhartinger, *Ber.* 1923, **56**, 2223.
[677] R. Ciusa and G. Grillo, *Gaz.* 1927, **57**, 322.
[678] A. Roux and J. Martinet, *C.R.* 1921, **172**, 385.
[679] A. Coppens, *Rec. Trav.* 1925, **44**, 907. [680] A. Meyer, *C.R.* 1927, **184**, 609.
[681] H. E. Fierz-David, *Helv. Chim. Acta*, 1927, **10**, 197.
[682] A. I. Zakharov, *J. Chem. Ind. Moscow*, 1927, **4**, 960.
[683] P. V. McKie, *J.C.S.I.* 1927, **46**, 262 T.
[684] K. Lauer, *J. prakt. Chem.* 1933, ii. **138**, 81.
[685] G. Travagli, *Gaz.* 1936, **66**, 525.
[686] D. R. Patent, *Chem. Centr.* 1897, i. 1040.

through to the di-compounds: thus mercuric oxide acts on methyl malonate to give $Hg(CH(COOCH_3)_2)_2$.[687] As a rule, however, the reaction stops at the first stage with the production of the mono-mercury salt R—Hg—X, which appears to be more stable than a mixture of R_2Hg and HgX_2.[688] Thus mercury diphenyl and mercuric chloride, if mixed in acetone or alcohol solution, immediately give a precipitate of phenyl mercury chloride, $\Phi \cdot HgCl$.[689]

The reverse action

$$2\,R\cdot Hg\cdot X = R_2Hg + HgX_2$$

seems only to occur when R is an α-thienyl radical.[690]

Usually the di-derivatives are made by the reduction of the mono- with sodium[691]:

$$2\,R\cdot Hg\cdot Cl + 2\,Na = R_2Hg + Hg + 2\,NaCl$$

with copper powder,[692] forming cuprous chloride (this is the best method as a rule), with an alkaline stannite,[693] or with other reducing agents such as hydrazine or hydroxylamine in sodium carbonate solution.[694]

The compounds can also be made by treating the mono-derivative with the Grignard reagent, by which means mixed di-derivatives can be obtained[695]:

$$R\text{—}Hg\text{—}Cl + Br\text{—}Mg\text{—}R' = R\text{—}Hg\text{—}R' + MgClBr.$$

Another series of reactions depends on the fact that the change

$$2\,R\text{—}Hg\text{—}X = R_2Hg + HgX_2$$

can be brought about if the salt HgX_2 is removed from the sphere of reaction. This can be done[691] by warming the sulphide

$$(R\cdot Hg)_2S = R_2Hg + HgS$$

owing to the insolubility of mercuric sulphide: or by forming a complex mercury salt:

$$2\,R\text{—}Hg\text{—}X + 2\,KX = R_2Hg + K_2HgX_4,$$

where X can be an iodine atom, or the cyanide or thiocyanate group.[696-7]

A further method is to carry the diazo-synthesis of R—Hg—X a stage farther with the help of more copper powder, in 25 per cent. aqueous ammonia.[698]

$$2\,Ar\cdot Hg\cdot Cl + 2\,Cu = Ar_2Hg + 2\,CuCl.$$

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[687] W. Schrauth and W. Schoeller, *Ber.* 1908, **41**, 2087.

[688] 'The mercury atom has a strong tendency to saturate its two valencies with different atoms or groups': K. A. Hofmann and E. C. Marburg, *Ann.* 1899, **305**, 196.

[689] W. Steinkopf, ib. 1917, **413**, 313, 329.

[690] Whitmore, p. 59.

[691] E. Dreher and R. Otto, *Ber.* 1869, **2**, 542.

[692] F. Hein and K. Wagler, ib. 1925, **58**, 1499; *Chem. Centr.* 1927, ii. 741.

[693] O. Dimroth, *Ber.* 1902, **35**, 2033.

[694] H. Gilman and M. M. Barnett, *Rec. Trav.* 1936, **55**, 563.

[695] H. Gilman and R. E. Brown, *J.A.C.S.* 1930, **52**, 3314.

[696] F. C. Whitmore and R. J. Sobatzki, ib. 1933, **55**, 1128.

[697] R. W. Beattie and F. C. Whitmore, ib. 1567.

[698] A. N. Nesmejanov and E. J. Kahn, *Ber.* 1929, **62**, 1018.

Physical Properties of Mercury-organic Compounds

Some of the more highly mercurated compounds such as the mercarbides are high-melting solids which are no doubt polymerized; but the simpler mono- and di-alkyl and aryl derivatives are monomeric.[699–700] The di-alkyls and diaryls are obviously covalent molecules; some of their melting-points and boiling-points are:

Dialkyls	*B.pt./760*	*Diaryls*	*M. pt.*	*B. pt.*
$Hg(Me)_2$	92°	$Hg(C_6H_5)_2$	125°	204°/10·5 mm.
$HgEt_2$	159°	Hg(*o*-tol)$_2$	107°	219°/14 mm.
Hg *n*. Pr_2	189°	Hg(α-naphth)$_2$	243°	
Hg *i*. Bu_2	206°			

For the compounds with long alkyl chains, such as the di-octodecyl, $Hg(C_{18}H_{37})_2$, melting-point 67°, see reference [701]. The dialkyls above the dipropyl decompose to some extent on boiling under atmospheric pressure. They are all soluble in organic solvents such as benzene and chloroform.

The dialkyl and diaryl compounds, but especially the former as they are the more volatile, are excessively poisonous: the alkyl-mercury halides are said to be even more so. Mercury diphenyl has an irritating effect on the eyes; the dibenzyl, the diethyl, and ethyl-hydroxide Et·Hg·OH have a strong vesicating action on the skin.

Dipole Moments of Hg—C compounds

The mercury diaryls have very small dipole moments; that of mercury diphenyl at 25° is 0·41 in benzene, 0·44 in decaline,[702–3] and 0·42 in dioxane.[704] This suggests that the C—Hg—C group is linear (as the crystal structures of the dihalides indicate), but with considerable flexibility, a conclusion supported by the larger moments of the di-para-substituted diphenyls $HgAr_2$, which are in decaline at 140°[703]:

Ar =	*p*-tolyl	*p*-$Cl\cdot C_6H_4$	*p*-$Br\cdot C_6H_4$	*p*-$F\cdot C_6H_4$
Moment	0·74	1·15	0·92	0·87

The moments of the mercury aryl and alkyl bromides R·Hg·Br (dealt with in the next section) at 50° in dioxane are[704]:

R =	C_6H_5	*p*-tolyl	*p*-$Cl\cdot C_6H_4$	Butyl	Amyl
Moment	3·06	3·39	1·57	3·45	3·53

Hence the moment of C—Hg—Br must be about 3·5 with the bromine negative. From the values C_6H_5—Hg—Br −3·06, and Alkyl—HgBr −3·50, with the difference −0·44, it follows on Sutton's rule[705] that substituents

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[699] A. Ghira, *Gaz.* 1894, **24**, 320.

[700] R. C. Menzies and H. Overton, *J.C.S.* 1933, 1290.

[701] R. N. Meals, *Iowa State Coll. J. Sci.* 1943, **18**, 62.

[702] E. Bergmann and W. Schutz, *Z. physikal. Chem.* 1932, B **19**, 401.

[703] G. C. Hampson, *Trans. Far. Soc.* 1934, **30**, 877.

[704] B. C. Curran, *J.A.C.S.* 1942, **64**, 830.

[705] L. E. Sutton, *Proc. Roy. Soc.* 1931, **133**, 668.

should go to the meta-position (difference for $-CN$ $-0{\cdot}43$, for $-NO_2$ $-0{\cdot}88$).

Mono-alkyl and -aryl Mercury Derivatives

The most important of these are the halides, the nitrates, and the hydroxides; but a variety of salts have been prepared. The melting-points of some of these are given in the following table:

Melting-points of Compounds Alk—Hg—X

X =	F	Cl	Br	I	CN	OH
Me—Hg—X	200°	167°	161°	152°	93°	137°
Et—Hg—X		192°	193°	186°	77°	37°
^{n}Pr—Hg—X		147°	135°	113°	28°	78°
^{i}Bu—Hg—X		110°	122°	110°	39°	50°

The halides are volatile with steam, and some of them even with ether vapour. They are very slightly soluble in water, except the fluorides, which dissolve readily; the other salts (nitrates, sulphates) are more soluble, especially the hydroxides; a carbonate, $(C_6H_5—Hg)_2CO_3$, can be made with silver carbonate, and is easily recrystallized from alcohol: it decomposes on heating, and evolves carbon dioxide when treated with acetic acid.[706] The electrolytic behaviour of these compounds is shown by their molecular conductivities in decinormal solution at 25°[707-8]:

$CH_3{\cdot}Hg{\cdot}OH$	$CH_3{\cdot}HgOAc$	$[CH_3{\cdot}Hg]_2(SO_4)$	$[CH_3{\cdot}Hg](NO_3)$
0·71	4·92	57·4	101·0

It is evident that these compounds dissociate in the same way as the simple mercuric salts; the salts of strong oxy-acids very highly, those of the half-strong acids much less, and those of the halogen acids (to judge from their solubility in water) very little, except the fluoride: the hydroxide is evidently a weak base; phenyl mercury hydroxide, which should be still weaker, is extremely weak: the pH of a saturated solution (0·7 per cent.) in water at 25° is 7 to 7·6[709]; it is less soluble in normal alkali, and so has no acidic properties.

Chemical Properties of Mercury-organic Compounds

These are marked by two peculiarities. (1) the mercury is expelled from its link to carbon by a great variety of reagents, sometimes as free mercury, sometimes as a compound: the conversion of a dialkyl HgR_2 into a monalkyl derivative $R{\cdot}Hg{\cdot}X$ is particularly easy. (2) There is a curious slowness of reaction, indicating a high heat of activation.

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[706] Whitmore, p. 177.

[707] J. L. Maynard and H. C. Howard, *J.C.S.* 1923, 123, 960.

[708] K. H. Slotta and K. R. Jacobi, *J. prakt. Chem.* 1929, [2] 120, 249.

[709] R. M. Schramm, *J.A.C.S.* 1947, 69, 1831.

The weakness of the Hg—C link is shown by the ease with which the dialkyls and diaryls separate metallic mercury:

$$\mathrm{HgR_2 = Hg + R\cdot R.}$$

All the dialkyls except the dimethyl undergo this reaction in the cold on keeping; mercury separates, ultimately collecting in drops, and pressure develops, owing no doubt to the formation of free paraffin.[713] The higher dialkyls undergo this change rapidly on distillation at temperatures below 200°. The diaryls behave in the same way; mercury diphenyl begins to decompose slowly at 200°. Some break up even more readily. Mercury dibenzyl, which is unstable in many ways, and can scarcely be prepared by any method except through the Grignard reagent, does so at 75°, and is completely broken up by 160°.[716] Mercury dicyclohexyl $\mathrm{Hg(C_6H_{11})_2}$ is readily decomposed by light or heat, and reacts with mercuric chloride at once in the cold.[712]

Mercury dimethyl is markedly more stable (in the same way cadmium dimethyl is much more stable than cadmium diethyl); it does not decompose in the cold, but it does so, producing mainly ethane, either on heating to 300°[718] or on exposure to mercury radiation of 2,537 A.[717]

The mercury-carbon link can also be broken by a whole series of reagents. Hydrogen promotes the separation of mercury from all these products, giving the reaction

$$\mathrm{HgR_2 + H_2 = Hg + 2\,R\cdot H.}$$

Thus mercury methyl in presence of hydrogen mainly forms methane,[718] and mercury diphenyl under 50 atm. pressure of hydrogen at 275° is converted into benzene.[714]

Again, almost any metal will take a hydrocarbon radical away from mercury: for example,

$$\mathrm{2\,Li + Hg(C_2H_5)_2 = Hg + 2\,Li\cdot C_2H_5.}$$

Similar reactions, with both the alkyls and the aryls, have been observed with sodium, beryllium, magnesium,[711] zinc, cadmium,[711] aluminium,[710] tin,[715] antimony,[715] bismuth,[715] and tellurium.[719]

The same fission is brought about by any of the halogens, including iodine, and by a large number of halides reacting in the form

$$\mathrm{Hg{-\!-}C + A{-\!-}hal = Hg{-\!-}hal + A{-\!-}C.}$$

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[710] S. Hilpert and G Grüttner, *Ber.* 1912, **45**, 2828.

[711] Id., ib. 1913, **46**, 1675.

[712] G. Grüttner, ib. 1914, **47**, 1655.

[713] E. Krause, ib. 1926, **59**, 935.

[714] G. A. Razuvaiev and M. M. Koton, ib. 1932, **65**, 613.

[715] A. E. Shurov and G. S. Razuvaiev, ib. 1507.

[716] G. A. Razuvaiev and M. M. Koton, ib. 1933, **66**, 854.

[717] J. W. Linnett and H. W. Thompson, *Trans. Far. Soc.* 1937, **33**, 501.

[718] J. P. Cunningham and H. S. Taylor, *J. Chem. Phys.* 1938, **6**, 359.

[719] Whitmore, p. 94.

Halides which will react in this way include those of hydrogen, boron,[723] silicon,[720] phosphorus,[721] arsenic,[722] and antimony.

In the same way acyl halides form ketones

$$R_2Hg + CH_3{\cdot}CO{\cdot}X \;=\; R{\cdot}Hg{\cdot}X + CH_3{\cdot}CO{\cdot}R.$$

The ease of this reaction falls off in the order[724]

$$R{\cdot}COI > R{\cdot}COBr > R{\cdot}COCl > R{\cdot}COF.$$

Thus benzoyl iodide gives a 29 per cent. yield of ketone in 10 hours at 80°, while the fluoride only gives 2 per cent. in 35 hours at 120°; this is the exact opposite of the order observed in the reaction of the Grignard reagent with acyl halides by Entemann and Johnson.[725]

Many other reagents will break the Hg—C link. Thus potassium cyanide decomposes the ethylene addition products with evolution of ethylene on warming.[726]

With the oxides of nitrogen it has been shown[727–8] that though nitric oxide has no action, nitrogen sesquioxide acts on mercury diphenyl to form phenyl mercury nitrate $C_6H_5{\cdot}Hg{\cdot}NO_3$ and benzene diazonium nitrate, while nitrogen tetroxide gives the same mercury compound along with nitrosobenzene. Sulphur trioxide reacts with mercury diphenyl with great violence, separating both the carbon atoms from the mercury, and forming mercury benzene sulphonate $(\Phi{\cdot}SO_3)_2Hg$.[730] Chlorine monoxide Cl_2O also acts violently, the products including carbon, mercuric chloride, and phenyl mercury chloride.[729]

The ease with which the mercury dialkyls and diaryls can lose one of their two hydrocarbon radicals to form R·Hg·X has already been emphasized. The relative strength of attachment of different radicals can be determined by observing which of two different groups is split off in these reactions. This has been investigated by Kharasch and his fellow workers.[731–6]

These mixed derivatives HgRR′* are not very stable, and slowly change

* They can of course be made from the mercury alkyl halide and a Grignard reagent, and sometimes by the peculiar loss of carbon dioxide from the substituted benzoates on heating [731]; thus alkyl-mercury trinitrobenzoates lose carbon dioxide at 160–230° to give alkyl mercury trinitrophenyls.

[720] A. Ladenburg, *Ann.* 1874, **173**, 151.

[721] A. Michaelis, ib. 1876, **181**, 288.

[722] Id., ib. 1880, **201**, 184.

[723] Id., *Ber.* 1894, **27**, 247.

[724] H. Gilman and J. F. Nelson, *J.A.C.S.* 1939, **61**, 743.

[725] C. E. Entemann and J. R. Johnson, ib. 1933, **55**, 2900.

[726] K. A. Hofmann and J. Sand, *Ber.* 1900, **33**, 1344.

[727] E. Bamberger, ib. 1897, **30**, 509.

[728] L. I. Smith and F. L. Taylor, *J.A.C.S.* 1935, **57**, 2460.

[729] E. Dreher and R. Otto, *Ann.* 1870, **154**, 127.

[730] R. Otto, *J. prakt. Chem.* 1870, [2] **1**, 183.

[731] M. S. Kharasch and M. W. Grafflin, *J.A.C.S.* 1925, **47**, 1948.

[732] M. S. Kharasch and R. Marker, ib. 1926, **48**, 3130.

[733] M. S. Kharasch and A. L. Flenner, ib. 1932, **54**, 674.

[734] M. S. Kharasch, H. Pines, and J. H. Levine, *J. Org. Chem.* 1938, **3**, 347.

into a mixture of the pure derivatives HgR_2 and HgR'_2, but their physical and chemical properties show that they are distinct individuals when they are first prepared.

The order of ease of separation ('electronegativity') of different radicals in the reaction

$$HgRR' + HCl = R \cdot HgCl + R'H.$$

is as follows (compare, however, p. 311).

Among the least electronegative (most firmly bound) is benzyl, followed by the alkyl groups in order beginning with the heaviest and ending with methyl. All the aryls and substituted aryls are more electronegative—more easily removed—than any of the alkyls, and naphthyl more than phenyl. The introduction of a chlorine atom into an aromatic nucleus diminishes the electronegativity, and a second chlorine does so still more.

Inertness of the Mercury Organic Compounds

Although the Hg—C link is broken by so many reagents, the mono- and di-alkyl and aryl compounds of mercury show in many ways a remarkable slowness to react. Alkyl mercury halides, unlike the Grignard reagents, are not affected by water, amines, alcohols, or organic carbonyl compounds, and are usually attacked by acids only when they are hot and concentrated.[737] The mercury dialkyls and diaryls differ most markedly from the other organo-metals (such as those of zinc) in being stable to air and water and fairly stable to acids.

They are remarkably inactive in other ways too. Thus mercury di-*p*-tolyl gives no reaction[742] on refluxing for 300-350 hours in toluene with a large variety of mono- and di-halogenated paraffins, olefines, aromatic hydrocarbons, ketones, esters, and ethers. The alkyl or aryl mercury halides, unlike the Grignard reagents, will not react with alkyl halides to give the hydrocarbon and mercury halide.[745] The di-derivatives also react very slowly[744] (unlike other organo-metallic derivatives) with the carbonyl group of Michler's ketone,[740] with ketenes to form methyl ketones,[743] with sulphonyl iodides to form sulphones,[738] and (except the thiophene derivatives[746]) with acyl halides to give ketones.[741]

In the same way the Hg—C link usually cannot be broken by alkalies, though occasionally the mercury can be made in this way to lose one of two carbon atoms; thus sodium hydroxide reacts with the mercury derivative

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[735] M. S. Kharasch and S. Swartz, ib. 405.

[736] M. S. Kharasch, R. R. LeGault, and W. R. Sprowls, ib. 409.

[737] Whitmore, p. 38.

[738] F. C. Whitmore and N. Thurman, *J.A.C.S.* 1923, **45**, 1068.

[739] K. A. Hofmann and L. Leschewski, *Ber.* 1923, **56**, 123.

[740] H. Gilman and F. Schulze, *J.A.C.S.* 1925, **47**, 2002.

[741] H. O. Calvery, ib. 1926, **48**, 1009.

[742] F. C. Whitmore and E. N. Thurman, ib. 1929, **51**, 1491.

[743] H. Gilman, B. L. Woolley, and G. F. Wright, ib. 1933, **55**, 2609.

[744] H. Gilman and J. F. Nelson, ib. 1939, **61**, 743.

[745] Whitmore, p. 79.

[746] W. Steinkopf and M. Baumeister, *Ann.* 1914, **403**, 58.

of phenyl acetate $(CH_3\cdot CO\cdot O\cdot C_6H_4)_2Hg$ to remove one phenyl group and give $CH_3\cdot CO\cdot O\cdot C_6H_4\cdot Hg\cdot OH$.[747]

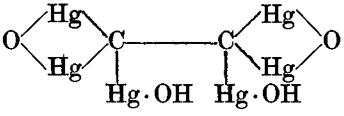
Again, in the mercurated phenols and anilines the OH and NH_2 groups can undergo a variety of transformations without the Hg—C link being disturbed. Thus a mercurated phenol $HO\cdot C_6H_4\cdot Hg\cdot X$ can have its hydroxyl acylated, or can be coupled with a diazonium salt; a mercurated aniline $H_2N\cdot C_6H_4\cdot Hg\cdot X$ can be acylated, and can be alkylated up to the $N(CH_3)_2$ or even further to a quaternary compound such as

$$Hg(C_6H_4\cdot N(CH_3)_3)_2[I]_2$$

(a stable compound melting at 230°), or its NH_2 group can be diazotized and then coupled to an amine or phenol to form a dye; and in all these reactions the mercury remains attached to the aromatic nucleus. Mercurated anilines will dissolve in aqueous ammonia, probably forming ammines of the mercury; but they are re-precipitated unchanged by acids.[748]

Similar inactivity is observed with the remarkable addition compounds of the mercury halides and oxyhalides to the double carbon link (above, p. 305), and is one of the strongest proofs that these are no 'loose addition products'; they react very unwillingly with all reagents other than acids[739]; the 'alcoholic' chloride $HO\cdot CH_2\cdot CH_2\cdot Hg\cdot Cl$ does not begin to decompose on heating below 154°. It is not broken up by alkalies or moist silver oxide, but merely converted into a strongly basic hydroxide; sodium or ammonium sulphide only precipitates the insoluble sulphide $(HO\cdot CH_2\cdot CH_2\cdot Hg)_2S$;* after shaking with alkali and potassium iodide it gives no traces of the Nessler reaction, showing that no mercury has been liberated; free hydroxylamine, which reduces HgClOH at once, only acts very slowly even on heating.

Some of the more highly mercurated compounds are even more inactive. Thus ethane hexamercarbide,[750]



(see above, p. 302) a yellow insoluble powder, forming equally insoluble salts with acids, is entirely unaffected by excess of acid, hydrogen sulphide, aqua regia, potassium permanganate, dichromate, or sodium hypochlorite, and its reduction by sulphur dioxide, hydroxylamine, or hydrazine is very slow. On heating it darkens with loss of water, but it does not decompose below the melting-point of tin (230°), where it detonates with great violence.

* Some of these sulphides will split off mercuric sulphide on heating; the pentamethylene derivative $[C_5H_9\cdot Hg]_2S$ does so slowly at 160°.[749]

[747] F. C. Whitmore and E. B. Middleton, *J.A.C.S.* 1921, **43**, 622.

[748] L. Vecchiotti, *Gaz.* 1918, ii. **48**, 80.

[749] S. Hilpert and G. Grüttner, *Ber.* 1914, **47**, 182.

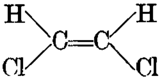
[750] K. A. Hofmann, ib. 1898, **31**, 1904.

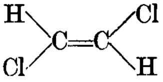
Acetylene Derivatives

The mercury derivatives of acetylene are especially easily formed, and are said to be to some extent salt-like in character; but they are scarcely more so than mercuric cyanide, of which the ionization in N/32 solution is less than 1 per cent. (p. 316). Acetylene precipitates from a solution of mercuric cyanide (i.e. a compound where the mercury is already attached to carbon) a white solid of the composition HgC_2, which is perhaps the salt $Hg[C{\equiv}C]$, and is highly explosive. The precipitates formed with other mercury salts are so completely insoluble that even their composition is uncertain. It is remarkable (since the products from ethylene regenerate the ethylene with acids) that when treated with mineral acids all these acetylene products produce acetaldehyde.[751] This is the basis of the technical production of acetaldehyde, acetic acid, and acetone from calcium carbide with a mercury catalyst.

If a stream of acetylene is passed into boiling 40 per cent. sulphuric acid containing a few per cent. of mercuric sulphate, a continuous evolution of acetaldehyde occurs. In the same way phenyl-acetylene gives acetophenone.[754–5] Mercury derivatives of many mono-substituted acetylenes, such as $(C_2H_5\cdot C{\equiv}C)_2Hg$, are readily prepared.[752]

Mercuric cyanide acts readily on *cis*-dichloroethylene $CHCl{=}CHCl$, one hydrogen atom being replaced by mercury and one HCl eliminated, with the formation of $(Cl\cdot C{\equiv}C)_2Hg$,[757] a white solid soluble in organic solvents, highly explosive, and forming mono-chloroacetylene with hydrochloric acid.[750] With *trans*-dichloroethylene no hydrogen chloride is lost, and one hydrogen is replaced by mercury, to give the doubly linked $(CHCl{=}CCl)_2Hg$. It is clear that the loss of hydrogen chloride only occurs from the *trans* positions of H and Cl, which are found in the *cis* but not in the *trans* compound





Derivatives in which both the hydrogen atoms of acetylene are replaced by mercury $R{-}Hg{-}C{\equiv}C{-}Hg{-}R$ are formed when alkyl or aryl mercury halides are treated with acetylene in alkaline solution.[753] They are clearly covalent, easily volatile, and soluble in most organic solvents, including benzene. They will dissolve in aqueous alkalies if more acetylene is passed into the solution, but if the excess of acetylene is removed by a stream of gas, or by lowering the pressure, they are re-precipitated. This seems to imply the reversible reaction

$$C_2H_2 + R\cdot HgC{\equiv}C\cdot Hg\cdot R \rightleftharpoons 2\,R\cdot Hg\cdot C{\equiv}C\cdot H.$$

If the R groups are both aryls the compounds are stable, but if even one is

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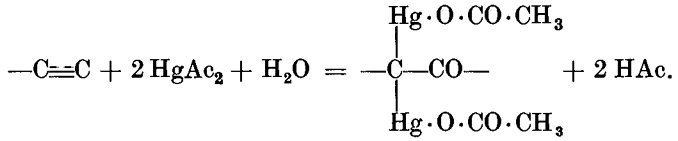
[751] M. Kutscheroff, ib. 1881, 14, 1540.
[752] J. R. Johnson and W. L. McEwen, *J.A.C.S.* 1926, 48, 469.
[753] J. R. Nieuwland *et al.*, ib. 1933, 55, 2465, 3728, 4206.

an alkyl they decompose in the air with the production of the corresponding aldehyde.

With long-chain acids containing a triple link, mercuric acetate will react in presence of water thus[756]:



$$—C{\equiv}C + 2\,HgAc_2 + H_2O = —\overset{\displaystyle Hg{\cdot}O{\cdot}CO{\cdot}CH_3}{\underset{\displaystyle Hg{\cdot}O{\cdot}CO{\cdot}CH_3}{C}}—CO— + 2\,HAc.$$

Sometimes the CO group is on the side nearer to the carboxyl, and at others a mixture of the two forms is produced. In presence of acid the mercury is split off with the production of the keto-acid ($—CO—CH_2—$), the reaction being precisely similar to that by which acetylene is converted into acetaldehyde.

Mercuric Cyanide, $Hg(CN)_2$

This is an unusual example of a metallic compound readily soluble in water but scarcely ionized in the solution. The solubility in water is 11·3/25°[758]; the molecular conductivity in N/32 solution at 25° is 0·14,[759] indicating an ionization of about 0·2 per cent. Hence its aqueous solution is not precipitated by hydroxyl or iodide ions, though it is by hydrogen sulphide, while it can be made by the action of mercuric oxide on complex cyanides like prussian blue. Hence also slightly soluble mercuric salts like the sulphate or phosphate dissolve in potassium cyanide solution.

The crystal structure has been examined by Hassel[761-2] and by Fricke,[763-4] but the facts, as well as their interpretation, seem to be doubtful.

On heating it decomposes into mercury and cyanogen; part of the latter remains behind as the polymer paracyanogen. Ley and Schaeffer[760] point out that while the mercuric derivatives of amides and imides are considerably decomposed by hydrochloric or nitric acid, mercuric cyanide is scarcely affected at all; they conclude from this that the mercury is attached to carbon and not to nitrogen.

Mercuric cyanide forms a very large number of complexes (p. 327), as might be expected from the high concentration of $Hg(CN)_2$ molecules in the aqueous solution (about 0·44-normal when saturated at 25°); the very

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[754] W. Manchot and J. Haas, *Ann.* 1913, **399**, 123.

[755] H. Biltz and K. Reinkober, ib. 1914, **404**, 219.

[756] W. W. Myddleton, A. W. Barrett, and J. H. Seager, *J.A.C.S.* 1930, **52**, 4405.

[757] M. Fitzgibbon, *J.C.S.* 1938, 1218.

[758] W. Herz and G. Anders, *Z. anorg. Chem.* 1907, **52**, 164, 271.

[759] H. Ley and H. Kissel, *Ber.* 1899, **32**, 1358.

[760] H. Ley and K. Schaeffer, *Z. physikal. Chem.* 1903, **42**, 690.

[761] O. Hassel, *Z. Krist.* 1926, **64**, 217.

[762] Id., *Z. anorg. Chem.* 1929, **180**, 370.

[763] R. Fricke and L. Havestadt, ib. 1928, **171**, 344.

[764] R. Fricke, ib. 1929, **180**, 374.

low (less than N/1000) concentration of CN ions prevents the formation of auto-complexes.

Mercury-Nitrogen Compounds

The affinity of mercury for nitrogen is of the same order as that for carbon, but is probably less intense. In particular there is reason to think[765-6] that in the mercuration, for example, of aniline the mercury attaches itself first to the nitrogen, and then migrates to the carbon.

The link has a very small tendency to ionize, though perhaps rather more than the link to carbon.

Hydrogen attached to trivalent nitrogen can practically always be replaced by mercury; the derivatives are easily made and comparatively stable; they can be obtained from ammonia and amines, and still more readily from amides and imides.

Mercuric Nitride, Hg_3N_2

This can be made[768] by the action of potassamide KNH_2 on mercuric iodide in liquid ammonia. It is a highly explosive chocolate powder, whereas all the other M_3N_2 nitrides of Group II are colourless and non-explosive. As mercury so readily forms covalent links, Hg_3N_2 may have a covalent molecule.

Derivatives of Ammonia and Amines

There are three types of compounds formed when ammonia acts on mercuric oxide or mercuric salts: (1) infusible white precipitate $H_2N \cdot Hg \cdot Cl$, (2) fusible white precipitate $Hg(NH_3)_2Cl_2$, and (3) Millon's base

$$(HO \cdot Hg)_2NH_2OH$$

and its salts. The white precipitates were examined by Kane (1836) and Rammelsberg (1846), and later the whole groups were re-examined and discussed by Hofmann,[767] who established the structures of these compounds on satisfactory evidence.

(1) Infusible white precipitate is made by the action of ammonia on an aqueous solution of mercuric chloride. Its composition is $H_2N \cdot Hg \cdot Cl$, and though it is obviously highly associated, its reaction agrees with this formula; for example, on prolonged boiling with 20 per cent. potassium hydroxide all the nitrogen is split off as ammonia, and nearly all the chlorine can be precipitated with silver nitrate. Ethylamine forms a similar compound $EtNH \cdot Hg \cdot Cl$. It is noticeable that the mercuric salts of oxy-acids such as nitric or sulphuric do not form analogous compounds, evidently because the mercury will not form a covalent link with the oxygen of their anions; instead of this they give salts of Millon's base, such as $OHg_2NH_2[NO_3]$.

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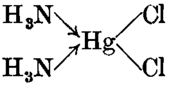
[765] M. S. Kharasch and I. M. Jacobsohn, *J.A.C.S.* 1921, **43**, 1894.

[766] A. F. Albert and W. Schneider, *Ann.* 1928, **465**, 257.

[767] K. A. Hofmann and E. C. Marburg, ib. 1899, **305**, 191.

[768] A. F. Wells, *Structural Inorganic Chemistry*, p. 425.

(2) Fusible white precipitate is formed when the mercuric chloride solution to which the ammonia is added contains much ammonium chloride; it is a diamine, and as such is discussed later (p. 328); it has the structure

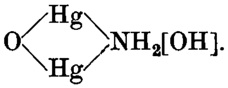


or perhaps $[Hg(NH_3)_2]Cl_2$.

(3) Millon's base is made by the action of aqueous ammonia on the yellow (more reactive) form of mercuric oxide. It has the composition $(HO \cdot Hg)_2NH_2OH$. Its exact structure is uncertain. Possibly it contains water of crystallization, and should be written $(HO \cdot Hg)_2NH,H_2O$. It behaves as a base, and with mineral acids forms a series of salts, all of which have lost a further molecule of water and are of the type

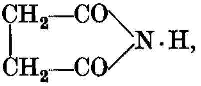
$$OHg_2NH_2[X] \ (X = Cl, Br, NO_3).$$

The free base also can be made to lose this water giving first OHg_2NH_2OH, and then at 125° OHg_2NH as a dark brown very heavy (density 8·52) powder, which explodes if it is touched or heated to 130°. The formulae given above seem probable; we may expand them as in



Rather similar compounds are formed by hydrazine.[767]

Mercury replaces the hydrogen attached to nitrogen more easily in amides than in amines, and still more easily in imides. Thus mercuric oxide dissolves in a solution of acetamide, or in fused acetamide,[769] to give $Hg(NH \cdot CO \cdot CH_3)_2$, and imides, especially cyclic imides like succinimide,



react equally easily. The products are very slightly ionized; their condition has been examined by Ley[770-1,773] by means of the conductivity. The conductivity of mercury acetamide was found to be little greater than that of mercuric cyanide, and that of the succinimide derivative even less, the values of μ at 25° and V 32 being

Mercury cyanide	0·18
,, acetamide	0·33
,, succinimide	0·10

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[769] W. Schoeller and W. Schrauth, *Ber.* 1909, **42**, 784.

[770] H. Ley and H. Kissel, ib. 1899, **32**, 1357.

[771] H. Ley and K. Schaefer, ib. 1902, **35**, 1309.

[772] R. Kiesseritzky, *Z. physikal. Chem.* 1899, **28**, 385.

[773] H. Ley and K. Schaefer, ib. 1903, **42**, 690.

The amide and imide solutions can be titrated with hydrochloric acid and methyl orange; hence they must contain hydroxyl ions (presumably derived from the half-hydrolysed product $CH_3 \cdot CO \cdot NH \cdot Hg[OH]$), and so the degree of ionization cannot be calculated directly from the conductivity.

The low ionization of these nitrogen compounds is supported by the observation that their solutions give no precipitate of mercuric oxide with alkali, and only slowly precipitate the iodide with potassium iodide.

It is remarkable that mercury fulminate has if anything a lower conductivity than the amide derivatives: it is so insoluble that it could not be measured above $V = 513$, but at this high dilution the value of μ is only 0·7.[770] Hence in the covalent form the mercury can scarcely be attached to oxygen. The fulminate radical contains the group $\mathrm{O{-}N{-}C}$; it is difficult to devise a formula in which it should be attached to the nitrogen, but the compound may have a Hg—C link, as in $\mathrm{O{=}N\underline{\underline{\rightarrow}}C{-}Hg{-}{-}}$, where the mercury has a valency quartet, and every other atom an octet.

Ley[771,773] has determined the extent of reaction of mercuric chloride with various amides and imides by means of the conductivity, the only reaction product that is sensibly ionized being the hydrochloric acid. He finds that only the first stage of the reaction occurs:

$$HgCl_2 + H \cdot NR = Cl \cdot Hg \cdot NR + HCl$$

(H·NR being the amide or imide). It proceeds much farther with imides than with amides; with succinimide (which gave a good equilibrium constant) it goes about 10 per cent. in N/64 solution, and about the same with camphorimide; with ordinary amides like acetamide, and with urea, the Hg—N compound is much less stable, and only 2 or 3 per cent. of it are formed. With mercuric nitrate, owing to its high ionization, much less reaction occurs.

These conclusions are in general supported by the E.M.F. measurements of Kieseritzky.[772]

Mercuric Oxide, HgO

This occurs in two forms, a yellow, prepared at low temperatures by precipitating a solution of a mercuric salt with alkali, and a red form, made by gently heating mercurous or mercuric nitrate, or by the action of air or oxygen on metallic mercury at temperatures above 300°. It is doubtful whether these differ in more than particle size. Garrett and Hirschler[774] find a 5 per cent. difference in solubility: yellow 51·3, red 48·7, mg. per litre at 25°; and calculate an energy difference of only 0·031 k.cals.; this suggests that the difference is only in particle size.

The direct combination of mercury with oxygen begins a little below its boiling-point of 357°; a little above this the oxide, as we should expect from the small affinity of mercury for oxygen, begins to dissociate again

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[774] A. B. Garrett and A. E. Hirschler, *J.A.C.S.* 1938, 60, 299.

(Lavoisier's experiment); the oxygen tension amounts to a few mm. at 440° and 1,240° mm. at 610°[775]; the heat of activation is 57·3 k.cals.[776]

The hydroxide $Hg(OH)_2$ cannot be isolated, as it loses water to give HgO. It is amphoteric in character, but more basic than acidic; according to Garrett and Hirschler[774] the two dissociation constants are at 25°:

$$K_b = \frac{[Hg^{++}]\cdot[OH]^2}{[Hg(OH)_2]} = 1{\cdot}8 \times 10^{-22}$$

$$K_a = \frac{[H^+]\cdot[HgO\cdot OH]}{[Hg(OH)_2]} = 1{\cdot}4 \times 10^{-15}.$$

The fact that K_b is numerically smaller than K_a is due to the different form of the constant.

Mercuric Alkylates. According to Hock and Stuhlmann[777] mercuric methylate $Hg(O\cdot CH_3)_2$ is formed as an orange-yellow precipitate when solutions of sodium methylate and mercuric chloride in methyl alcohol are mixed; they did not analyse it, but judged its formula from its formation and its reactions. The ethyl and propyl compounds seem to be similar.

Mercuric Sulphide, HgS

This occurs in a red form (cinnabar, the chief ore of mercury) and a black. The black, produced at lower temperatures, is unstable below 386°, and goes over to the red with the evolution of 0·381 k.cals.[778] It changes to the red form spontaneously, especially in presence of alkaline polysulphides, mercurous chloride, and mercury-sulphur-chlorine compounds, the rate increasing with temperature up to 290°.[779] Its solubility product in water is only 3×10^{-54} at 26°[780] (3 individual molecules in 1,000 litres). Hence mercuric sulphide is precipitated by hydrogen sulphide even from the stablest complexes.

Cinnabar has a distorted sodium chloride (probably ionic) lattice; but a second form (metacinnabarite) has a zinc-blende structure.[783]

Mercuric selenide[781] and telluride[782] are known; they have covalent zinc-blende lattices.

Mercaptan Derivatives

Mercuric oxide reacts with mercaptans with some violence[784] (hence the name, from *mercurium captans*), and gives a series of derivatives $Hg(S\cdot Alk)_2$, which have low melting-points (e.g. methyl compound 175°, ethyl 76°, propyl 71°, heptyl 76°[785]) and are soluble in chloroform and benzene.[786]

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[775] H. Pelabon, *C.R.* 1899, **128**, 825.

[776] B. V. Erofeev and K. I. Trusova, *J. Phys. Chem. Russ.* 1938, **12**, 346.

[777] H. Hock and H. Stuhlmann, *Ber.* 1929, **62**, 2690.

[778] G. B. Heisig, *J.A.C.S.* 1938, **60**, 359.

[779] J. Krustinsons, *Z. anorg. Chem.* 1941, **245**, 352.

[780] I. M. Kolthoff, *J. Phys. Chem.* 1931, **35**, 2720.

[781] W. H. Zachariasen, *Z. physikal. Chem.* 1926, **124**, 436.

[782] Id., ib. 277.

[783] A. F. Wells, *Struct. Inorg. Chem.*, pp. 391, 513.

[784] P. Klason, *Ber.* 1887, **20**, 3410.

[785] E. Wertheim, *J.A.C.S.* 1929, **51**, 3661.

[786] E. Ott and E. E. Reid, *J. Ind. Eng. Chem.* 1930, **22**, 878.

On heating they readily break up into mercury and the disulphide Alk_2S_2 (the phenyl compound $Hg(S \cdot C_6H_5)_2$ does this reversibly),* whereas the alkaline mercaptides decompose much less easily, and give metallic sulphides and thioethers.

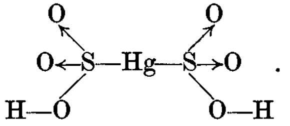
These properties indicate that the compounds are covalent; here again we find mercury compounds ionizing to about the same extent as the hydrogen compounds they come from.

Like so many compounds of the HgR_2 type these are readily converted into the half-halides R—Hg—hal; thus treatment with hydrogen chloride or mercuric chloride[785] gives Et—S—Hg—Cl, and ethyl iodide reacts on gentle warming to give Et—S—Hg—I.[787-8] These halide products are colourless or yellow crystals very stable to water or alcohol; with nitric acid the iodine is replaced by NO_3[788]; we may assume that the iodide is covalent Et—S—Hg—I, and the nitrate ionized as [Et—S—Hg]NO_3. At higher temperatures (80–100°) the reaction of the mercaptide with ethyl iodide goes farther, with the formation of a sulphonium complex iodide $Et_3S[HgI_3]$.[787-9]

Mercury Disulphonic Acid

This compound shows how easily mercury forms covalent links with sulphur. Mercuric oxide dissolves easily in alkaline sulphite solutions to give products of the composition $M_2Hg(SO_3)_2$, aq. (also formed from mercurous salts with separation of mercury).

It has been shown by Barth[790] that they are alkaline salts of mercury disulphonic acid



Barth prepared a series of these salts: Na_2, 1 aq.; K_2, 2 aq.; $(NH_4)_2$; Ag_2, 2 aq.; Sr, 2 aq.; Ba, 1 aq. They are reasonably soluble, and fairly stable; but they change very slowly on standing in the cold, or more rapidly on boiling, with the separation of metallic mercury according to the equation

$$Na_2[Hg(SO_3)_2] = Na_2SO_4 + Hg + SO_2.$$

The constitution of these salts is evident from their behaviour; the solutions have a very low concentration of mercuric ions; they give no precipitate with alkaline hydroxides, carbonates, phosphates, oxalates, or ferro- or ferricyanides, though they do so with hydrogen sulphide. The

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* Hence in this reaction, in which 2 Hg—S links are replaced by one S—S, the heat effect must be very small; so that as H_a for S—S is 64 k.cals. that of Hg—S must be about 32.

[787] K. A. Hofmann and W. O. Rabe, *Z. anorg. Chem.* 1897, **14**, 293.

[788] Id., ib. 1898, **17**, 26.

[789] S. Smiles, *J.C.S.* 1900, **77**, 163.

[790] K. Barth, *Z. physikal. Chem.* 1892, **9**, 193.

metal is clearly linked covalently to sulphur; that it is so linked by both its valencies is shown by the fact that the alkaline salts in solution are tri-ionic, as their freezing-points and the change of conductivity with dilution show[790]; the mobility of the $[Hg(SO_3)_2]^{--}$ ion (62·0) is almost the same as that (71·1) of the anion of methylene disulphonic acid $CH_2(SO_3H)_2$.[791]

In the presence of alkaline chlorides or hydroxides mixed compounds of the types of $M[Cl—HgSO_3]$ and $M[HO—Hg—SO_3]$ are formed; the sodium salt has the composition $Na[Cl—Hg—SO_3]$, H_2O; the E.M.F. measurements of Spacu[792-3] have confirmed the existence of this mixed chloro-sulphonate in the solution. This is a further example of the increased stability of a mixed R—Hg—X compound.

Mercuric Halides

All four mercuric halides are known; the fluoride is very different in behaviour from the other three. The melting- and boiling-points[794] are as follows:

	HgF_2	$HgCl_2$	$HgBr_2$	HgI_2
B. pt. . .	650°	302·5°	318°	351°
M. pt. . .	645°	280°	238°	257°

Mercuric Fluoride, HgF_2

The anhydrous salt cannot be prepared by the dehydration of the hydrate, but it can be made in other ways, e.g. from mercurous fluoride, by passing chlorine or bromine over it,[795] or by heating it to 450°, when it breaks up into mercury and mercuric fluoride. Mercuric fluoride forms colourless octahedra, melting at 645° and boiling a few degrees higher. It has a fluorite lattice,[796] with the Hg—F distance 2·40 A; this is an ionic lattice, and the distance is that to be expected for ions (Hg[F] 2·45: Hg—F 2·12 A). With a small amount of water it gives a yellow crystalline hydrate HgF_2, 2 H_2O (with mercury the formation of a hydrate is a sign of ionization) (see p. 325). With more water it is largely hydrolysed, giving first a basic fluoride and then mercuric oxide. This is very unlike the other halides (which are only slightly ionized, and scarcely hydrolysed) and much more like the oxy-acid salts such as the nitrate. It is clear that with mercury as with aluminium or tin, the fluoride is far more ionized than the other halides. The link of mercury to fluorine is ionic like that to oxygen; mercuric fluoride is a strong electrolyte.

The crystal structure of the anhydrous salt supports this, and also the fact that fluorine, unlike the other halogens, gives no complex halide anions with mercury. Further mercuric fluoride is less soluble in water in

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[791] G. Bredig, *Z. physikal. Chem.* 1894, **13**, 271.

[792] G. Spacu and C. Dragulescu, *Z. anorg. Chem.* 1935, **224**, 273.

[793] Id., ib. 1936, **226**, 416.

[794] F. M. G. Johnson, *J.A.C.S.* 1911, **33**, 77.

[795] O. Ruff and G. Bahlau, *Ber.* 1918, **51**, 1752.

[796] F. Ebert and H. Woitinek, *Z. anorg. Chem.* 1933, **210**, 269.

presence of potassium fluoride (common ion effect), in striking contrast to the other halides, whose solubility is greatly increased by the presence of an alkaline halide, owing to the formation of a halide complex.

Mercuric Chloride Bromide and Iodide

The remaining mercuric halides resemble one another very closely, and differ markedly from the fluoride; they are almost wholly covalent even in water, and so are very slightly hydrolysed.

Their covalency is shown by the relatively low boiling-points (see above), and also by the small conductivities in the fused state, the specific values just above the melting-points being: $HgCl_2$ $0{\cdot}82 \times 10^{-4}$ at 276°[797-8]; $HgBr_2$ 15×10^{-4} at 238°.[799] The same thing is shown by the photo-dissociation of the vapour of the chloride and bromide into a halogen atom and an excited Hg—hal molecule,[800] and by the Raman spectra of these halides both in the vapour[802] and in the solid and liquid,[810] which indicate a symmetrical linear molecule.

The linear shape of the molecule has been established for all three dihalides by electron diffraction in the vapour[812,813]; in the solid it has been found by X-ray analysis for the chloride and the bromide.[809,811] The relations of the crystal lattices of the four mercury dihalides are remarkable.[814] The numbers of halogen neighbours surrounding the mercury in each of these compounds are:

Compound	*2 at*	*2 at*	*2 at*
HgF_2		8 at 2.40 A	
$HgCl_2$	2·25	3·34	3·63
$HgBr_2$	2·48	3·23	3·23
HgI_2		4 at 2·78 A	

(Theory for covalent links Hg—F 2·12; Hg—Cl 2·47; Hg—Br 2·62; Hg—I 2·81.)

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[797] W. Biltz, ib. 1924, **133**, 312.

[798] W. Biltz and W. Klemm, ib. 1926, **152**, 267.

[799] G. v. Hevesy, *Kgl. Danske Vid. Selsk. Med.* 1921, **3**, 13.

[800] K. Wieland, *Z. Phys.* 1932, **77**, 157.

[801] H. F. Fromherz and K. H. Lih, *Z. physikal. Chem.* 1933, **167**, 103.

[802] M. Wehrli, *Helv. Phys. Acta*, 1938, **11**, 339.

[803] W. J. Curran and H. H. Wenzke, *J.A.C.S.* 1935, **57**, 2162.

[804] B. C. Curran, ib. 1941, **63**, 1470 (corrects the previous reference).

[805] E. B. R. Prideaux and J. R. Jarratt, *J.C.S.* 1938, 1203.

[806] M. L. Delwaulle, *C.R.* 1938, **206**, 1965.

[807] G. Tammann, *Nachr. K. Ges. Wiss. Gött.* 1916, 292 (*Chem. Centr.* 1917, i. 1065).

[808] D. Gernez, *C.R.* 1899, **129**, 1234.

[809] W. Scholten and J. M. Bijvoet, *Z. Krist.* 1941, **103**, 415.

[810] K. V. K. Rao, *Proc. Ind. Acad. Sci.* 1941, **14**, A 521.

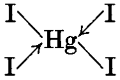
[811] H. Braekkon and W. Scholten, *Z. Krist.* 1934, **89**, 448.

[812] H. Braune and S. Knoke, *Z. physikal. Chem.* 1933, B **23**, 163.

[813] A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. F. L. Jones, and L. E. Sutton, *Trans. Far. Soc.* 1937, **33**, 852.

[814] A. E. Wells, *Struct. Inorg. Chem.*, p. 514.

The fluoride clearly has an ionized (fluorite) lattice; the chloride lattice is molecular, with two (linear) Cl atoms much nearer than the rest; that of the bromide is similar, but the more distant halogen atoms are more strongly attracted; finally, in the iodide the attraction is still greater, and the whole has passed over into a giant molecule formed of tetrahedral



groups. The dipole moments in dioxane solution are[803-4] $HgCl_2$ 1·43, $HgBr_2$ 1·53, HgI_2 1·67; these may be due to flexibility, or to some co-ordination with the solvent. The parachors[805] are for some reason exceptionally low, being $HgCl_2$ 169·7, $HgBr_2$ 199·0 (calculated 177·8, 205·0). The solubilities in water at 25° are $HgCl_2$ 7·09, $HgBr_2$ 0·613, HgI_2 0·0591 (in moles/litre 0·26, 0·017, 0·00013).

The molecular conductivities at 25° and *V*128 are $HgCl_2$ 5·1, $HgBr_2$ 1·3. This shows that the ionization is very small, but owing to the presence of $Hg\cdot X^+$ ions and of hydrolytic products, the exact amount cannot be calculated (see Fromherz and Lih[801]); the degree of ionization must be in centinormal solution of the order of 1 per cent. or less.

These halides are readily soluble in organic solvents, as we should expect. Some values (mainly from Seidell's *Solubilities*) are given in the table below, in moles of solute to 100 moles of solvent at 25°.

TABLE

Solvent	$HgCl_2$	$HgBr_2$	HgI_2
Water	0·484	0·0308	0·00023
Ethyl alcohol	8·14	3·83	0·396
Ethyl acetate	9·42	..	0·566
Chloroform	0·0466	0·0418	0·0034
Carbon tetrachloride	0·00114	0·00128	0·000831
Benzene	0·152	..	0·0671

Of the individual halides *mercuric chloride* is corrosive sublimate: lethal dose for a man from 0·2 to 0·4 g. The molecular weight is normal in urethane by the freezing-point, and in methyl and ethyl alcohol by the boiling-points. From methyl alcohol solution $HgCl_2,CH_3OH$ separates.

Mercury chlorobromide, HgClBr, is shown by the Raman spectrum[806] to be present in a mixed solution of the chloride and bromide in alcohol.

Mercuric iodide occurs in a red form, and in a much less dense yellow form, which is stable above 126°.[808] A third form has been obtained by Tammann[807] by cooling the vapour by sudden expansion; it appears as a colourless snow, which rapidly changes over into the red form.

Mercuric Salts of Oxy-acids

These are peculiar in being ionized to about the same extent as the acids from which they are derived. Mercuric salts of strong oxy-acids such as nitric sulphuric and perchloric are strong electrolytes, and owing to the weakness of the hydroxide $Hg(OH)_2$ as a base are considerably hydrolysed in dilute aqueous solution; those of weak oxy-acids like the carboxylic acids are among the very few salts that are (like those acids themselves) 'half-strong' electrolytes in Ostwald's sense; their low ionization also prevents them from being very greatly hydrolysed. Unlike most mercuric compounds, those which are strong electrolytes are nearly always hydrated; thus we have $Hg(NO_3)_2$, 8 and 1 H_2O; $HgSO_4$, H_2O[815]; $Hg(ClO_4)_2$, 6 H_2O; even some slightly ionized salts are hydrated, such as $HgCl_2$, 2 H_2O, and mercuric benzoate, 1 H_2O.

Mercuric Salts of Carboxylic Acids

Mercuric carbonate is only known as a basic salt, which suggests that the ionization of the normal salt is greater than one would expect from the weakness of the free acid.

The salts of the 'half-strong' carboxylic acids have conductivities roughly the same as those of the acids from which they are formed, and this is true over a range of dilutions, the effect of dilution on the conductivity being much the same for both, as is shown by the following molecular conductivities at 25°[816]:

	Propionate		*Acetate*		*Glycollate*		*Mono-chloracetate*	
	Hg	H	Hg	H	Hg	H	Hg	H
$V = 32$	5·22	7·4	5·4	8·7	11·2	24·8	28·4	72·4
$V = 64$	7·6	10·4	8·1	12·1	17·3	34·4	44·1	96·8
Ratio $V32/V64$	0·69	0·71	0·67	0·72	0·65	0·72	0·64	0·75

Mercuric formate has a curious reaction, a partial oxidation of the anion by the cation; when it is warmed in water the less soluble mercurous formate crystallizes out.

$$2\,\mathrm{Hg(O\cdot CO\cdot H)_2} = \mathrm{Hg_2(O\cdot CO\cdot H)_2} + \mathrm{CO_2} + \mathrm{CO} + \mathrm{H_2O}.$$

The acetate behaves to a small extent in the same way, but not the propionate.

The following are some of the solubilities: [mercurous acetate 0·75/13°][817]; mercuric acetate 25/10°[817]; benzoate 0·209/20°[819]; oxalate 0·0107/12°; fulminate 0·070/12°.[818]

Oxy-salts of Nitrogen

Mercuric nitrate, $Hg(NO_3)_2$ 8 and 1 (possibly 1/2) H_2O: in dilute solution it is highly hydrolysed, and at sufficient dilutions it can be completely broken up into mercuric oxide and nitric acid.

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[815] C. Hoitsema, *Z. physikal. Chem.* 1895, **17**, 651.

[816] H. Ley and H. Kissel, *Ber.* 1899, **32**, 1361.

[817] T. W. B. Welsh and H. J. Broderson, *J.A.C.S.* 1915, **37**, 816.

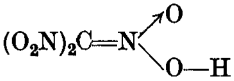
[818] A. F. Holleman, *Rec. Trav.* 1896, **15**, 159.

[819] F. Ephraim and A. Pfister, *Helv. Chim. Acta*, 1925, **8**, 369.

Mercuric nitrite, $Hg(NO_2)_2$, is a very soluble and highly deliquescent salt (Rây).[816] Its conductivity is about the same as that of the acetate,[816] which suggests that nitrous acid should be about as strong as acetic; it has since been found that the dissociation constant of nitrous acid is $4{\cdot}5 \times 10^{-4}$, about half-way between acetic and monochloracetic. This suggests that the undissociated part of the salt has an Hg—N rather than an Hg—O link.

So too mercuric fulminate $Hg(ONC)_2$ (p. 319) is much less ionized than we should expect for a compound with mercury linked to oxygen. On the other hand, the mercury salt of methyl nitramine $CH_3{\cdot}NH{\cdot}NO_2$ has[816] $\mu = 2{\cdot}3$ at $V256$, while methylnitramine itself at this dilution has $\mu = 5{\cdot}0$. Here again we probably have an Hg—O link.

The mercuric salt of *nitroform*, $CH(NO_2)_3$, has a remarkable behaviour. Nitroform itself[820] is colourless in the pure state both as liquid and as solid; no doubt it has the true nitro-structure. In water it gives a strongly acid solution of a bright-yellow colour; it is too highly ionized to give an Ostwald dissociation constant, but its strength is of the same order as that of trichloracetic acid; the alkaline salts are bright yellow. This yellow modification is obviously the aci-form



$$(O_2N)_2C{=}N\begin{matrix}\nearrow O\\ \searrow O{-}H\end{matrix}$$

or its anion.

The remarkable point is that the mercuric salt behaves just like free nitroform[816]; it is colourless in the solid state and in solution in benzene or ether (in which its solubility is unusually high), but bright yellow when dissolved in water or pyridine. It is clear that in ethereal solution (where the boiling-points show it to be monomeric) it is present as the Hg—C compound $(O_2N)_3C{-}Hg{-}C(NO_2)$, while the yellow solution in water no doubt contains (so far as it is not ionized) the oxy (aci) structure.

In more concentrated aqueous solutions the molecular conductivity (e.g. $72{\cdot}4$ at $V = 32$) is about half that of the mercuric salt of the (about) equally strong acid trichloracetic; the solution has a strong acid reaction, and is highly hydrolysed; all these facts are to be expected if the molecule in the un-ionized state has an Hg—O link.

Thus we have the unusual relations:

State	*Free nitroform*	*Alkaline salt*	Hg'' *salt*
Solid	Colourless	Yellow	Colourless
Ether solution	Colourless	. .	Colourless
Water solution	Yellow	Yellow	Yellow

With cyanuric acid, $C_3N_3O_3H_3$,[821] two isomeric mercuric salts are formed.

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[820] A. Hantzsch and A. Rinkenberger, *Ber.* 1899, **32**, 628.

[821] A. Hantzsch, ib. 1902, **35**, 2717.

Oxy-salts of Sulphur

The only well-known salt (apart from mercury disulphonic acid) is the sulphate. This forms a hydrate $HgSO_4, H_2O$; excess of water hydrolyses it to give various basic compounds, including 'Turpeth mineral' $HgSO_4$, 2 HgO, or Hg_3SO_6, which might be called an ortho-sulphate.

Oxy-salts of the Halogens

The mercuric salts of acids of the chloric and perchloric series are highly ionized and hydrolysed in water. The solubilities of the series chlorate—bromate—iodate fall off rapidly in this order, the last being almost insoluble.

The best-known mercuric salt of this group is the perchlorate, which forms a hexahydrate and is very soluble in water. Unlike the mercuric salts of all the other strong oxy-acids (nitrate, sulphate, chlorate, etc.) its aqueous solution remains clear even at the highest dilution; it is highly hydrolysed, but the products are soluble.

Mercuric Complexes

These are fairly numerous; the more important are those in which the metal is attached to carbon (in the cyanides), nitrogen, sulphur, and the halogens.

Complex Cyanides

These are numerous and stable; the more important are of the type $M_2[Hg(CN)_4]$; in the potassium salt the anion is tetrahedral,[822] as in the corresponding zinc and cadmium complexes.

In the system KCN, $Hg(CN)_2$, H_2O at 25° $K_2Hg(CN)_4$ is the only solid complex formed.[823-4]

A few salts, however, are known of a second type $M[Hg(CN)_3]$, such as $Ca[Hg(CN)_3]_2$[825] and mixed salts of the type $M[Hg(CN)_2X]$, where X = Cl, Br, or I.[826-7]

Complex Ammines

These are definite but not very stable compounds. So far as they have been isolated they are almost all of two types, diammines $Hg(NH_3)_2X_2$ and tetrammines $Hg(NH_3)_4[X_2]$; but some trichelate ethylene diamine salts have been isolated,[829] and there are signs that a simple hexammine can sometimes be formed in solution.

Our knowledge of the diammines is mainly due to Hofmann,[828] and that of the tetrammines to Weitz.[829] Ammonia can act on a mercuric salt in

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[822] R. G. Dickinson, *J.A.C.S.* 1922, **44**, 774.

[823] A. S. Corbet, *J.C.S.* 1926, 3190.

[824] H. T. S. Britton and E. N. Dodd, ib. 1932, 1940.

[825] H. Grossmann and P. v. d. Forst, *Ber.* 1904, **37**, 4141.

[826] E. Rupp and S. Goy, *Arch. Pharm.* 1909, **247**, 100.

[827] R. Varet, *Ann. Chim. Phys.* 1896, [7] **8**, 278.

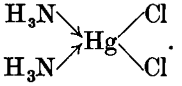
[828] K. A. Hofmann and E. C. Marburg, *Ann.* 1899, **305**, 191.

[829] E. Weitz, K. Blasberg, and E. Wernicke, *Z. anorg. Chem.* 1930, **188**, 344.

two ways, either by replacement of its anion by NH_2, or by addition to form an ammine. This reaction occurs very readily, giving such amino- or imino-compounds as infusible white precipitate $H_2N \cdot Hg \cdot Cl$ and Millon's base OHg_2NH_2OH. If the ammines are to be produced, this substitution must be prevented by adding an excess of an ammonium salt, which depresses the ionization of the ammonia and makes the solution less alkaline.

This is why ammonia acts on mercuric chloride in water alone to give the amino-compound $H_2N \cdot Hg \cdot Cl$ (p. 317), while in presence of much ammonium chloride the diammine $Hg(NH_3)_2Cl_2$, fusible white precipitate is formed. The structure may be either

$[H_3N \rightarrow Hg \leftarrow NH_3]Cl_2$ or



The halides no doubt will have the covalent form, but there is a nitrate which must be a true salt, with di-covalent mercury.

In the absence of water the stability of the diammines is considerable; as usual it falls off in the order $Cl > Br > I$; the dissociation pressure of ammonia is one atmosphere with the chloride at 239° and with the bromide at 186°.[830]

Ethylamine gives a similar diammine $(Hg(EtNH_2)_2)Cl_2$, as well as a monammine $Hg(EtNH_2)Cl_2$.[831] Under suitable conditions, provided always that excess of ammonium ions are present, two more ammonia molecules can be taken up, giving a tetrammine. These tetrammines can also be made in the absence of ammonium salts if water is excluded, as when liquid or gaseous ammonia acts on the dry salt[832-4] or on its solution in acetonitrile.[835] The best method is[829] to pass ammonia into a saturated solution of the required ammonium salt, with the mercury salt in suspension; in this way the very soluble nitrate $[Hg(NH_3)_4](NO_3)_2$, the less soluble sulphate, and the slightly soluble perchlorate have been made, as well as the cyanide,[832] thiocyanate,[833] acetate,[833] and sulphite.[835]

If the solution of the tetrammine nitrate is treated with the salt of a strong oxy-acid or with a fluoride, no precipitation occurs, except with ammonium perchlorate, which gradually precipitates the rather insoluble tetrammine perchlorate.

But with a chloride, bromide, or iodide, there is an immediate precipitation of the diammine halide $Hg(NH_3)_2(hal)_2$, and no excess of ammonia will dissolve this up.

Evidently the normal covalency of mercury (like that of the preceding element gold) does not exceed 4, so that if the mercury remains ionized, as it does when the anion is that of a strong oxy-acid, it can take up 4 molecules of ammonia; but the halogens (excluding fluorine as before, see

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[830] M. François, *Ann. Chim.* 1929, [x] **11**, 22.

[831] H. Köhler, *Ber.* 1879, **12**, 2321.

[832] R. Varet, *C.R.* 1891, **112**, 1313.

[833] W. Peters, *Ber.* 1908, **41**, 3180.

[834] Id., *Z. anorg. Chem.* 1912, **77**, 147.

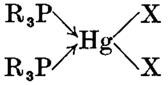
[835] A. Naumann, *Ber.* 1914, **47**, 1378.

p. 322) form covalent links with the mercury, which then has room only for 2 NH_3, and the diammine so formed being relatively insoluble is precipitated.

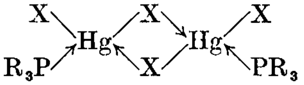
A covalency of more than 4, though rare, is possible for mercury; hexammines are known in the tri-chelate ethylene diamine salts $[Hg(en)_3]X_2$; also the less soluble tetrammine perchlorate, and in a smaller degree the nitrate, are much more soluble in water in presence of a large excess of ammonia, and will crystallize out when the excess is driven off.

*Phosphine and Arsine Complexes**

The mercuric halides form complexes with tertiary phosphines and arsines, which are of five types; the first three are exactly like the cadmium complexes (p. 280) and are (P stands for P or As):



(I)

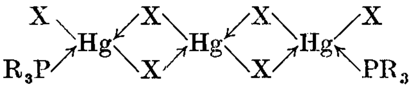


(II)

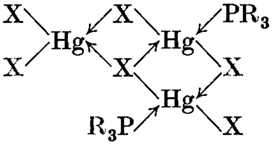
Possibly a *trans* form of II occurs.

III. A compound of the composition $(R_3P)_2(HgX_2)_4$, of uncertain structure.

IV and V are peculiar to mercury; they are two modifications of the compound $(R_3P)_2(HgX_2)_3$; the structures, established by X-ray analysis are:



(IV)

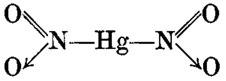


(V)

For distances and angles, see Mann.[523]

Nitro-complexes

The low dissociation of mercuric nitrite (p. 326) indicates that it is a nitro-compound



and not a nitrito-compound O=N—O—Hg—O—N=O, and the complex nitrites (like the more stable forms of all complex nitrites) are no doubt similar. The most probable types of complex mercuric nitrites are[836] $M[Hg(NO_2)_3]$, $M_2[Hg(NO_2)_4]$, and $M_3[Hg(NO_2)_5OH_2]$. The first type is very unusual: the salts should perhaps be written $M_2Hg[Hg(NO_2)_6]$, though the

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* See Mann *et al.*[523] [p. 280 above].

[836] A. Rosenheim and K. Oppenheim, *Z. anorg. Chem.* 1901, **28**, 171.

mercury in the cation cannot be replaced by any other metal.[837] The last type, which certainly exists, is remarkable owing to the rarity with mercury of a covalency of more than 4.

Oxygen Complexes

Owing to the weakness of the covalent link of mercury to oxygen the oxygen complexes are few, not very stable, and mostly chelate.

Mercuric chloride bromide and iodide form 1:1 compounds with dioxane[838-9]; but these occur only in the solid state, their heats of formation are very small (less than 8 k.cals.), and they are probably only crystal aggregates. Otherwise it needs the extra stability of chelation to overcome the weakness of the Hg—O link.

The acetylacetonate $Hg(C_5H_7O_2)_2$ is made[840-1] by the action of sodium acetylacetonate on mercuric chloride in water. It is a white solid slightly soluble in water but almost insoluble in the ordinary organic solvents; the true mercuric salt of so weak an acid would be completely hydrolysed by water; also the mercury is not precipitated by potassium hydroxide, though it is by hydrogen sulphide. Mercurous chloride forms the same mercuric acetylacetonate, with separation of metallic mercury.[841]

Of the supposed mercuric ato-compounds some are of doubtful structure, such as the salicylic derivatives, which probably have the mercury attached at least one on one side to carbon. Among the most certain are the dichelate oxalato-complexes such as the ammonium salt

$$(NH_4)_2[Hg(C_2O_4)_2],\ 2\ H_2O.$$

Their true complexity is shown by the ready solubility of mercuric oxalate in solutions of alkaline oxalates, by the values of the freezing-points of the solutions,[842] and by the failure of reactions for the mercuric and oxalate ions[843]; for example, the oxalate is only partly precipitated by barium salts.

E.M.F. measurements suggest that complex nitrito- and sulphato-compounds are formed to some extent in solution, though much less than with the complex halides.[844]

Sulphur Complexes

Mercury has a much stronger affinity for sulphur than for oxygen, and so the sulphur complexes are much more numerous. The most important are the polysulphides and the addition compounds with organic sulphides.

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[837] A. Ferrari and C. Colla, *Gaz.* 1935, **65**, 789.

[838] H. T. Clarke, *J.C.S.* 1912, **101**, 1803.

[839] J. L. Crenshaw, A. C. Cope, N. Finkelstein, and R. Rogan, *J.A.C.S.* 1938, **60**, **2308**.

[840] S. Tanatar and E. Kurowski, *J. Russ. Phys.-Chem. Ges.* 1908, **40**, 580 (*Chem. Centr.* 1908, ii. 1096).

[841] G. T. Morgan and H. W. Moss, *J.C.S.* 1914, **105**, 195.

[842] M. Roloff, *Z. physikal. Chem.* 1894, **13**, 327.

[843] H. Schaefer, *Z. anorg. Chem.* 1905, **45**, 299.

[844] G. Infeldt and L. G. Sillén, *Svensk Kem. Tidskr.* 1946, **58**, 104.

Complex Sulphides[845-6]

Mercuric sulphide, which is almost absolutely insoluble in water (p. 320), dissolves in concentrated solutions of alkaline sulphides, and complex sulphides of the composition $M_2[HgS_2]$ will crystallize out; like other polysulphides they usually have large amounts of water of crystallization, as in $K_2[HgS_2]$, 5 and 7 H_2O.

The solubility of the mercuric sulphide is strictly determined by the concentration of S^{--} ions in the solution. It will not dissolve in ammonium sulphide solutions, because owing to the weakness of ammonia this salt is almost wholly hydrolysed, and the solution contains HS^- ions but no S^{--}. For the same reason if hydrogen sulphide is passed into a solution of mercuric sulphide in sodium sulphide the mercuric sulphide is reprecipitated, because the sulphide ions are all destroyed by the reaction

$$H_2S + S^{--} = 2\ HS^-.$$

The complex anion $[HgS_2]$ could be written either $[S \leftarrow Hg \rightarrow S]^{--}$ or $[S{=}Hg{=}S]^{--}$. With any B metal other than mercury the latter would obviously be the more stable, as providing a complete octet; but mercury is so readily satisfied with the shared quartet that the first structure may correspond more nearly to the state of the molecule; no doubt there is resonance between the two; both will be linear.

Dialkyl Sulphide Complexes

Dialkyl sulphides combine with mercuric halides especially on warming, with evolution of heat;[847] mercurous salts do the same, with separation of mercury.[848] The conditions of the last reaction depend on the mercurous salt used. Mercurous nitrate, sulphate, and iodide will react in presence or absence of water; but water promotes the reaction, and with mercurous acetate is necessary except with dimethyl sulphide. Mercurous chloride will react only with dimethyl sulphide, and then only in presence of water. These differences are presumably partly due to the heats of linkage (although the reaction involves only the change from X—Hg—Hg—X to X—Hg—X) and partly to solubility relations.

The products are of three types: (1) R_2S, 2 HgX_2; (2) R_2S,HgX_2; (3) $(R_2S)_2HgX_2$. The second of these is the commonest. Their structures presumably correspond to those of the analogous trialkyl phosphine complexes (p. 329).

Complex Halides

While cadmium chloride in water has its conductivity lowered by auto-complex formation, mercuric chloride, with a still lower conductivity, forms no auto-complexes. But this does not mean that mercury has no tendency to form complexes; the tendency, though less than that of cadmium, owing to the stability of the mercury quartet, is still consider-

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[845] R. Abegg and S. Jander, *Z. Elektrochem.* 1902, **8**, 689.

[846] J. Knox, ib. 1906, **12**, 477.

[847] S. Smiles, *J.C.S.* 1900, **77**, 163.

[848] W. F. Faragher, J. C. Morell, and S. Comay, *J.A.C.S.* 1929, **51**, 2774.

able. The absence of auto-complexes in aqueous mercuric chloride solutions is due to the low concentration of chlorine ions, just as with barium chloride it is largely due to the small amount of undissociated $BaCl_2$ molecules. In a saturated (0·27-normal) solution of mercuric chloride at 25° the factor $C = [HgCl_2]\cdot[Cl^-]^2$ on which the formation of $[HgCl_4]^{--}$ depends, is about 10^{-7}. It is quite different if an alkaline chloride is present: on addition of normal potassium chloride to this solution C rises to 0·22—2 million times.

We find, in fact, that the mercuric halides, other than the fluoride, readily form complex halides when treated with alkaline halides, or even hydrogen halides. These are all of two types, $M[HgX_3]$ and $M_2[HgX_4]$. With fluorine no sign of complex formation has been observed; this is a further proof of the reluctance of fluorine (as of oxygen) to form a covalent link with mercury. The other three halogens readily form complexes, as is shown by the solubility of mercuric halides in solutions of alkaline halides. The equilibrium in the solutions has been examined mainly by Sherrill[851-2] and by Garrett[862]; various methods were used involving the measurement of E.M.F., of solubilities, of freezing-points, and of partition between water and another solvent such as benzene. They all agree in showing that complexes are formed, and that the predominant type in presence of excess of alkaline halide is the tetrahalide $M_2[HgX_4]$. There is a good deal of uncertainty about the quantitative interpretation of these measurements, but they agree in showing that the stability rises rapidly in the order $Cl < Br < I$. A covalency of more than 4, always rare with mercury, never seems to be reached in the halides.

The HgX_4'' ion has a tetrahedral structure,[857] as is natural since the mercury in it has an inert gas number of 86. The crystal lattices of various peculiar complex halides have been determined, such as Ag_2HgI_4,[857-8] one form of which has gaps in the lattice, accounting for its high conductivity; K_2HgI_4, H_2O has a complicated structure[860]: the trichloride $(NH_4)HgCl_3$ has a layer lattice.[859] The trihalides readily complete the mercury octet by co-ordination; thus $KHgCl_3$ forms a monohydrate and a monoalcoholate.[856] Gallais[861] finds from the conductivities and the Raman spectra that in solutions containing one mol. KI to one HgI_2 the main complex ions are those of $K[HgI_3(OH_2)]$.

The complex diazonium chlorides[849] and iodides[853] have been prepared; the latter on decomposition give some iodonium salt $(C_6H_5)_2I[HgI_3]$.

It has been said[850] that optically active sulphonium salts are racemized by conversion into their mercuri-iodides, but Kenyon and his co-workers[854] have shown that this is not so.

[849] A. Hantzsch, *Ber.* 1895, **28**, 1734.

[850] W. J. Pope and H. A. D. Nevill, *J.C.S.* 1902, **81**, 1552.

[851] M. S. Sherrill, *Z. physikal. Chem.* 1903, **43**, 705.

[852] Id., ib. 1904, **47**, 103.

[853] A. N. Nesmejanov, *Z. anorg. Chem.* 1929, **178**, 300.

[854] M. P. Balfe, J. Kenyon, and H. Phillips, *J.C.S.* 1930, 2554.

These sulphonium salts $(R_3S)[HgI_3]$ and $(R_3S)_2[HgI_4]$ (whose formation by the action of alkyl iodides on dialkyl sulphide complexes of mercury salts has been mentioned, p. 321) were examined by Cavell and Sugden,[855] who found that the variation of the conductivity in acetone with concentration is that required by the Debye–Hückel–Onsager theory. The parachors (the melting-points are Et_3S 116°: Bu_3S 81°) are anomalous.

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[855] H. J. Cavell and S. Sugden, ib. 2572.

[856] M. Pernot, *Ann. Chim.* 1931, [x] **15**, 5.

[857] J. A. A. Ketelaar, *Z. Krist.* 1931, **80**, 190.

[858] Id., *Z. physikal. Chem.* 1934, B **26**, 327.

[859] E. J. Harmsen, *Z. Krist.* 1938, **100**, 208.

[860] C. H. Macgillavry, J. H. de Wilde, and J. M. Bijvoet, ib. 212.

[861] F. Gallais, *Ann. Chim.* 1938, [x] **10**, 117.

[862] A. B. Garrett, *J.A.C.S.* 1939, **61**, 2744.

GROUP III

THIS group is peculiar in many ways. Owing to the inclusion of the rare earth metals it contains twenty-three elements, more than twice as many as any other group; and of these twenty-three, one, aluminium, is the most abundant of the metals (nearly twice as abundant as iron) and the third commonest element in the earth's crust, of which it forms 8·8 per cent.: all the rest are rare; boron is only 3 parts per million, and the others vary from 44 (cerium) to 0·1 (indium) parts per million, except the short-ived actinium, which is estimated at 2·3 parts in 10^{16}.

In atomic structure, these are the first elements in which the valency electrons are in more than one subgroup.

Typical and B elements: ——(8), (2, 1)
A elements: ———(8+1), 2.

Owing to the fact that the first electron entering a new type of orbit has not a very different stability from that in the previous type, this difference does not appear at all in their chemical properties.

In general we have to regard the group as consisting of the normal forked arrangement, with the elements 58–71 forming a side growth:

$$\begin{tikzcd}
 & \text{21 Sc} \arrow[r, dash] & \text{39 Y} \arrow[r, dash] & \text{57 La} \arrow[r, dash] \arrow[d, dash] & \text{89 Ac} \\
\text{5 B 13 Al} \arrow[ur, dash] \arrow[dr, dash] & & & 58 \cdot\cdot 71 & \\
 & \text{31 Ga} \arrow[r, dash] & \text{49 In} \arrow[r, dash] & \text{81 Tl} &
\end{tikzcd}$$

We may consider the main lines first, and deal with the rare earth metals n the narrower sense afterwards.

The tendency to covalency formation is greater in the third than in the second group, owing to the increase of the ionic charge, and as usual diminishes from above downwards, and is more marked in the B than in he A elements. There is, however, less difference between the A and the B elements in the third than in the second group, just as there was less n the second than in the first.

In boron we have for the first time an element which is always covalent and never forms a simple ion. Aluminium, with its larger size, is on the ine between ionization and covalency, like beryllium; it forms both covaent and ionized compounds, but on the whole the covalent tendency is tronger than in beryllium, as may be seen from the conductivities of the used chlorides: the value for beryllium chloride, 0·0032, is intermediate between that of a true salt (about 1) and that of a non-conducting covalent halide like carbon tetrachloride, while aluminium chloride (10^{-6}) is pracically a non-conductor in the liquid state. The A elements scandium, yttrium, and lanthanum become increasingly metallic (less tendency to ovalency) with increase of atomic number and size, as do the alkaline arths; presumably this is even more true of actinium.

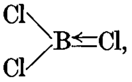
The change is most clearly shown in the behaviour of the hydroxides $M(OH)_3$. $B(OH)_3$ is a definite though weak acid with no basic properties. $Al(OH)_3$ is amphoteric, giving, on the one hand, salts such as the sulphate and, on the other, acting as an acid towards strong alkalies, and forming aluminates such as $K[AlO_2]$ analogous to the metaborates. Scandium hydroxide acts only as a base but a weak one: its salts are largely hydrolysed. Yttrium forms a stronger base, and lanthanum stronger still: thus in N/10 solution $ScCl_3$ is 0·9 per cent. hydrolysed, YCl_3 0·01 per cent., and $LaCl_3$ 0·003 per cent. The peculiar change of basicity of the rare earths will be discussed later.

The B elements gallium, indium, and thallium have a stronger tendency to covalency formation than any of the others except boron and aluminium. As in the zinc-cadmium-mercury series we find a considerable resemblance between the first two elements but more difference in the third, thallium, which has various peculiarities, especially a tendency to form a $[TlR_2]^+$ ion, in which the thallium has the same E.A.N. and much the same stability as mercury in the mercuric compounds.

Boron and aluminium have so many individual peculiarities that they will be treated separately. The A elements can then be taken together, including the rare earth metals.

BORON

BORON is the first element we have met with which is always covalent and never forms monatomic ions. It is very unusual in its behaviour in many ways, largely because it is the only one of those elements that never ionize which in its normal covalent state has less than a complete valency octet. The other non-ionized electronegative elements all belong to the fourth or later groups, and so their normal covalency leads to a complete and more or less fully shared octet, as in CH_4, $\underline{\mathbf{8}}$; NH_3 2, $\underline{\mathbf{6}}$; OH_2 4, $\underline{\mathbf{4}}$; ClH 6, $\underline{\mathbf{2}}$; but with boron in the normal valency of 3 the valency group is only a 3-covalent sextet $\underline{\mathbf{6}}$. The result is that boron has a very strong tendency to complete its octet by co-ordination, even on occasion by 'back-co-ordination', as in



where this is indicated by the interatomic distances.[1]

But the strain of the 3-covalent sextet can be relieved in another way also. The nearness of the electronegativity values of boron (2·0) and hydrogen (2·1),[2] and also probably the extreme lightness of these two elements, are peculiarly favourable to the formation of 1-electron bonds between them. Hence boron can form comparatively stable molecules in which it is attached to itself and to hydrogen, and sometimes to carbon (2·5) or the halogens (Cl 3·0, Br 2·8, I 2·4) as well, which do not contain enough valency electrons to supply two for every covalent link. It can thus acquire the more stable covalency of 4 and at the same time approach, though not reach, the full octet.*

The strongest affinities—the most stable links—of boron are (in this order) with F, N, O, Cl, and B. The heats of formation are only known for very few of them; if we accept the value of 115 k.cals. for the heat of atomization of boron,[3] we get with the halogens the following values, compared with those for carbon. The remarkable value for B—F is to be noticed; the values for boron are always higher than for carbon, and more so, the lighter the halogen, owing no doubt to the greater importance of the ionic form of linkage. Both have a greater affinity for fluorine than for any other element, but with carbon the affinity for oxygen comes lower (just above chlorine) and that for nitrogen lower still (just below it).

Ht. of linkage:	B—F 140·6	B—Cl 96·7	B—Br 76·9
	C—F 103·4	C—Cl 78·0	C—Br 65·5
	Diff. +37·2	+18·7	+11·4

The fact that the group valency of 3 only gives boron a sextet leads to a very strong tendency to complex formation. The covalency limit is 4,

* An alternative formulation of these compounds has been proposed, but it is not yet established; see p. 339.

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[1] H. A. Levy and L. O. Brockway, *J.A.C.S.* 1937, **59**, 2085.

[2] L. Pauling, *Chem. Bond*, p. 64.

[3] Bichowsky and Rossini, p. 105.

which is thus reached by one co-ordinate link. As we should expect, the complexes with fluorine ($[BF_4]^-$) are the most stable: then comes nitrogen, and (less stable) the complexes formed through oxygen.

The radius of the boron atom in various states of combination is a difficult problem. Many of the data are collected by Laubengayer *et al.*,[4] who also determine the parachors of B_2H_6, BBr_3, and BEt_3, and discuss the relation between the radius and the parachor. See also Bauer and Beach.[5] We may provisionally accept Pauling's values of B— 0·88, B= 0·76, B≡ 0·68.

Elementary Boron

Boron is a rare element, present in the earth's crust to about 3 parts per million (3 g. per ton: only half as common as beryllium). This rarity is partly due to the nucleus being disrupted in natural atomic bombardments. It is very widely distributed in small concentrations; its read accessibility commercially is due to its occurring in a few places in a concentrated form, e.g. in the volcanic gases (fumaroles) of Tuscany, and as sodium borate in certain salt deposits in eastern California and Nevada. Owing to its high affinity for oxygen it is always found as oxide—boric acid or borates.[6]

Elementary boron is usually got in a black form which is believed to be amorphous; it has recently (see below) been obtained in the crystalline state. The supposed crystalline boron which is described in many textbooks is now known not to be boron, but one or another of several compounds, especially the black AlB_{12} and the transparent yellow $Al_3C_2B_{44}$.[7] These formulae look improbable, but are well established. Boron has a singular power of forming a series of compounds with metals which have long strings of united boron atoms, and whose composition is determined rather by geometrical than chemical considerations. Thus there is a series of the composition MB_6 where M = Ca, Sr, Ba, La, Ce, Pr, Nd, Er, all of the same lattice structure, in which the shortest distances between the boron atoms are practically the same, 1·64 A, and show that the borons must be joined to one another directly[8] (theory for B—B 1·76 A).

Elementary boron can be made in the form of a black and probably amorphous powder, by the reduction of the oxide with sodium or of a fluoroborate with potassium. It is extremely difficult to get in the pure form[9]; it melts at 2,200° and boils at about the same temperature. Quite

[4] A. W. Laubengayer, R. P. Ferguson, and A. E. Newkirk, *J.A.C.S.* 1941, **63**, 559.

[5] S. H. Bauer and J. Y. Beach, ib. 1394.

[6] An idea of its great importance to vegetation can be got from an article on 'Boron in Agricultural and Horticultural Practice', *Nature*, 1940, **145**, 766.

[7] F. Halla and R. Weil (*Z. Krist.* 1939, **101**, 435) make an X-ray study of AlB_{12}, a 'graphite-like' form, previously known as crystalline boron; two modifications of this occur.

[8] F. Laves, *Z. physikal. Chem.* 1933, B **22**, 114.

[9] See A. W. Laubengayer, A. E. Newkirk, and R. L. Brandaur, *J. Chem. Ed.* 1942, **19**, 382.

recently, however, Laubengayer *et al.*[10] have been able to prepare massive crystalline elementary boron and to study its properties. It was made by passing a mixture of hydrogen and boron tribromide vapour at rather less than an atmosphere over a tantalum filament heated to 1,100-1,300° C.; at this temperature the tribromide is reduced and the boron deposited on the filament in hexagonal plates and needles, which are practically pure. It is harder than carborundum, and as hard as boron carbide, the second hardest known solid. It is black and opaque, but the thinnest plates appear orange-red in a strong light. Its density is 2·310. The crystalline structure is complex, and it may be dimorphic. The needles are probably tetragonal, with a spacing of 5·06 A along the needle's axis. Its electrical conductivity is small, and increases less than 100-fold (not, as has been stated of some less pure specimens, a million times) between 20° and 600°, even at 1,800° it does not seriously increase the conductivity of a tungsten wire.

Chemically this form of boron is extremely inert. It is not affected by boiling with concentrated hydrochloric or even hydrofluoric acid, and only reacts very slowly with hot concentrated nitric or sulphuric acid. It reacts with fused sodium hydroxide only above 500°, and then slowly.

This inertness is in strong contrast to the great reactivity of the finely divided form. The large heat of oxidation makes the powder a very strong reducing agent at high temperatures: it catches fire at about 700° and then burns by itself while the massive crystals oxidize superficially if heated to incandescence in oxygen, but cease to do so as soon as the external heat is removed. The powder reduces many metals from their oxides, chlorides, and sulphides, and at 800° reduces orthophosphoric acid to elementary phosphorus.

BORON COMPOUNDS

Boron, as we have seen, has an almost unique power of forming covalent molecules with less than 2 electrons per link: in these (except in the borohydrides, p. 364) the boron is always united to a second boron and to at least one hydrogen atom.

Hence the first section of boron compounds, that of the hydrides and their derivatives, includes all these abnormal compounds, as well as many that are normal.

BORON HYDRIDES

All statements about the hydrides of boron earlier than 1912, when Stock began to work upon them,[11] are untrue. Stock has prepared a whole series of these hydrides and determined their properties, and recently others, especially Schlesinger and Burg in America, largely using his technique but extending his methods, have added to our knowledge of them and their

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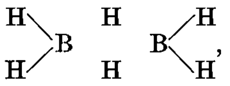
[10] A. W. Laubengayer, D. T. Hurd, A. E. Newkirk, and J. L. Hoard, *J.A.C.S.* 1943, 65, 1924.

[11] A. Stock and C. Massenez, *Ber.* 1912, 45, 3539. (The last paper on this subject in which Stock took part was published 24 years later: A. Stock, E. Wiberg, and W. Mathing, ib. 1936, 69, 2811.)

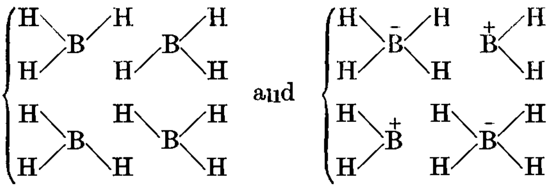
derivatives. A full account of the work up to 1932 is given in Stock's Cornell lectures.[12]

A normal hydride of boron with an open chain of singly linked boron atoms would have the general formula B_nH_{n+2} (BH_3, B_2H_4, B_3H_5, B_4H_6, etc.). Six or perhaps seven different volatile hydrides, from B_2H_6 to $B_{10}H_{14}$, are known and have had their molecular weights determined; all of them have more hydrogen than this general formula requires, some two more and the rest four more. These compounds can have most but not quite all (up to all but two) of their hydrogen atoms replaced by certain other atoms or groups such as alkyls and halogens; the products retain the peculiar valency relations of the hydrides, but disproportionate with increasing ease to form normal trivalent boron derivatives like $B(CH_3)_3$ and BCl_3. They are also able to make up the normal number of electrons either directly, by becoming anions, or by co-ordination as acceptors.

Numerous theories have been suggested to account for these facts, but up to a few years ago there had come to be a general agreement that the boron atoms in these compounds were united to one another, and that their abnormally high covalencies were due to the presence of 1-electron links, or rather to a deficiency of shared electrons, which was itself shared among the links by resonance. In 1943 a rival theory was put forward by Longuet-Higgins and R. P. Bell,[13] who ascribed to B_2H_6 a bridged structure



which might be written as a resonance between the structures



This theory was first suggested by Dilthey,[15] and discussed by others, especially Syrkin,[16] but no serious arguments had been put forward in its support.

In their first paper Longuet-Higgins and Bell[13] examine the physical properties which such a model should have, and compare them with the observed results of electron diffraction, X-ray analysis of the crystal, specific heats, etc.; they get a better agreement than with the ethane-like model. In a second paper[14] they discuss the vibrations of such a molecule

[12] A. Stock, *Hydrides of Boron and Silicon*, Cornell Press, 1933.

[13] H. C. Longuet-Higgins and R. P. Bell, *J.C.S.* 1943, 250.

[14] R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc.* 1945, **183**, 357.

[15] W. Dilthey, *Z. angew. Chem.* 1921, **34**, 596.

[16] J. Syrkin and M. Diatkina, *Acta Phys.-Chem. U.R.S.S.* 1941, **14**, 547; *C.R. Acad. Sci. U.R.S.S.* 1942, **35**, 180.

in detail, and find that the observed infra-red and Raman spectra of diborane can be satisfactorily assigned, 15 of the 17 possible frequencies being observed, with an agreement within 2 per cent.; the derived specific heats also agree with observation. See further references.[17-18]

The calculated entropies for the ethane-like and the protonated models are practically identical, so that the entropy will not decide between them.[20]

A general review of the situation suggests that with diborane B_2H_6 the bridge theory gives a better agreement with observation than the usual ethane-like model. Of the higher hydrides of boron, however, to which the older theory assigns satisfactory structures, the new view gives no probable account.[13] Hence in what follows the older theory, which formulates the compounds after the manner of paraffins, will be followed. If, however, it becomes possible to apply the bridge theory to these (and also to the borohydrides, p. 364) with as good an agreement as it gives with diborane, it will have a strong claim to be accepted.[21] See, however, p. 364.[47a] See further reference.[21a]

A modification of this theory, which claims to account for the higher boranes, has been proposed by Pitzer.[19] A modified hydrogen-bridge theory has been suggested[22] in which it is assumed (much as by Pitzer) that two electrons can be donated to form a co-ordinate link even when they are already shared. Infra-red measurements on B_2H_6 are considered to rule out the ethane-like structure, and to be compatible with that of Bell and Longuet-Higgins.[23]

The factor which on the 'paraffin' theory determines the abnormal valency seems to be the presence of the B—B group together with B- -H links; these two are present in every abnormal boron compound except the borohydrides. According to Mulliken[24] the deficiency of electrons is shared among all the links, but from the properties it is fairly obvious that it is more fully shared among the B—B and B—H links, and in a diminishing degree by the B—C and B—halogen. On theoretical grounds it would be expected that the 1-electron state of the link would be more stable the nearer the electronegativity values (in Pauling's sense) of the atoms composing it; and the following list of values[25] shows that this is so: **B 2·0**; H 2·1; C 2·5; N 3·0; O 3·5; F 4·0, and Cl 3·0.

Mainly through the work of Stock, six or perhaps seven different volatile hydrides have been prepared and purified, and their molecular weights

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[17] R. P. Bell and H. C. Longuet-Higgins, *Nature*, 1945, **155**, 328.

[18] H. C. Longuet-Higgins, *J.C.S.* 1946, 139.

[19] K. S. Pitzer, *J.A.C.S.* 1945, **67**, 1126.

[20] Id., ib. 1947, **69**, 184.

[21] Rather similar views were put forward by R. E. Rundle, ib. 1327.

[21a] V. H. Dibeler and F. L. Mohler, ib. 1948, **70**, 987.

[22] A. D. Walsh, *J.C.S.* 1947, 89.

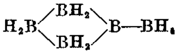
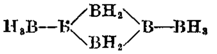
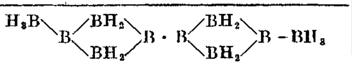
[23] W. C. Price, *J. Chem. Phys.* 1947, **15**, 614.

[24] R. S. Mulliken, ib. 1935, **3**, 635.

[25] L. Pauling, *Chemical Bond*, 1939, p. 64.

determined. The simplest possible hydride, BH_3, does not exist as such, but at once polymerizes to B_2H_6, unless it can co-ordinate as an acceptor with such donor molecules as ether or ammonia. The structures of the first four of the others (B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11}) have been determined by electron diffraction; those of the rest (with more than 5 boron atoms) can with some probability be guessed, as Bauer and Pauling[26] have pointed out. The electronic defect is to some extent dependent on the structure; there is no reason to assume that double B=B bonds exist anywhere, but the presence of a ring (established in one case and probable in two others) increases the defect by two (for a B_5 hydride the normal structure with an open chain would be B_5H_7, and with a closed B-ring B_5H_5). The structures of these hydrides are discussed later (p. 347). The following list gives (1) the formula; (2) the atomic structure of the molecule (ascertained by electron diffraction except in the last three hydrides); (3) the electron deficiency; (4) the m. pt.; (5) the boiling-point; (6) the average number of valency electrons per link; (7) the vapour pressure in mm. at 0°.

TABLE

Formula	*Structure*	*El. def.*	*M. pt.*	*B. pt.*	*Els./link*	*V.p./0°*
B_2H_6	$H_3B—BH_3$ as ethane	2	−165·5°	−92·5°	1·71	V. high
B_4H_{10}	$H_3B-BH_2—BH_2—BH_3$ as butane	4	−120°	+18°	1·69	388 mm.
B_5H_9		4	−46·9°	*ca.* +65°	1·71	66 mm.
B_5H_{11}	$BH_3-BH_2—BH—BH_2—BH_3$	4	−123·3°	*ca.* +60°	1·73	53 mm.
B_6H_{10}		4	−65·1°	*ca.* 110°	1·75	7·2 mm.
?? B_6H_{12}	?? $H_3B—BH_2-BH—BH—BH_2—BH_3$?	4	−91·5°	*ca.* +50°	1·76	?
$B_{10}H_{14}$*		6	+99·5°	*ca.* 213°	1·76	V. low

A comparison of certain of the boiling-points with those of analogous compounds is interesting.

	B_2H_6	C_2H_6	Si_2H_6	B_4H_{10}	C_4H_{10}	Si_4H_{10}	B_2H_5Br	C_2H_5Br
B. pts.	−92·5°	−88·3°	−15°	+18°	+0·6°	+80–90°	*ca.* +10°	38·4°
M. pts.	−165·5°	−172·1°	−132·5°	−120°	−135°	−93·5°		

The figures in col. 6 for the average number of electrons per link are remarkably close; the mean is 1·73±0·04 (2 per cent.). The value of course depends on the structures assumed (thus an open-chain B_5H_9 would give 1·85), and though there is no obvious reason for the agreement it gives some support to the ring-formulae for B_5H_9 and $B_{10}H_{14}$.

* The alternative 5-ring structure (p. 346) gives the same number of valency electrons per link.

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[26] S. H. Bauer and L. Pauling, *J.A.C.S.* 1936, **58**, 2403.

Methods of Preparation

These are essentially two: (1) Stock's original method[11] of treating magnesium boride Mg_3B_2 with acid, which gives B_4H_{10}, from which the other hydrides can be obtained; in this way 750 c.c. B_2H_6 were obtained from 4 kg. of magnesium boride, or 0·19 c.c. of gas per gramme. (2) The second method is that of Schlesinger and Burg,[27] who exposed a mixture of boron trihalide and hydrogen to the electric discharge; the main product of this reaction is B_2H_6, from which again the other hydrides can be prepared. These are practically the only methods now used for the preparation of these hydrides. The predominance of the B_4 hydride in the first reaction is mainly due to two causes: (1) water acts so much more rapidly on B_2H_6 than on B_4H_{10} (it can be used to remove traces of B_2H_6 from B_4H_{10}) that any diborane that may be formed in Stock's reaction will be destroyed by the water present, and (2) there is some reason to think that the magnesium boride itself contains a B_4 group.[28-30]

The method now used is Schlesinger and Burg's except where B_4H_{10} is wanted; in that case a yield of 1 c.c. B_4H_{10} gas per gramme of magnesium boride (about 0·1 per cent. of theory) can be obtained[31] by using finely divided boride and 8-normal phosphoric acid.[32] To avoid silicon compounds, which are difficult to remove, beryllium boride can be used in place of magnesium.[33]

Schlesinger and Burg's method[27] is very peculiar. Hydrogen at about 20 mm. is mixed with a tenth of its volume of boron trihalide, and exposed to a discharge of about 15,000 volts; the products, which are condensed with liquid air, are mainly (with the trichloride) composed of B_2H_5Cl, but on letting them warm up to 0° this is almost completely converted into $B_2H_6+BCl_3$. Since it is difficult to separate hydrogen chloride (b.pt. $-85°$) by fractionation from diborane (b. pt. $-92·5°$), it is better to use boron tribromide (b.pt. of HBr $-68°$).[34-5]

Diborane, B_2H_6

This is the simplest of the boranes, since no binary hydride of boron with only one boron atom in the molecule exists. It is best made by the method of Schlesinger and Burg already described[27]; with 20 mm. boron trichloride and 15,000 volts they got from 5 to 10 g. of diborane per week in a 55 per cent. yield. Diborane is also the chief product of heating B_4H_{10} to 100°, and was first made in this way by Stock[11]; it is also formed from other hydrides and their derivatives.

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[27] H. I. Schlesinger and A. B. Burg, *J.A.C.S.* 1931, **53**, 4321.

[28] M. W. Travers, R. C. Ray, and N. M. Gupta, *J. Ind. Inst. Sci.* 1914, **1**, 1.

[29] R. C. Ray, *J. Chem. Soc.* 1914, **105**, 2162.

[30] R. C. Ray, *J. Ind. Chem. Soc.* 1924, **1**, 125.

[31] A. Stock, F. Kurzen, and H. Laudenklos, *Z. anorg. Chem.* 1935, **225**, 243.

[32] B. D. Steele and J. E. Mills, *J. Chem. Soc.* 1930, 74.

[33] A. Stock, E. Wiberg, and H. Martini, *Ber.* 1930, **63**, 2927.

[34] A. Stock, H. Martini, and W. Sütterlin, ib. 1934, **67**, 396.

[35] A. Stock and W. Mathing, ib. 1936, **69**, 1456.

Diborane melts at $-165{\cdot}5^\circ$ and boils at $-92{\cdot}5^\circ$; its vapour density gives no indication of its dissociation into BH_3 up to 100°, where it begins to decompose; it is slightly soluble in carbon disulphide. When pure, and free from the hydrides of silicon, it is not spontaneously inflammable, unlike the hydrides of silicon and also the boron trialkyls; at the ordinary temperature, unlike some of the higher hydrides, it is stable for days in dry air or oxygen. At 100–200° it changes into B_4H_{10} together with some B_5H_9 and B_5H_{11}, but no B_6H_{10}[22]; at 300° it dissociates practically completely into boron and hydrogen; an electric discharge converts it into the solid $(BH)_x$.[36]

The structure of diborane has been examined by X-ray analysis of the crystals,[37] by electron diffraction,[38] and by means of the Raman spectrum.[39] The results are concordant (see, however, p. 340). Both in the gas and in the solid it has the same type of structure as ethane, but the distances are rather greater: B—B $1{\cdot}86 \pm 0{\cdot}04$ A; B—H $1{\cdot}27 \pm 0{\cdot}03$ A (theory B—B 1·76, B—H 1·18): the angles are tetrahedral. The Raman spectrum gives the force constants (with 10^5 dynes per cm. as unity) B—H stretching 3, bending 0·26; B—B stretching 3·6 (for the pseudo-aromatic $B_3N_3H_6$ the force constants for the B—H links are stretching 3·42, for bending 0·35 in the plane of the molecule, 0·23 across it). It is diamagnetic.

The following table gives the properties of diborane as compared with those of ethane and ethylene (since it has been maintained that the B—B link in diborane is double).

Properties of B_2H_6, C_2H_6, C_2H_4

	B_2H_6	C_2H_6	C_2H_4
M. pt.	$-165{\cdot}5^\circ$	-172°	-169°
B. pt.	$-92{\cdot}5^\circ$	-84°	-105°
Distance A—A .	1·86	1·54	1·38
Distance A—H .	1·27	1·09	1·06 A.U.

The B—B distance is unusually long (the usual value is 1·76), which proves that the B—B link cannot be double, and probably shares in the electron deficiency. The value of the parachor is 121·9,[42] which is 13·5 less than would be calculated for the molecule if all its links contained 2 electrons.

Diborane is in general a stable compound, but it is exceptionally rapidly hydrolysed by water to boric acid and hydrogen; it can be removed from B_4H_{10} in this way. Stitt,[40-1] from the specific heats, finds in B_2H_6 a barrier to complete rotation of *ca.* 5 k.cals./mole. Various of its reactions are

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[36] Id., ib. 1469.
[37] H. Mark and E. Pohland, *Z. Krist.* 1925, **62**, 103.
[38] S. H. Bauer, *J.A.C.S.* 1937, **59**, 780.
[39] T. F. Anderson and A. B. Burg, *J. phys. Chem.* 1938, **6**, 586.
[40] F. Stitt, *J. Chem. Phys.* 1940, **8**, 981.
[41] Id., ib. 1941, **9**, 1096.
[42] A. Stock, E. Wiberg, and W. Mathing, *Ber.* 1936, **69**, 2811.

described later: with sodium (p. 348), with ammonia (pp. 351-5), with halogens (p. 363), and with sodium hydroxide (p. 361).

B_4H_{10}[33]

This can be made in three ways.

A. By the action of acids (preferably phosphoric)[32] on magnesium boride Mg_3B_2; the borides of beryllium, aluminium, cerium, or manganese can also be used.

B. By the action of sodium on the mono-iodide of diborane B_2H_5I[43]; this reaction is of importance as proving the structure of tetraborane. The iodide was agitated with dilute sodium amalgam, and the product distilled off, freed from admixed diborane by treatment with water, and identified by its vapour pressure.

C. Burg and Schlesinger[44] showed that B_5H_{11} reacts with hydrogen to give a mixture of B_4H_{10} and B_2H_6; at 100° B_4H_{10} is the main product.[35]

B_4H_{10} has been shown by electron diffraction[45] to have the structure of normal butane, with the distances B—B $1{\cdot}84 \pm 0{\cdot}04$: B—H $1{\cdot}28 \pm 0{\cdot}03$. It melts at $-120°$ and boils at $+18°$. It is not spontaneously inflammable if it is free from silanes. It decomposes slowly in the cold, more rapidly if it is heated, mainly to hydrogen, diborane, and solid hydrides $(BH)_x$; its rate of decomposition is much hastened by impurities or by ultra-violet light.

On heating it gives B_2H_6, B_5H_9, B_5H_{11}, B_6H_{12}, $B_{10}H_{14}$, and non-volatile hydrides. To convert it into diborane it is heated to 90° for some hours; after 4 hours at 180° the main product is B_5H_{11}[27]; B_5H_9 is made by passing it through a tube at 200°; at 300° the only products are boron and hydrogen.

Water hydrolyses it to boric acid, but quite slowly in the cold, about 50 per cent. in 2 hours. With hydrogen chloride it gives diborane and boron trichloride, and with ammonia the compound $B_4H_{10}, 4NH_3$ (see p. 355); its reactions with potassium and potassium hydroxide are discussed later.

B_5H_9

This can be made from B_4H_{10} by heating it to 100°, or by passing it through a tube at 200° (17 per cent. yield), or more easily from B_2H_6 either by heating it to 250–300° in the presence of mercury vapour as a catalyst,[27] or by treating it with hydrogen chloride for 48 hours at 120-30°[35] (yield 20 per cent.). It is a mobile liquid, melting at $-46{\cdot}9°$ and boiling at about $+65°$ (vapour pressure 66 mm./0°).

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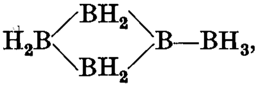
[43] A. Stock and E. Pohland, *Ber.* 1926, **59**, 2223.
[44] A. B. Burg and H. I. Schlesinger, *J.A.C.S.* 1933, **55**, 4009.
[45] S. H. Bauer, ib. 1938, **60**, 805.
[46] A. Stock and E. Kuss, *Ber.* 1923, **56**, 802.

By electron diffraction Bauer and Pauling[26] found the remarkable structure



corresponding to methyl cyclobutane. All the 5 boron atoms lie in one plane, with the distances B—B 1·76+0·02; B—H 1·17. The presence of this 4-ring is very unexpected, as with carbon it is a rare form; but the defect of electrons may probably make deformation of the angles easier. Bauer and Pauling assume with some probability that a similar 4-ring occurs in B_6H_{10}, and two of them in $B_{10}H_{14}$ (see structures above, p. 341).

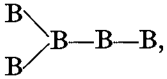
B_5H_9 is one of the three stablest hydrides of boron, the other two being B_2H_6 and $B_{10}H_{14}$. It is not spontaneously inflammable in air; on standing it changes very slowly into hydrogen and a non-volatile hydride; if it is passed through a tube at 300° half of it comes through unchanged, the remainder going to boron and hydrogen. Hydrogen chloride has no action on it, even in presence of aluminium chloride.

To water it is much more stable than B_2H_6 or even B_4H_{10}; it is not completely hydrolysed in 3 days at 90°. Ammonia forms the addition product B_5H_9, $4NH_3$; it dissolves in 30 per cent. sodium hydroxide (this is the initial stage of hydrolysis; see later, p. 361) almost without evolution of hydrogen; if the solution is acidified hydrogen is evolved, but only 85 per cent. of the theoretical amount after 24 hours' treatment with the alkali, which shows the stability of the intermediate hydrolytic products.

B_5H_{11}

This is made[14] by passing the diborane through a tube at 100-115°, when it is practically all converted into a mixture of B_4H_{10}, B_5H_{11}, and hydrogen, or[22] in a 75 per cent. yield by passing B_2H_6 at 150-450 mm. pressure through a tube at 180°.

It melts at −123·3° and boils at +60°; its vapour density is normal. Electron diffraction[31] shows it to have an open chain of 5 boron atoms, probably normal, B—B—B—B—B, but possibly branched, as



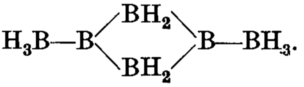
with B—B 1·81+0·03 and B—H 1·26+0·03 A (theory 1·76, 1·18).

B_5H_{11} is unstable, and decomposes in a few hours in the cold, mainly to hydrogen, $B_{10}H_{14}$, and a solid hydride; if heated with excess of hydrogen it is almost quantitatively converted into $B_2H_6+B_4H_{10}$.

B_6H_{10}

This is present in small quantity in the mixed gases from magnesium boride, and can be separated by fractionation (2 kg. Mg_3B_2 gave 1·5 c.c.

liquid or 300 c.c. gaseous B_6H_{10}). Its structure has not yet been determined, but Bauer and Pauling suggest that it may be



$$H_3B—B\begin{matrix}\diagup BH_2 \diagdown \\ \diagdown BH_2 \diagup\end{matrix}B—BH_3.$$

It is a colourless liquid melting at −65·1°, with a vapour pressure of 7·2 mm. at 0° (b. pt. extrapolated *ca.* 110°); the vapour density is normal. It decomposes at the ordinary temperature or at 100° into hydrogen and a non-volatile compound, and does so quicker than B_2H_6 or B_5H_9, but slower than B_4H_{10} or B_5H_{11}. If it is passed through a tube at 300° most of it comes out unchanged, showing that it belongs to the more stable group of hydrides. After 15 hours with water at 90° hydrolysis is not complete.

B_6H_{10} dissolves in 30 per cent. sodium hydroxide without any evolution of hydrogen, which, however, comes off quantitatively and at once on acidification, as with B_2H_6 and B_4H_{10}, but not with B_5H_9.

B_6H_{12}?

The original B_6H_{12}[11] was withdrawn; but this may probably be the formula of an impurity found in the B_5H_9 formed by heating B_4H_{10}, and imperfectly separated by means of its greater volatility.[47] It is too unstable for accurate analysis or vapour-density determination, but it seems to have the composition $B_6H_{>10}$. In the analogy of B_5H_{11} we may assign it an open-chain structure such as $BH_3—BH_2—BH—BH—BH_2—BH_3$.

$B_{10}H_{14}$

This is the heaviest of the volatile hydrides of boron, and the only one which is solid at the ordinary temperature. It is formed by the action of heat on the lower hydrides, for example, by heating diborane to 115-120° for 48 hours, or B_4H_{10} to 90–95° for 5 hours.[35]

It forms white crystals, with a vapour pressure of about 0·3 mm. at 0°; m.pt. 99·6°, b.pt. extrapolated 213°; it is thus easily purified by sublimation. The molecule from the vapour density at 145° and the freezing-point in benzene is monomeric. It has a peculiar smell unlike those of the other hydrides (they all have unpleasant smells) and resembling osmium tetroxide. Recent electron diffraction measurements[47a] suggest that the molecule may be formed of two 5-boron rings joined by a B—B link; they are definitely against a 'protonated' or hydrogen-bridge structure. But see further the X-ray results.[47b]

$B_{10}H_{14}$ is one of the stablest of the hydrides; it can be kept in air or oxygen at 50-60° for days without change; in the absence of air it decomposes very slowly at 200°, but even at 250° only 93 per cent. was found to be decomposed after 24 hours.

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[47] A. Stock, and W. Siecke, *Ber.* 1924, **57**, 562.

[47a] G. Silbiger and S. H. Bauer, *J.A.C.S.* 1948, **70**, 115.

[47b] J. S. Kasper, C. M. Lucht and D. Harker, ib. 881.

It is insoluble in water, but soluble in alcohol, ether, benzene, and especially carbon disulphide.

Water hydrolyses it very slowly in the cold (10 per cent. in 10 days), more rapidly on heating (94 per cent. in 20 hours at 100°), especially if air has access to the system.

Chlorine and bromine substitute (but not at all violently) in the cold; the residue after 6 months with bromine had a composition between $B_{10}H_{12}Br_2$ and $B_{10}H_{11}Br_3$; iodine gave a di-iodo-derivative as well as other more highly iodinated compounds. Hydrogen chloride has no action on it even at 100° in the presence of aluminium chloride. The complicated reactions with ammonia and with sodium hydroxide are discussed later.

Non-volatile Solid Hydrides

When the volatile hydrides are decomposed by heat or otherwise, non-volatile solid deposits are often formed; these have a composition not far from BH, and are hydrolysed by water in much the same way as the volatile hydrides, to give solutions containing hypoborates and similar reducing substances. None of them have been purified, and it is not certain how many individuals are included under this description.

Stock and Mathing[36] found that by the action of the electric discharge on diborane none of the higher volatile hydrides is formed, but only hydrogen, and a solid which, if the silent discharge in an ozonizer is used, looks like chrome yellow, and has the composition $(BH)_x$. It is stable in dry air and insoluble in indifferent solvents like benzene or chloroform. Above 100° it gives off hydrogen, and about 5 per cent. of B_6H_{10}. It is hygroscopic, and with water 2 atoms of hydrogen for every 3 atoms of boron present are replaced by 1 oxygen atom, which again suggests that the structure contains B_6 units of some kind.

Structures of the Volatile Hydrides

All the seven volatile hydrides were discovered by 1932; no new ones have been found since then. We may therefore conclude that the hydrides of boron are a very limited group of compounds, practically all of which are known. Since they can contain up to 10 boron atoms in the molecule, it should be possible to find out what conditions limit their number to the half-dozen or so that have been made. From the structures of the first four compounds it seems that they contain either (1) a normal boron chain; or (2) a 4-boron ring. In B_4H_{10} we have a straight chain of 4; the addition of the tricovalent group BH would give from this first B_5H_{11} (which we know to be an open chain), and then B_6H_{12}, which we may assume to be one too. The closing of a 4-ring removes 2 hydrogen atoms, to give B_5H_9 and B_6H_{10}, with one and two side chains; this ring-closure seems to involve in both a marked increase in stability. Finally, we have only one hydride with more than 6 boron atoms, and that is the very stable one with 4 more, $B_{10}H_{14}$, for which the structure with two 4-rings has been suggested (p. 341), though more recent work[47a, b] is more in favour of two 5-rings. We thus have the boron skeletons B—B, B—B—B—B, B—B—B—B—B, B—B—B—B—B—B, and B_4—B, B—B_4—B, and B—B_4—B_4—B, or B_5—B_5.

Derivatives of Boron Hydrides

The numerous and varied substitution products of the boron hydrides (especially diborane), and their addition compounds in which the electron deficiency is made up, are so closely connected that they are better treated together, classified as usual according to the periodic groups of the attached atoms (alkali metals, p. 348: C, p. 349: N, p. 351: O, p. 360: halogens, p. 363: borohydrides, a special class, p. 364.

Alkaline Salts

Most of the boranes (as well as some of their amino-derivatives) form solid addition products with alkali metals, of a salt-like character.* The best known are the salts of diborane. If this hydride is treated with dilute sodium amalgam in the cold it takes up 2 atoms of sodium (but never more) per B_2H_6.[46,48]. The product $Na_2[B_2H_6]$ is a white powder insoluble in benzene; in water it evolves hydrogen and gives an alkaline solution with all the properties of a hypoborate ($M_2[BH_2OH—BH_2OH]$; see p. 361), including the power of precipitating black nickel boride from a solution of a nickel salt; gaseous hydrogen chloride acts on the solid to liberate most of the diborane, showing that no profound change has occurred. The potassium salt,[49] from which the excess of potassium can be distilled off in a vacuum, is a fine white powder of remarkable stability, not affected by heating to 300°. It forms regular crystals, stable in dry air, insoluble in benzene or ether, and diamagnetic[50]; it is hydrolysed by water to a hypoborate. The methylated diboranes form similar alkaline salts.

The structure of the salts is obvious. The molecule must be dimeric since it is diamagnetic, and so must have the divalent anion $[B_2H_6]^{--}$ which has the exact ethane structure. Since all its links are di-electronic it is much more stable than diborane itself; it forms the first member of the series:

$$K_2[H_3B—BH_3] : H_3C—CH_3 : [H_3N—NH_3]SO_4.$$

Similar alkaline salts are formed by B_4H_{10} and B_5H_9. B_4H_{10} when treated with dilute amalgam for some hours at the ordinary temperature will take up 2 atoms of sodium or potassium per B_4H_{10}. The products are very like the diborane salts[18]; the potassium salt is rather more sensitive to heat than $K_2B_2H_6$; it begins to lose hydrogen at 130°, and ultimately at

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* These are sharply contrasted with the addition compounds which the boron triaryls form with these metals (p. 378). The latter are only formed by the triaryls and the tribenzyl, not by the trialkyls; they only have one boron atom in the molecule, and the result of their formation is to give the molecule apparently more electrons than it needs for its three covalencies.

[48] A. Stock and E. Pohland, *Ber.* 1926, 59, 2210.

[49] A. Stock, W. Sütterlin, and F. Kurzen, *Z. anorg. Chem.* 1935, **225**, 225.

[50] L. Klemm and W. Klemm, ib. 258.

450° leaves a stable white solid of the composition $K_2B_4H_6$, of which little is known.

B_5H_9 in the same way forms $K_2B_5H_9$, which is stable at 265°; it gives an alkaline solution in water, which evolves no hydrogen until it is acidified, and does not precipitate black nickel boride.

The structures of these salts, other than those of diborane, are uncertain, as is indeed the individuality of some of them.

Similar salts can be obtained from the amino-compounds of the boranes (see later under the ammonia compounds[51]); thus a solution of

$$NH_4[H_3\overset{-}{B}—\overset{+}{N}H_2—\overset{-}{B}H_3]$$

in liquid ammonia reacts with sodium to give $Na[H_3\overset{-}{B}—\overset{+}{N}H_2—\overset{-}{B}H_3]$, which is left behind on evaporation. So, too, if sodium is added to a solution of $(CH_3)_2O \rightarrow BH_3$ in liquid ammonia, there remains on evaporation the salt $Na[H_3\overset{-}{B}—NH_2]$.

Alkyl Diboranes

The only binary hydride of boron from which alkyl derivatives have been prepared is diborane. This reacts[52] reversibly with boron trimethyl at the ordinary temperature to give a mixture of mono- di- tri- and tetramethyl diborane, which can be separated by fractionation. Later[53] a number of ethyl and propyl derivatives were made in the same way. The constitution of the products is proved by their reaction with water, in which every hydrogen atom attached to boron is replaced by hydroxyl. In this way it was found that the last three of these four methyl derivatives all give dimethyl boric acid $(CH_3)_2B—OH$. Hence their structures are $RBH_2—BH_3$, $R_2BH—BH_2$, $R_2BH—BH_2R$, and $R_2BH—BHR_2$. The fact that the dialkyl product is entirely the unsymmetrical form is an example of the singular instability of the RBH_2 group in the diboranes, whatever R may be, so that the substitution occurs exclusively here and not in the BH_3.

Schlesinger and Burg were, however, able to make the symmetrical compound $CH_3BH_2—BH_2CH_3$ by an indirect method.[54] Ethers are able, like tertiary amines, but less energetically, to form co-ordination products with the BH_3 group, and will split diborane in order to do so. If monomethyl diborane is treated with dimethyl ether, the ether breaks up the molecule and combines with the BH_3, but having less affinity apparently for the CH_3BH_2 radicals it leaves them to polymerize.

$$2\,CH_3BH_2{\cdot}BH_3 + 2\,(CH_3)_2O = 2\,(CH_3)_2OBH_3 + CH_3BH_2{\cdot}BH_2CH_3.$$

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[51] H. I. Schlesinger and A. B. Burg, *J.A.C.S.* 1938, **60**, 290.
[52] H. I. Schlesinger and A. O. Walker, ib. 1935, **57**, 621.
[53] H. I. Schlesinger, L. Horvitz, and A. B. Burg, ib. 1936, **58**, 407.
[54] H. I. Schlesinger, N. W. Flodin, and A. B. Burg, ib. 1939, **61**, 1078.

The physical properties of these compounds are:

Formula	*M. pt.*	*B. pt. or vap. press.*
$H_3B—BH_3$	−165·5°	−92·5°
$CH_3·BH_2—BH_3$	. .	*ca.*—15° (55 mm./—78·5°)
$CH_3·BH_2—BH_2·CH_3$	−124·9°	+4·9°
$(CH_3)_2BH—BH_3$	−150·2°	−2·6°
$(CH_3)_2BH—BH_2CH_3$	−122·9°	+45·5°
$(CH_3)_2BH—BH(CH_3)_2$	−72·5°	68·6°
$C_2H_5·BH_2—BH_3$	. .	(7 mm./—78·5°; decp. at −30°)
$(C_2H_5)_2BH—BH_3$	+67·1°	. .
$(C_2H_5)_2BH—BH_2C_2H_5$	. .	(4 mm./0°)
$(C_2H_5)_2BH—BH(C_2H_5)_2$	−56·3°	(0·5 mm./0°)
$n—C_3H_7BH_2—BH_3$	. .	(2·8 mm./0°)

The chemical properties are little known. Their behaviour with water shows the hydrogen atoms are much more easily removed from the borons than the methyl groups, as we should expect. The general points to be noticed about them are:

I. The monoalkyl compound is the least stable. This is a general characteristic of compounds containing the RBH_2 group, whatever R may be, as the following examples show:

1. $H_3B—BH_2CH_3$ very readily changes over to B_2H_6 and $B(CH_3)_3$.
2. $H_3B—BH_2C_2H_5$ decomposes at −30°.[53]
3. $CH_3BH_2—BH_2CH_3$ changes spontaneously into the isomeric $H_3B—BH(CH_3)_2$,[54] which is the sole product of the direct dimethylation of diborane.
4. $CH_3BH_2—BH(CH_3)_2$ goes spontaneously into a mixture of tetramethyl and unsymmetrical dimethyl diborane.[53]

The same thing happens when carbon is replaced by oxygen or halogen:

5. $CH_3·O·BH_2$ is unstable and changes spontaneously into $(CH_3·O)_2BH$.
6. B_2H_5Cl and B_2H_5Br go spontaneously into $B_2H_6+B(hal)_3$.

II. It is not possible to put more than 2 alkyl groups on to one boron atom, whatever excess of boron trimethyl is used; hence the product always contains at least two hydrogen atoms; this is an argument for the bridge structure of diborane.

III. The methyl, ethyl, and propyl compounds are similar to one another, though the latter seem to disproportionate rather more easily. (Methyl substitution products of triborine triamine, p. 358.)

Carbonyl Addition Compound, $H_3B \leftarrow C \equiv O$

This is a complex boron compound and a boron hydride derivative.

Diborane combines reversibly with carbon monoxide, rapidly at 100° and slowly at the ordinary temperature.[55] The equilibrium constant

$$K = \frac{[CO]^2 \cdot [B_2H_6]}{[H_3B \leftarrow CO]^2}$$

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[55] A. B. Burg and H. I. Schlesinger, *J.A.C.S.* 1937, **59**, 780.

is at 100° 3×10⁴. This means that at 100° $H_3B \leftarrow CO$ having an initial pressure of 200 mm. would be 95 per cent. dissociated.

$H_3B \leftarrow CO$ melts at $-137°$ and boils at $-64°$; the Trouton constant is 23·0. It is monomeric (apart from dissociation) in the vapour. It reacts with ammonia to give a white solid of the composition $H_3B \leftarrow CO, 2\ NH_3$, which when treated with sodium in liquid ammonia gives off 2 atoms of hydrogen per boron atom, and so would seem to have two NH_4 ions; but it has not been further examined and may be a mixture. The structure of $H_3B \leftarrow CO$ has been determined by means of electron diffraction by Bauer[56]; he finds the atoms B—C—O to be linear; the angle H—B—C is tetrahedral; the distances are

$$B—H\ 1·20 \pm 0·03;\ B—C\ 1·57 \pm 0·03;\ C—O\ 1·13 \pm 0·03$$

(theory 1·18, 1·65, $C{\equiv}O$ 1·10) as in carbon monoxide itself and the other carbonyls.

NITROGEN COMPOUNDS

The nitrogen derivatives of the hydrides of boron may be divided into the following classes:

1. True Ammines (co-ordination compounds).
2. Amines and Imines.
3. Ammonium Salts.
4. B_2NH_7, probably $H_3B \leftarrow NH_2—BH_2$.
5. The semiaromatic 6-ring triborine triamine $B_3N_3H_6$ and its derivatives.

1. *True Ammines*

Ammonia and amines can react with boron hydrides to produce (1) by substitution amino- or imino-compounds (p. 352); (2) by addition either true ammines with the group $R_3N \rightarrow B$, or ammonium salts (sect. 3, p. 353). Nearly all the known ammines are produced by trimethylamine, not because the tertiary amine co-ordinates more strongly, but because the ammonia reacts further to give an ammonium salt, which, as we now realize, involves the replacement of hydrogen attached to nitrogen (see sect. 3, p. 354).

$H_3B \leftarrow N(CH_3)_3$[55]; formed rapidly and completely from its components, and also from trimethylamine and the carbonyl compound $H_3B \leftarrow CO$, with expulsion of carbon monoxide. M.pt. +94°, b.pt. (extrapolated) 171°; monomeric in the vapour. It is a remarkably stable compound. It cannot be a trimethylammonium salt (the addition compound with ammonia is an ammonium salt) as it does not evolve hydrogen when it is treated with sodium in liquid ammonia. This is confirmed by the results of electron diffraction (Bauer[38]), which give a pattern like that of tetramethyl methane $C(CH_3)_4$; the distances are B—N 1·62+0·15; N—C 1·53+0·06 A.U. (theory 1·58, 1·47).

Methylated diboranes react in the same way, but the methyl groups

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[56] S. H. Bauer, **59**, 1804.

weaken the B—N link; thus $Me_3B \leftarrow NMe_3$ is 70 per cent. dissociated in the vapour at 80°; $Me_2BH \leftarrow NMe_3$ not perceptibly at 68°; $MeBH_2 \leftarrow NMe_3$ and $H_3B \leftarrow NMe_3$ not at all at 100°. At the same time the fully methylated boron atom is more stable than the partly methylated, and so

$$CH_3BH_2 \leftarrow NMe_3,$$

though it is stable at 100°, goes over at 200° into the trimethylamine compounds of BH_3 and BMe_3, and the dimethyl compound in the same way at 70° to the mono- and the tri-; it is surprising that here the di-substituted BH_3 disproportionates so much more readily than the mono-substituted.

The boiling-points, the Trouton constants, and the melting-points of these methyl-borane ammines are:

Compound	*B. pt.*	*Trouton*	*M. pt.*
$H_3B \leftarrow NMe_3$	171°	23·0	+94°
$CH_3BH_2 \leftarrow NMe_3$	176·4°	21·9	+0·8°
$(CH_3)_2BH_2 \leftarrow NMe_3$	171·4°	21·6	−18·0°
$(CH_3)_3B \leftarrow NMe_3$	*ca.* 115°	. .	+120°

The remarkable fall in the boiling-points with the rise in the number of methyl groups must be due to the increasing dissociation, which in the last compound must be nearly complete at the boiling-point, as it is 70 per cent. some 25° lower.

The trimethylamine compounds of BH_3 and its mono- and dimethyl derivatives react with hydrogen chloride at low temperatures (in a few minutes at −80°: diborane itself scarcely reacts with it at all) to replace hydrogen attached to boron by chlorine—a reaction peculiar to boron and silicon—giving, for example, $CH_3BHCl \leftarrow NMe_3$. The reaction goes quicker the more methyl groups are present: thus $BHCl_2 \leftarrow NMe_3$ is formed only by long heating at 100°, but $CH_3BCl_2 \leftarrow NMe_3$ completely in 20 minutes at the ordinary temperature. $(CH_3)_3B \leftarrow NMe_3$ is the only known compound whose B—N link is broken by hydrogen chloride: it gives of course $(CH_3)_3B+(CH_3)_3NH[Cl]$.

The compound $H_3B \leftarrow NH_2—BH_2$ (sect. 4, p. 356) can take up one molecule of ammonia or trimethylamine as its formula requires.[57]

Other amines, especially tertiary amines, can replace trimethylamine; it is remarkable[58] that while pyridine expels NMe_3 from $Me_3B \leftarrow NMe_3$ it is itself expelled by NMe_3 from $H_3B \leftarrow py$.

2. *Amines and Imines*

Molecules with such groups as $B—NH_2$ or B—NH—B are often assumed as intermediate products in the reactions of the boranes with ammonia, but few have actually been identified.

The addition compound B_2H_6, $2NH_3$ is now known to be of this kind,

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[57] H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *J.A.C.S.* 1938, 60, 2297.

[58] H. I. Schlesinger and H. C. Brown, ib. 1940, 62, 3429.

being the ammonium salt $(NH_4)[H_3\overset{-}{B}—\overset{+}{N}H_2—\overset{-}{B}H_3]$ (see sect. 3, p. 354); the corresponding neutral compound $H_3\overset{-}{B}—\overset{+}{N}H_2—BH_2$ has also been prepared (sect. 4, p. 356). A similar B—N—B grouping occurs in the benzene-like triborine triamine $B_3N_3H_6$ (sect. 5, p. 357), which is very stable and gives numerous derivatives.

Simpler amino-derivatives with only one boron atom in the molecule are also known. For example, if B_2H_6, 2 NH_3 is treated with sodium in liquid ammonia, one hydrogen atom is evolved for every two borons, and the residue has the composition (and no doubt the structure) of $Na[H_3\overset{-}{B}—NH_2]$.[57] A neutral molecule of the same kind (which has been isolated) is $(CH_3)_2B—NH_2$.[59] When ammonia acts on the methyl diboranes the chief products are the B-methyl derivatives of $B_3N_3H_6$; but they include this $(CH_3)_2B—NH_2$, which melts about −55° and has a vapour pressure of 2 mm. at −78·5°; the formula is supported by the vapour density and the analysis. We may suppose that the methyl-diboranes react with ammonia to give $CH_3BH—NH_2$ and $(CH_3)_2B—NH_2$; the former then condenses, losing hydrogen, with itself and $H_2B—NH_2$ to the triborine compound, while the latter having no hydrogen left on the boron stays put. When ammonia acts on tetramethyldiborane, $(CH_3)_2B—NH_2$ is the sole product.

3. *Ammonium Salts*

All the volatile boranes except B_6H_{10} and B_6H_{12} have been found to take up ammonia with the formation of solid salt-like products soluble in liquid ammonia; this is in sharp contrast to the behaviour of C_2H_6, Si_2H_6, or SiH_4. The compounds formed by B_2H_6 and B_5H_9 are quite stable even when heated, and behave as ammonium salts, especially on electrolysis in liquid ammonia; they are quite different in behaviour from the ammonia addition compounds of the boron trialkyls; thus $(CH_3)_3B \leftarrow NH_3$ does not act as a salt, is volatile, low-melting, soluble in benzene, and its conductivity in liquid ammonia is less than 1 per cent. of that of diborane. The other boranes, and the methyl diboranes, combine with ammonia at low temperatures, but the products are less stable.

$B_2H_6+NH_3$

Diborane combines with ammonia at the ordinary temperature with evolution of heat to form a solid of the composition B_2H_6, 2 NH_3 whatever excess of ammonia is used. This substance[60] is an obvious salt: it is white, stable, non-volatile, and water-soluble. It can be recrystallized from liquid ammonia, in which it is so soluble that it deliquesces in gaseous ammonia at less than one atmosphere pressure[48]; it burns if heated in air. At 90° it melts with evolution of hydrogen, and at 200° it forms the triborine $B_3N_3H_6$. The depression of the vapour pressure of liquid ammonia[60-1]

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[59] H. I. Schlesinger, L. Horvitz, and A. B. Burg, ib. 1936, 58, 409.

[60] A. Stock, and E. Pohland, *Ber.* 1925, 58, 657.

[61] Id., ib. 1926, 59, 2215.

indicates a molecular weight little less than that of $B_2H_6, 2\,NH_3$; the conductivity in liquid ammonia,[60, 62] while much larger than that of liquid ammonia itself, is much less than one would expect for a tri-ionic [or indeed for a di-ionic] salt. The products of electrolysis in liquid NH_3 are those to be expected for an ammonium salt; the solid residue after electrolysis has the composition $B_2H_4(NH_2)_2$, and a conductivity in the solvent much less than that of B_2H_6.[60]

The compound is obviously an ammonium salt, and Stock originally suggested the probable formula $(NH_4)_2[H_2\overset{-}{B}{=\!=}\overset{-}{B}H_2]$, in which the anion has a structure like that of ethylene, the double negative charge making the borons behave like carbons. But later Schlesinger and Burg[51] suggested a new formula, that of the mono-ammonium salt of the amino-anion $(NH_4)\cdot[H_3\overset{-}{B}{-\!-}\overset{+}{N}H_2{-\!-}\overset{-}{B}H_3]$, in which the electron complement is normal. Their reasons were: (1) The compound causes less lowering of the vapour pressure of liquid ammonia than would be expected for a tri-ionic salt[60]* and has a smaller conductivity. (2) If its solution in liquid ammonia is treated with sodium at —77° (i.e. just above its m. pt.) only one hydrogen atom is evolved for every two borons, and on evaporation the sodium salt $Na[B_2H_6NH_2]$ is left.[51] This last salt can also be made in another way. If the ether compound $H_3B{\leftarrow}OMe_2$ is treated with sodium in ammonia it gives $Na[H_3B{-\!-}NH_2]$, and if this is treated with more diborane it takes up another BH_3 and forms $Na[H_3\overset{-}{B}{-\!-}\overset{+}{N}H_2{-\!-}\overset{-}{B}H_3]$.[51]

This formulation must be correct. The compound is very readily converted into others which can be shown to contain the B—N—B group: if diborane is passed over it at 80° $H_3B{\leftarrow}NH_2{-\!-}BH_2$ is formed; if it is heated alone, it gives the benzene-like $B_3N_3H_6$. $B_2H_6, 2\,NH_3$ has the stability characteristic of molecules with normal boron atoms, and none of the unsaturation to be expected of the B=B link, a link which is not known to occur in any other molecule.

If $(NH_4)[H_3B\cdot NH_2\cdot BH_3]$ is dissolved in heavy ammonia ND_3 there is an exchange between N—H (not B—H) and N—D, rapid even at —78°.[63] This is an argument against any formula involving $B[H^+]$, but it does not discriminate between the ethane-like and the Bell and Longuet-Higgins structures.

The methyl-diboranes all (including the tetra-methyl) form similar compounds with $2\,NH_3$.[53, 80] The tetramethyl derivative, which must have the formula $(NH_4)\cdot[Me_2\overset{-}{B}H{-\!-}\overset{+}{N}H_2{-\!-}\overset{-}{B}HMe_2]$, is very unstable and decomposes at a low temperature. The rest, which are white crystalline solids at the ordinary temperature, are more stable than the methyl diboranes themselves, and no migration of methyl groups was observed; thus

$$CH_3BH_2{-\!-}BH_3,\ 2\,NH_3$$

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* Indeed the values found do not indicate any dissociation of the compound.

[62] A. Stock, E. Wiberg, H. Martini, and A. Nicklas, *Ber.* 1932, 65, 1711.

[63] A. B. Burg, *J.A.C.S.* 1947, 69, 747.

can be heated to 50° without perceptible decomposition, while the dimethyl compounds at 0° and the tri- and tetra- at −35° slowly evolve hydrogen. This increased stability is common among the anions derived from the boranes, in which the ionic charge completes the octets of the boron atoms.

An interesting analogue of these ammonia compounds is that formed by phosphine.[64] This has the composition B_2H_6, 2 PH_3 (or BH_3,PH_3). With liquid ammonia it gives off half its PH_3 and a compound B_2H_6,PH_3,NH_3 is left. Now all the phosphorus that was present as PH_4 ion must be expelled by the ammonia, so that only half of it can be in this form, and the structure of the compound must be $(PH_4)[H_3\overset{-}{B}—\overset{+}{P}H_2—\overset{-}{B}H_3]$.

Our knowledge of the compounds formed by ammonia with the other volatile hydrides of boron is much less detailed, and though no doubt all or most of them are ammonium salts, any more precise structures are guess-work.

B_4H_{10} *and* NH_3[33]

At −70° they give a salt-like product B_4H_{10}, 4 NH_3, soluble in liquid ammonia; at the ordinary temperature it slowly loses ammonia and hydrogen, probably giving an amino-compound. At 200°, like the ammonia compounds of B_2H_6 and B_5H_9, it is converted into triborine triamine: this is probably the best source for that compound. On electrolysis the compound behaves just like B_2H_6, 2 NH_3; products of the compositions $B_2H_6(NH_2)_2$ up to $B_4H_4(NH_2)_6$ can be obtained.

A probable structure for this compound is

$$(NH_4)_2[H_3\overset{-}{B}—\overset{+}{N}H_2—\overset{-}{B}H_2—\overset{-}{B}H_2—\overset{+}{N}H_2—\overset{-}{B}H_3],$$

in which all the borons and the nitrogens have their full valency octets.

B_5H_9 *and* NH_3[47, 51]

The product has the composition B_5H_9, 4 NH_3, and resembles the others in appearance. It dissolves in water with a slight evolution of hydrogen. B_5H_9 seems to have less affinity for ammonia than B_2H_6; at low pressures the addition of ammonia is quite slow.

B_5H_{11} *and* NH_3[48]

In the reaction hydrogen is given off, and the product seems from its reactions to be identical with that formed by B_5H_9.

$B_{10}H_{14}$ *and* NH_3[65]

At −75° a solid compound $B_{10}H_{14}$, 6 NH_3 is formed, but at the ordinary temperature all the ammonia comes off again. If $B_{10}H_{14}$ is heated with ammonia to 120° hydrogen is evolved, apparently with the formation of amino-compounds.

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[64] E. L. Gamble and P. Gilmont, ib. 1940, 62, 717.

[65] A. Stock and E. Pohland, *Ber.* 1929, 62, 90.

Though its amine is so unstable, $B_{10}H_{14}$ behaves on electrolysis in liquid ammonia like the others, and so seems to form an ammonium salt.

Reactions of the Ammonium Salts with Hydrogen Chloride

The normalized salts, both the ammonium and the alkaline, substitute halogen for hydrogen very easily, either with hydrogen halide or with the halogen itself.

B_2H_6, 2 NH_3 reacts with gaseous hydrogen chloride at −60°,[48] the main product having the composition and presumably the structure of

$$(NH_4)\cdot[H_2BCl—\overset{+}{N}H_2—\overset{-}{B}H_2Cl].$$

B_4H_{10}, 4 NH_3 reacts with hydrogen chloride vigorously at −60°,[33] though B_4H_{10}, like B_2H_6 itself, only reacts very slowly even at the ordinary temperature. The main product has the composition of $(NH_4)_4[B_4Cl_8]$; it is very stable to water; even after 20 hours at 90° it is not completely hydrolysed. The formula should probably be halved: $(NH_4)_2[B_2Cl_4]$ can then be written in the usual form $NH_4[\overset{-}{B}HCl_2—\overset{+}{N}H_2—\overset{-}{B}HCl_2]$.

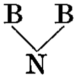
B_5H_9, 4 NH_3 reacts very readily with hydrogen-chloride at the ordinary temperature,[47] and in a few minutes is converted into $(NH_4)_4B_5HCl_4$ with loss of hydrogen; further substitution up to B_5Cl_7 can be effected.

The compound formed by B_5H_{11} with ammonia reacts with hydrogen chloride exactly like that of B_5H_9, which suggests that the two ammonia compounds are identical.

4. B_2NH_7, $H_3\overset{-}{B}—\overset{+}{N}H_2—BH_2$

This compound is made[57] by passing diborane over its ammonia compound $NH_4[H_3B—NH_2—BH_3]$ at +65°. It melts at −66·5° and boils at +76·2°; the Trouton constant is 21·0; the vapour is monomeric. It can be kept unchanged in the cold for days, but after some months it goes over into diborane and a solid $(BH_4N)_x$.

With trimethylamine at −80° it gives B_2NH_7, NMe_3, a white solid which on heating gives some $H_3B\leftarrow NMe_3$. If B_2NH_7 is heated to 200° with ammonia it is converted into triborine triamine; with a solution of sodium in liquid ammonia it forms a sodium salt of the composition B_2NH_7, NH_2Na (perhaps $Na[H_3\overset{-}{B}—\overset{+}{N}H_2—\overset{-}{B}H_2—NH_2]$).

Bauer has shown[66] by electron diffraction that the B_2NH_7 molecule has the group  $\overset{B\quad B}{\diagdown\!\diagup}_{N}$ with the angle 109±4°, and a B—N distance of 1·56±0·03 A (theory 1·58). This gives two possible formulae:

$$\text{(I) } H_3\overset{*}{B}—NH—\overset{*}{B}H_3 \quad\text{and}\quad \text{(II) } H_3\overset{-}{B}—\overset{+}{N}H_2—BH_2.$$

The electron diffraction results are more in favour of (I), but they are not

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[66] S. H. Bauer, *J.A.C.S.* 1938, **60**, 524.

conclusive, and on general, especially chemical, grounds the second structure is far more likely: by sharing all its valency electrons the nitrogen enables the covalent links to have 2 electrons apiece. Thus both the boron atoms are normal, but the second has only a sextet, which explains why the molecule takes up only one NMe_3 for the 2 Bs. This structure also enables us to give a reasonable structure to the product of the action of sodium on the solution in ammonia:

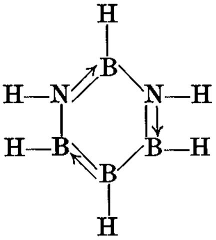
$$H_3\overset{-}{B}—\overset{+}{N}H_2—\overset{-}{B}H_2—\overset{+}{N}Me_3 \rightarrow Na[H_3\overset{-}{B}—\overset{+}{N}H_2—\overset{-}{B}H_2—NH_2]$$

as well as to the amine. (A tautomeric shift of hydrogen atoms in the reactions of these substances is not of course excluded.)

5. *Triborine triamine*, $B_3N_3H_6$

This was first made by Stock and Blix in 1901[67] by the action of ammonia on the complex sulphide B_2S_3,H_2S or HBS_2. It is more conveniently made[61] by heating[55a] B_2H_6, 2 NH_3, or B_4H_{10}, 4 NH_3, or B_5H_9, 4 NH_3 to about 200° for several hours. The yield is not good, but it may be as high as 40 per cent. The formula is supported by analysis, hydrolysis, and vapour-density determination.

$B_3N_3H_6$ is a colourless mobile liquid melting at $-58{\cdot}0°$ and boiling at $+55°$. It is far more stable than any other compound containing a B—H link. It will remain unchanged for months in the absence of water; even at 500° only 27 per cent. is decomposed in 30 minutes, and 81 per cent. in 12 hours. Oxygen has no action on it in the cold unless it is sparked. It dissolves in water to give a solution with a strong reducing power, and this hydrolyses, very slowly in the cold, to hydrogen, boric acid, and ammonia.



The suggestion of Stock[61] that this substance is the analogue of benzene, with 3 B—N pairs replacing the 6 carbon atoms, is supported by all the evidence. The physical properties are very similar to those of benzene:

	B. pt.	*M. pt.*	*Ht. of evapn.*	*Trouton*	*Parachor*
$B_3N_3H_6$	55·0°	—58°	7·03 k.cals.	21·1	207·9
Benzene	80·2°	+6°	7·36 k.cals.	21·4	206·1

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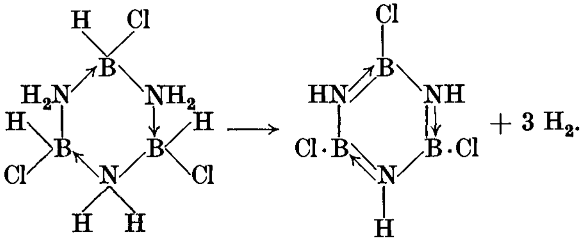
[67] A. Stock and M. Blix, *Ber.* 1901, **34**, 3043.

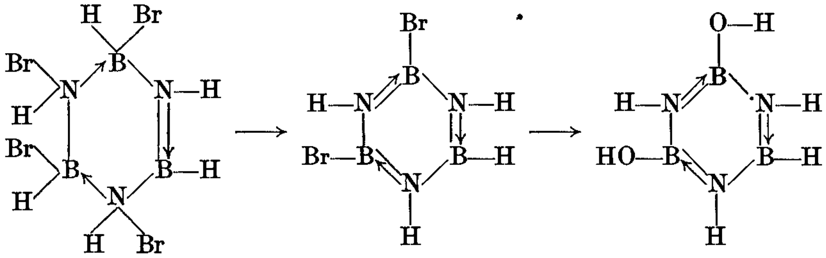
[68] E. Wiberg and A. Bolz, ib. 1940, **73**, 209.

The concordant results on the electron diffraction of Stock and Wierl[69] and Bauer[66] show that the molecule has a plane structure, giving a pattern just like that of benzene, with the B—N distance 1·44±0·02 A (theory for (B—N+B=N)/2 is (1.58+1·36)/2 = 1·47), and the angles 120°. This is supported by the infra-red and the Raman spectra.[45,70-1]

This structure agrees equally well with the chemical behaviour of the compound. The presence of B—H and N—H groups is proved by the fact that two kinds of methyl derivatives are known: one (from methylamine and diborane) hydrolysing to boric acid, methylamine, and hydrogen, and the other (from methyl-diboranes such as $(CH_3)_2B_2H_4$ and ammonia) to ammonia, hydrogen, and methyl boric acid $CH_3 \cdot B(OH)_2$ (see further, p. 359). The remarkable stability of $B_3N_3H_6$ is quite incompatible with the presence of B—B links, and indeed strongly suggests resonance; the formation from $H_3B—NH_2—BH_2$ (above, p. 356) supports the B—N—B grouping. The threefold symmetry of the structure is exactly reproduced in its reactions. It readily takes up[33,68] in the cold and in absence of a catalyst three molecules of HCl, HBr, H_2O, or CH_3OH to give a symmetrically trisubstituted 'inorganic cyclohexane', which at 50-100° loses three molecules of hydrogen to form the corresponding substituted 'inorganic benzene':



At 0° C. $B_3N_3H_6$ takes up 2 molecules of bromine; the product at 60° loses 2 HBr to give 'inorganic* meta dibromobenzene', readily hydrolysed to 'inorganic resorcinol':



The methyl derivatives of $B_3N_3H_6$ have been examined by Schlesinger and Burg.[53,72] Just as the ammonium salt of diborane when heated gives

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* Wiberg[68] suggested that $B_3N_3H_6$ should be called 'inorganic benzene' or 'borazol'.

[69] A. Stock and R. Wierl, *Z. anorg. Chem.* 1931, **203**, 228.

[70] R. M. Badger, *J. Chem. Phys.* 1934, **2**, 128.

[71] Id., ib. 1935, **3**, 710.

[72] H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *J.A.C.S.* 1938, **60**, 1296.

triborine triamine, so its methyl derivatives give the methyl triborines[53]; the mono-, di-, and tri-methyl compounds were all prepared, more than one of them from each methylated diborane, since there is considerable transference of methyl groups. When the diborane contains a $(CH_3)_2BH$ group, this is converted into the simple amine $(CH_3)_2B—NH_2$, the only product when ammonia is heated with tetramethyl diborane. That the methyl groups in these products are attached to boron and not to nitrogen is shown (1) by their method of formation, and (2) by the volume of hydrogen they produce on hydrolysis, which is always that required by the equation

$$B—H + H_2O = B—OH + H_2.$$

The N-methyl triborines and some of the mixed B,N-methyl derivatives were also prepared[72]; the mono-, di-, and tri-N-methyl compounds were got by heating diborane with ammonia and methylamine in the right proportions, while from the mono-N-methyl triborine and boron trimethyl the mono-, di-, and tri-B-methyl mono-N-methyl compounds were made. The compounds with the methyls attached to boron are all monomeric in the vapour, and so are the N-methyl compounds at higher temperatures, but at lower the latter tend to polymerize: thus the mono-N-methyl derivative is monomeric at 101°, but at the ordinary temperature its vapour density is 35 per cent. above the calculated value.

In the following table the boiling-points, Trouton constants, and melting-points of these methyl triborine triamines are given; the boiling-points of the corresponding benzene derivatives (or their mean values where the position of the methyls on the triborine ring is uncertain) are added, to point out the surprising fact that the boron compounds all have the lower boiling-points, and the more so, the more methyl groups they contain.

Benzene analogue					
B. pts.	*Diff.*	*Compound*	*B. pt.*	*Trouton*	*M. pt.*
80°	−27°	$B_3N_3H_6$	+53°	..	−58°
111°	−24°	Mono-B-methyl	+87°	23	−59°
139°	−32°	Di-B-methyl	107°	24	−48°
165°	−36°	Tri-B-methyl	129°	23	−31·5°
111°	−27°	Mono-N-methyl	84°	22·3	
139°	−31°	Di-N-methyl	108°	21·9	
165°	−31°	Tri-N-methyl	134°	22·7	
141°	−17°	Mono-N-mono-B-methyl	124°	20·2	
170°	−31°	Mono-N-di-B-methyl	139°	21·6	
198°	−40°	Mono-N-tri-B-methyl	158°	24·2	

Derivatives of the tri-N-phenyl compound are also known; Jones and Kinney[78] have prepared the tri-B-chloro- and tri-B-hydroxy-compounds.

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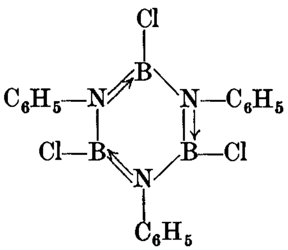
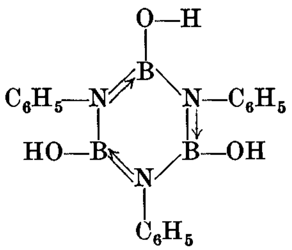
[78] R. G. Jones and C. R. Kinney, ib. 1939, 61, 1378.

The first of these is produced in 85 per cent. yield when aniline and boron trichloride, or the co-ordination compound of the two, is warmed in benzene up to the boiling-point of the solvent, the reaction being





$$9\ \Phi\cdot NH_2 + 3\ BCl_3 = (\Phi\cdot N)_3B_3Cl_3 + 6\ \Phi\cdot NH_2\cdot HCl.$$

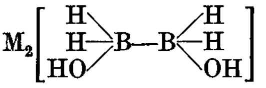
The product melts at 255-260° with decomposition. It is monomeric by the rise of the boiling-point in benzene and in chloroform. 100 g. of benzene will dissolve 2 g. at the ordinary temperature and about 40 g. at 80°. See further, reference[73a].

On standing in water for 3 hours this is hydrolysed to the corresponding tri-hydroxy-compound (the second formula above). Its molecular weight in boiling ethyl alcohol agrees at first with the trimeric formula given above, but it rapidly falls to half this value and stays there; the nature of the change does not seem to be understood. Neither of these compounds forms a hydrate with water, as the compounds do which have hydrogen or methyl groups attached to the nitrogen.

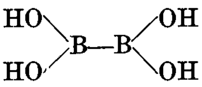
OXYGEN COMPOUNDS

The boron hydrides form far fewer compounds with oxygen than with nitrogen. They may be divided into:

1. Co-ordination compounds with the ethers, as $H_3B \leftarrow O(CH_3)_2$.
2. The intermediate products of the hydrolysis of the borane derivatives. Of these at least two kinds have been identified, the hypoborates



and the sub-boric acid



with its salts, esters, and acid chloride. These last are conveniently described here, though they are not hydrides. Excepting certain metallic borides (see pp. 337, 367), they are the only known B—B compounds with no hydrogen attached to the boron.

[73a] C. R. Kinney and M. J. Kolbezen, *J.A.C.S.* 1942, **64**, 1584.

1. *Addition Compounds of Ethers*

The oxygen of an ether molecule can co-ordinate with a trivalent boron atom, and (as we have seen) can split up the diborane molecule in order to do so. In particular methyl ether reacts readily but reversibly with diborane thus[31]:

$$2\,(CH_3)_2O + H_3B—BH_3 \longrightarrow 2\,(CH_3)_2O{\rightarrow}BH_3.$$

The product, a white solid, is rather unstable; the dissociation tension of methyl ether at $-80°$ is nearly half that of methyl ether itself.

In general the affinity of the ethereal oxygen for trivalent boron is less than that of the nitrogen in trimethylamine; this is why ether was used[54] in the preparation of symmetrical dimethyl diborane (p. 349).

2. *Boron Alkyl-oxides*

These are of the type $H\cdot B(OR)_2$. If diborane and methyl alcohol are condensed with liquid air[74] and allowed to warm up, they react on melting with effervescence:

$$B_2H_6 + 4\,CH_3OH = 2\,H\cdot B(OCH_3)_2 + 4\,H_2.$$

It is very unusual for the B—B links to be broken (except in co-ordination) before all the B—H links have been destroyed. These compounds can also be made[75] by the action of diborane on aldehydes, ketones, and esters, which are thereby reduced to the alcoholic state:

$$B_2H_6 + 4\,Me_2CO = 2\,H\cdot B(O\cdot CH(CH_3)_2)_2$$

$$B_2H_6 + 2\,CH_3\cdot CO\cdot OEt = 2\,HB(O\cdot C_2H_5)_2.$$

They are volatile liquids, for example:

$H\cdot B(OCH_3)_2$	b. pt. + 25·9°: m. pt. −130·6
$H\cdot B(OC_2H_5)_2$	v.p. 37·5 mm./0°
$H\cdot B(OCHMe_2)_2$	„ 10 mm./0°.

They are monomeric in the vapour; they are unstable and go over readily but reversibly[72] to a mixture of diborane and the alkyl borate $B(OAlk)_3$. They are not spontaneously inflammable, but are at once hydrolysed by water to the alcohol, hydrogen, and boric acid.

3. *Hypoborates and Sub-borates*

All the borane derivatives can be hydrolysed by water or alkali with the ultimate production of boric acid $B(OH)_3$ (or alkyl boric acids); in this reaction at least two of the intermediate stages have been identified, and the products isolated. The original compounds contain two sensitive links B—B and B—H. It seems clear[80, 74] that the first change is the conversion of a B—H into a B—OH, and that when all the hydrogen has been

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[74] A. B. Burg and H. I. Schlesinger, ib. 1933, **55**, 4020.

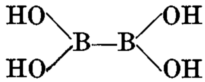
[75] H. C. Brown, H. I. Schlesinger, and A. B. Burg, ib. 1939, **61**, 673.

removed from the boron in this way the separation of the boron atoms, and the formation of boric acid, begins.

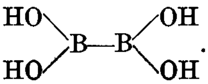
If B_4H_{10} or B_2H_6 is treated with concentrated potassium hydroxide in the cold, and the solution evaporated *in vacuo* at 0°, a solid salt separates, of the composition $KOBH_3$, which is known as a hypoborate; with B_4H_{10} the reaction is nearly quantitative. The product is very stable to heat; it begins to lose water at 100°, but retains much of its character up to 400–500°, where it gives off hydrogen and in a vacuum potassium distils over.[76] It is unaffected by dry air; it is hygroscopic, but it does not decompose in moist air unless it is heated; in water it gives an alkaline solution, which decomposes very slowly with evolution of hydrogen and formation of boric acid; if it is acidified (even with acetic acid) this change occurs at once. The aqueous solution has strong reducing powers[80.49,76]; it converts the salts of silver, mercury, arsenic, antimony, and bismuth into their metals; it reduces a cupric salt to the hydride at once, whereas a hypophosphite only does so slowly. A particularly characteristic reaction is that a nickel salt gives a black precipitate of the boride Ni_2B (the only known case of the precipitation of a boride from water) which is visible even in very dilute solution.

The composition of the potassium salt is $KOBH_3$. The great rarity of compounds with a single boron atom attached to hydrogen suggested that the formula should be doubled and written $K_2[\bar{B}H_2(OH)—\bar{B}H_2(OH)]$; this doubling is supported by the diamagnetism of the salt (Klemm and Klemm).[50] In this structure the boron atoms have their full octets as in the borofluorides $M[BF_4]$ or as in the salt $K_2[H_3B—BH_3]$, which the hypoborates resemble in their stability to oxygen, to heat, to water, and to alkali, and also in their reducing power. There seems no doubt that this glycol-like double formula is correct.

Sub-boric Acid



A different product is obtained by the hydrolysis of the subchloride B_2Cl_4.[77] This halide dissolves in water with no evolution of hydrogen to speak of, even on warming, but with separation of hydrogen chloride; the solution has a strong reducing power, but not so strong as that of a hypoborate; it reduces a silver salt to the metal, but a mercuric salt only to the mercurous, and a cupric salt to copper and not the hydride; also it does not give the characteristic reaction with nickel. From its method of formation Stock suggests the structure



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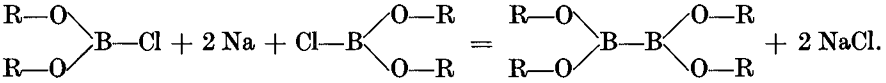
[76] A. Stock and E. Kuss, *Ber.* 1914, 47, 810.

[77] A. Stock, A. Brandt, and H. Fischer, ib. 1925, 58, 643.

This has been completely confirmed by Wiberg and Ruschmann.[78] They call the acid, of which boron subchloride may be taken to be the acid chloride, 'Unterborsäure', which may be translated sub-boric acid, since the name hypoboric is preoccupied for $H_2[B_2H_2(OH)_4]$.

They made the esters of this acid by a reaction which proves their structure, a 'Wurtz synthesis' from sodium and the boric ester halides $(RO)_2B\cdot Cl$. The reaction goes in a few days in the cold:

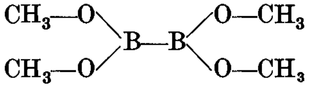


The free acid, a white solid, is made by the hydrolysis of the ester with water *in vacuo*, which is complete in a few hours at the ordinary temperature; it is accompanied by some formation of boric acid and hydrogen.

An aqueous solution of $B_2(OH)_4$ has strong reducing properties; it reduces permanganate and precipitates metallic silver from silver nitrate; but this power disappears (along with the peculiar unpleasant smell of the acid and its esters) after standing for 2 hours in the cold (longer in alkaline or acid solution), owing to atmospheric oxidation:

$$B_2(OH)_4 + H_2O + O = 2\ B(OH)_3.$$

The methyl ester



(from sodium and $(CH_3\cdot O)_2B\cdot Cl$) is a colourless liquid, easily decomposed. It melts at −24°; its extrapolated boiling-point is +93° and its Trouton constant 23·2; it is monomeric in the vapour. On standing in the cold, especially if it is not quite dry, its vapour pressure slowly rises, while a black deposit of finely divided and very active boron is formed:

$$3\ B_2(OCH_3)_4 = 4\ B(OCH_3)_3 + 2\ B.$$

The same occurs if it stands in pure dry oxygen, without any oxidation. Boron subchloride B_2Cl_4 seems to undergo a similar change.[77]

The ethyl ester $B_2(OC_2H_5)_4$ is similar (vapour pressures at 18°; methyl ester 35 mm., ethyl ester 4 mm.).

Halogen Derivatives of the Boranes

These are made by the action of the halogen, or the halogen hydride, or the boron trihalide, on the borane or its alkaline or ammonium salt, or by submitting a mixture of boron trihalide and hydrogen to the electric discharge.

They are unstable, and little is known of any but the diborane

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[78] E. Wiberg and W. Ruschmann, ib. 1937, 70, 1393.

monohalides. They undergo with great readiness two reversible reactions[27, 46, 79-80]:

$$\text{(I)}\ B_2H_5Cl + H_2 = B_2H_6 + HCl$$

$$\text{(II)}\ 6\,B_2H_5Cl = 5\,B_2H_6 + 2\,BCl_3.$$

In the latter,[34] the equilibrium is far over on the right-hand side. It is on reaction (I) that Schlesinger and Burg's method of preparing diborane depends, the chief primary product being B_2H_5Cl.

Chlorine and bromine react readily with diborane. Chlorine, which acts violently, gives no product except boron trichloride, even when it is in defect, but with bromine, which reacts only slowly even at 100°, the main products are a mixture of the monobromide B_2H_5Br and boron tribromide; the di- and tribromides were shown to be formed, but could not be isolated. With $B_{10}H_{14}$ bromine acts only very slowly. Iodine does not act on diborane.

With the hydrogen halides the activities are in the reverse order, hydrogen chloride scarcely acts on diborane at all; hydrogen bromide will not react in the cold, but at 90° in presence of aluminium bromide the reaction goes three-quarters of the way in 2 hours, the products being mainly boron tribromide and B_2H_5Br,[46] which goes over to $B_2H_6+BBr_3$ in a few days at the ordinary temperature. Hydrogen iodide reacts still more easily; the reaction proceeds at 50° without any catalyst.[43] Eighty per cent. of the B_2H_5I went over to $B_2H_6+BI_3$ in three weeks at the ordinary temperature. The melting- and boiling-points of these compounds are given below, the melting-point of the chloride being taken from Burg.[81]

Compound	*B. pt.*	*M. pt.*
B_2H_5Cl	−92°	−142°
B_2H_5Br	(160 mm./0°)	−104°
B_2H_5I	(60 mm./0°)	−110°

Both the ammonium and the alkaline salts of the boranes, especially of diborane, are readily halogenated by the halogen hydrides, and the products are much more stable than the simple halides, possibly owing to the negative charge, but also no doubt owing to their having the full complement of electrons. Little is known of the products.

Borohydrides —BH_4

The discovery of the first of these remarkable compounds, the volatile AlB_3H_{12}, was announced by Schlesinger, Sanderson, and Burg in 1939[82]; detailed accounts of this[83] and the beryllium[84] and lithium[85] compounds

[79] A. Stock, E. Kuss, and O. Priess, *Ber.* 1914, **47**, 3115-49.

[80] E. Wiberg, ib. 1936, **69**, 2816.

[81] A. B. Burg, *J.A.C.S.* 1934, **56**, 499.

[82] H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, ib. 1939, **61**, 536.

[83] Id., ib. 1940, **62**, 3421.

[84] A. B. Burg and H. I. Schlesinger, ib. 3425.

[85] H. I. Schlesinger and H. C. Brown, ib. 3429.

[86] J. Y. Beach and S. H. Bauer, ib. 3440.

[87] H. I. Schlesinger, H. C. Brown, and G. W. Schaeffer, ib. 1943, **65**, 1786.

followed. Recently it has been shown[87] that a similar derivative of Gallium can be prepared. The structure of aluminium borohydride was determined by means of the electron diffraction by Beach and Bauer.[86,90]

The compounds can be made by the action of the metallic alkyl on diborane, the aluminium and beryllium methyls reacting at 80–90°, and lithium ethyl and gallium trimethyl at the ordinary temperature:

$$\begin{aligned} AlMe_3 + 2\,B_2H_6 &= AlB_3H_{12} + BMe_3 \\ 3\,BeMe_2 + 4\,B_2H_6 &= 3\,BeB_2H_8 + 2\,BMe_2 \\ 3\,LiEt + 2\,B_2H_6 &= 3\,LiBH_4 + BEt_3. \end{aligned}$$

The compositions of the products (the gallium compound is discussed later) show that they must contain the monovalent BH_4 group, and should be written $Al(BH_4)_3$, $Be(BH_4)_2$, and $LiBH_4$, whatever the link between the metal and the boron may be. This view is completely confirmed by the results of the electron diffraction with the aluminium compound; the discoverers have given these substances the convenient name of borohydrides.

The melting-point, boiling-point, and vapour pressure are as follows; the values for diborane are added for comparison.

Property	$H_3B—BH_3$	$Al(BH_4)_3$	$Be(BH_4)_2$	$LiBH_4$	$(CH_3)_2Ga\cdot BH_4$
M. pt	−165·5°	−64·5°	+123°	+275°	+1·5°
B. pt.	−92·5°	+44·5°	+91·3°	subl. 275° decp.	92°
V.p. mm./0°	15,000	119	0·5	$< 10^{-4}$	*ca.* 1 mm.

Aluminium Borohydride, $Al(BH_4)_3$

It is colourless, spontaneously inflammable in air, and hydrolysed by cold water to hydrogen, boric acid $B(OH)_3$ and aluminium hydroxide $Al(OH)_3$. It reacts with lithium ethyl in benzene solution to give $LiBH_4$. Davidson and Brown[91] have tried in vain to make the methyl derivative of this, $Al(BMe_4)_3$; they showed by the lowering of the vapour pressure that Al_2Me_6 in dilute solution in BMe_3 was still dimeric. It forms 1:1 addition compounds with dimethyl ether and with trimethylamine, in which no doubt the aluminium acts as the acceptor. The first of these, $(CH_3)_2O{\rightarrow}Al(BH_4)_3$, is formed at −80°; its vapour pressure is 0·5 mm. at 67°, and it slowly decomposes at +50° and above. The ammine $(CH_3)_3N{\rightarrow}Al(BH_4)_3$ melts at +79°: its vapour pressure is very small at 250°, but it can be sublimed *in vacuo*.

Gallium Borohydride

Only a preliminary note on this has yet been published.[87] Gallium trimethyl reacts with diborane slowly at the ordinary temperature

$$GaMe_3 + 3\,B_2H_6 = Ga + 3\,MeB_2H_5 + 3/2\,H_2.$$

[88] A. M. Soldate, ib. 1947, 69, 987.

[89] P. M. Harris and E. B. Meibohm, ib. 1231.

[90] G. Silbiger and S. H. Bauer, ib. 1946, 68, 312.

[91] N. Davidson and H. C. Brown, ib. 1942, 64, 316.

No $Ga(BH_4)_3$ could be isolated. At −45° the product of this reaction is practically pure dimethyl gallium borohydride:

$$2\,GaMe_3 + 3\,B_2H_6 = 2\,Me_2GaBH_4 + 2\,MeB_2H_5.$$

It is colourless liquid, which has a monomeric vapour, an extrapolated boiling-point of 92°, giving a Trouton constant of 23·5. It is stable at −80°, but slowly decomposes even at room temperature.

Beryllium Borohydride, $Be(BH_4)_2$[84]

Diborane and beryllium dimethyl react at 95° and give a succession of products of which one, a sublimable solid, is probably $CH_3\cdot Be\cdot BH_4$, and the last is the borohydride $Be(BH_4)_2$. This resembles the aluminium compound in many ways; it is spontaneously inflammable; it reacts violently with water; and it forms a relatively stable addition compound with trimethylamine. But it is much less volatile than aluminium borohydride and melts at least 180° higher; it sublimes under one atmosphere pressure at 91·3° and melts under pressure at 123°.

The trimethylamine compound $Me_3N\rightarrow Be(BH_4)_2$ is spontaneously inflammable in air; it melts at +35° and its boiling-point extrapolated is 260°; it is stable enough to give normal vapour densities at 65–140°. It reacts at 100° with more trimethylamine, the molecule breaking up to give $H_3B\leftarrow NMe_3$ and a compound of the composition $Me_3N\cdot Be\cdot BH_5$, a white solid which loses trimethylamine easily and should probably be written $(NMe_3H)\cdot[Be—BH_4]$.

Lithium Borohydride, $LiBH_4$[85]

Lithium ethyl reacts very readily at the ordinary temperature either with diborane or with aluminium borohydride in benzene to give lithium borohydride, $LiBH_4$, a white solid, stable up to 240° and above, where its vapour pressure is less than 10^{-4} mm.; at 275–280° it melts to a colourless liquid which evolves hydrogen slowly. With methyl alcohol down to −100° it gives the reaction

$$LiBH_4 + 4\,CH_3OH = LiOCH_3 + B(OCH_3)_3 + 4\,H_2.$$

Like the aluminium and beryllium compounds it reacts readily with hydrogen chloride at −80° or above to form lithium chloride, diborane, and hydrogen. But it differs markedly from these substances in its stability and its non-volatility. The aluminium and beryllium compounds are spontaneously inflammable in air: lithium borohydride is not affected by dry air at all. The aluminium and beryllium compounds boil below 100°, whereas the lithium compound has no measurable vapour pressure up to its melting-point at nearly 300°, where it begins to decompose. Trimethylamine, which removes BH_3 groups easily from the aluminium compound, and rather less easily from the beryllium compound, has no action on $LiBH_4$.

The sodium compound $NaBH_4$ has recently been obtained; it is stable up to 400°, and X-rays show it to have a face-centred cubic lattice of

Na and BH_4 ions. The distances (Na··B 3·07, B··B 4·35 A) are large enough to let the BH_4 ions rotate.[88] Preliminary measurements[89] show that $LiBH_4$ has a similar structure.

Structures of the Borohydrides

Up to a certain point the structures of these borohydrides are clear, though very unusual. The aluminium compound, since it boils at 44·5°, must be covalent, and this conclusion is supported by the results of electron diffraction,[90] which show that the 3 valencies of the aluminium lie in a plane with angles of 120°, like those of boron in the trimethyl. Each boron atom is attached to 4 hydrogen atoms and 1 aluminium, these 5 atoms being at the angular points of a trigonal bipyramid (the invariable structure of a 5-covalent atom) with the aluminium at a pole: the distances are Al—B 2·14±0·02: B—H 1·27±0·04 (theory 2·14, 1·18). The large B—H distance (the same as in diborane) and the normal Al—B suggest that the electron deficiency is confined to the B-H links. The most interesting point is the bearing on the covalency rule; the boron has a complete and fully shared octet, but this maintains 5 covalencies, so that the covalency rule may limit the atoms of the first period to a valency octet, but it does not limit their covalency to 4.

The structure of aluminium borohydride is thus fairly clear. The very remarkable fall in volatility, and the accompanying rise in stability, when we go from aluminium to beryllium, and from beryllium to lithium, have still to be explained. The change in volatility is very like that of the alkyls; the boiling-points of the corresponding methyls are $Al(CH_3)_3$ 130°; $Be(CH_3)_2$ *ca.* 200°; $LiCH_3$ non-volatile. The differences may perhaps be described by saying that the aluminium compound is covalent, while the lithium is ionized (this is now established by the X-ray results), and the beryllium occupies (through resonance) an intermediate position. Beryllium borohydride has been shown by the electron diffraction of the vapour[90] to have a structure like that of the aluminium compound. The group H—B—Be—B—H is linear, with Be—B 1·66 and B—H 1·15 A; the three other hydrogens form a ring round the boron at 1·19 A; the Be—B—H angle is 85±5° (theory Be—B 1·78, B—H 1·18); these results are not compatible with Pitzer's theory for diborane. It might also be said that the effect is due to a rapid increase in association; our answer must depend on the view that we take of the alkaline alkyls and similar compounds. One point in favour of the view that $LiBH_4$ is ionized is that this would account for the great increase in stability, since we know that molecules containing the B—H group are much more stable when the boron has its octet complete, as in $K_2[B_2H_6]$.

METALLIC BORIDES

Boron has a peculiar behaviour in its binary compounds with metals; it is in some ways an electropositive element, and its metallic compounds are usually not ionized. It further has a strong tendency (also possessed in a rather different sense by carbon) to form links with itself, both long chains and two- and three-dimensional structures, into which the atoms of the other element are in some way fitted. Hence the binary metallic borides seldom have the simple compositions to be expected from the valencies, and usually contain more, and sometimes much more, boron atoms than these valencies require. Many metals are very reluctant to combine with boron; the alkali metals will not do so directly: no borides at all seem to be formed by copper, silver, zinc, mercury, thallium, tin, and lead. The following list of binary borides is given by Ephraim[92]:

Cu_3B_2	Mg_3O_2	AlB_2	CB_6	CrB	MnB	Fe_2B
	CaB_8	AlB_{12}	SiB_3	Cr_3B_2	MnB_2	Co_2B
	SrB_6	LaB_6	SiB_6	Mo_3B_4		CoB
	BaB_6	CeB_8	ThB_6	WB_2		CoB_2
		PrB_6				Ni_2B
		NdB_6				NiB_2
		ErB_6				

The characteristic reaction of the hypoborates of precipitating black Ni_2B from a solution of a nickel salt (above, p. 362) is the only known case of the precipitation of a boride from an aqueous solution.

The types of boride of frequent occurrence are MB_2 (M = Al, W, Mn, Co, Ni) and MB_6 (M = Ca, Sr, Ba, La, Ce, Pr, Nd, Er, C, Th). The structure of AlB_2 has been determined by X-ray analysis.[93-4] The B atoms form a graphitic lattice (B—B 1·73 A: theory B—B 1·76; B=B 1·52) with the aluminium atoms inserted between the sheets, as alkali metal atoms can be between those of graphite itself in compounds like KC_6 and KC_{16}. In CaB_6[95] (and in the MB_6 borides generally) the boron atoms form a three-dimensional lattice in which every boron has 5 equidistant boron neighbours at 1·71 A and the calcium atoms are arranged in the interstices.

CARBIDES, AND ALKYL AND ARYL COMPOUNDS

Boron Carbide

Various carbides of boron have been described, hard infusible substances of compositions from BC to B_6C, made from the elements, or by heating boron trioxide with carbon in an electric furnace. The most certain is B_4C (or $B_{12}C_3$), of which the crystal structure has been examined with concordant results by Shdanov and Sevasianov[96] and by Clark and Hoard.[97] It has a continuous network of boron atoms, which accounts for its great hardness and perceptible electric conductivity; there is room in the network for more atoms, and much commercial boron

[92] F. Ephraim, *Anorg. Chemie*, ed. 5, 1934, p. 751.

[93] W. Hofmann and W. Jänicke, *Naturwiss.* 1935, **23**, 851.

[94] L. Pauling, *Chemical Bond*, 1939, p. 400.

[95] L. Pauling and S. Weinbaum, *Z. Krist.* 1934, **87**, 181.

[96] G. Shdanov and N. Sevastianov, *C.R. Acad. Sci. U.R.S.S.* 1941, **32**, 432; *J. Phys. Chem. Russ.* 1943, **17**, 326.

[97] H. K. Clark and J. L. Hoard, *J.A.C.S.* 1943, **65**, 2115.

carbide contains more boron than the formula requires, being a solid solution of boron in B_4C. In the crystal units 3 carbon atoms form a linear chain, with 12 boron atoms at the points of a nearly regular ikosahedron, and each boron bonded to 5 others practically equidistant from it. The distances, with others for comparison,[98] are:

C—C in B_4C 1·39; normal C—C 1·54; C═C 1·33; C—C aromatic 1·39.
B—B in B_4C 1·74; in CaB_6 1·72; AlB_2 1·73; FeB 1·77; B_2H_6 1·86; B_4H_{10} 1·84; B_5H_{11} 1·81; B_5H_9 1·76.
B—C in B_4C 1·64; in BMe_3 1·56; $H_3B\cdot CO$ 1·57; $(BOCH_3)_3$ 1·57.
Mean = $\frac{1}{2}$ (1·54+1·72 to 1·80) = 1·63 to 1·67.
(For the other normal values see Introd., p. xxix.)

They suggest possible resonance formulae, but these do not take us very far. The crystal must contain C═C═C or C—C≡C.

The alkyl and aryl compounds of boron are numerous. Some have already been described among the boron hydrides. There are also many in which the covalent linkages are di-electronic, and the boron atoms are not united to other boron atoms.

They may be divided into these classes:

1. Trialkyls and triaryls.
2. Dialkyl and diaryl boric acids R_2BOH and their derivatives.
3. Monoalkyl and monoaryl boric acids $R\cdot B(OH)_2$ and their derivatives.
4. Mixed alkyl or aryl boron halides.
5. Alkali metal addition products of the triaryl borons.

The ammines, such as $H_3N\rightarrow B(CH_3)_3$, and the complex salts $M[BR_3X]$ will be discussed among the boron complexes (p. 401).

1. *Boron Trialkyls and Triaryls*

The trialkyls were discovered by Frankland and Duppa[99,100] in 1860, being made by the action of zinc alkyl on boron trichloride[101] or ethyl borate. A better way[102] is to treat boron trifluoride with the Grignard reagent. With excess of the trifluoride the mono- and dialkyl fluorides can be made, but no mixed trialkyl compounds have been prepared.[103] Recently certain of the trialkyls, especially tri-*n*-butyl boron, have been examined in detail by Johnson and his colleagues.[104]

The boiling- and melting-points of some of the trialkyls are given below.

Boiling-points and melting-points[101.103] *of* BR_3

R =	CH_3	C_2H_5	*n*—Pr	*n*—Bu	*i*—Bu	*i*—Am.
B. pt.	—20·2°	+95°	156°	109°/20 mm.	188°	119°/14 mm.
M. pt.	—161·5°	—92·5°	—56°	. .	. .	. .

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[98] S. H. Bauer and J. Y. Beach, ib. 1941, **63**, 1402.

[99] E. Frankland and D. F. Duppa, *Ann.* 1860, **115**, 319.

[100] E. Frankland, ib. 1862, **124**, 129.

[101] A. Stock and F. Zeidler, *Ber.* 1921, **54**, 531.

[102] E. Krause and R. Nitsche, ib. 2784.

[103] A. Michaelis and P. Becker, ib. 1880, **13**, 58.

[104] J. R. Johnson, H. A. Snyder, and M. G. van Campen, *J.A.C.S.* 1938, **60**, 115.

Boron trimethyl $B(CH_3)_3$ has a very sharp smell; its vapour density is exactly monomeric from −25° to +100°. Electron diffraction shows that the $B(CH_3)_3$ molecule in the vapour is planar and symmetrical, with angles of 120°.[105] It is spontaneously inflammable in air or chlorine, but is not acted on by water or iodine. It forms an ammine with ammonia, but does not combined with phosphine.

Boron triethyl is very similar and likewise spontaneously inflammable. At any temperature above its boiling-point it decomposes very slowly (some 4 per cent. in 60 hours at 100°), giving ethane and hydrogen. It is converted by slow oxidation into the alkylates $Et_2B\text{-}O\text{-}Et$ and $Et\text{-}B(O\text{-}Et)_2$.[106]

The normal butyl compound $B(n\text{-}Bu)_3$ is a colourless liquid which boils at 108–110° under 20 mm. It is rapidly oxidized by air, and catches fire if it is poured on cloth.

In the aromatic series Michaelis and his colleagues[102, 107-9] obtained the mixed aryl boron halides $ArBX_2$ and Ar_2BX by the action of mercury diaryls on boron trichloride or tribromide. The triaryls were made (like the trialkyls) by Krause and his colleagues from the Grignard reagents and boron trifluoride.[110-11] The boiling-points and melting-points of some of these compounds are as follows (refs. phenyl[110]: rest[112]).

	$B(C_6H_5)_3$	$B(p\text{-}tol)_3$	$B(xyl)_3$	$B(a\text{-}Nph)_3$	$B(Bz)_3$	$B(Hex)_3$
B. pt.°/mm.	203/15	233/12	..	..	..	194/15
M. pt.	142°	175°	147°	203°	47°	99°

Boron triphenyl[110, 112] forms large colourless crystals, soluble in benzene and in ether; alcohol at once attacks it to give the ester. The trialkyls and triaryls[113] are all, so far as is known, monomeric in the vapour and in solution.

The reactions of the trialkyls and the triaryls, as J. R. Johnson has pointed out, afford a rare example of atoms with a valency sextet. These reactions may be considered under the various reagents.

Water. This has no action on the trialkyls or the triaryls, which is in striking contrast to the behaviour of the beryllium and the aluminium alkyls and aryls.

Alcohol, on the other hand, acts on boron triphenyl and converts it into an ester.

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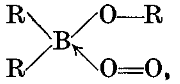
[105] H. A. Lévy and L. O. Brockway, *J.A.C.S.* 1937, **59**, 2085.
[106] E. Frankland, *J.C.S.* 1862, **15**, 363.
[107] A. Michaelis and P. Becker, *Ber.* 1882, **15**, 180.
[108] A. Michaelis, ib. 1889, **22**, 241.
[109] A. Michaelis, M. Behrens, and W. Geisler, ib. 1894, **27**, 244, 258.
[110] E. Krause and R. Nitsche, ib. 1922, **55**, 1261.
[111] E. Krause, ib. 1924, **57**, 216.
[112] E. Krause and H. Polack, ib. 1926, **59**, 777.
[113] E. Krause and P. Dittmar, ib. 1930, **63**, 2347.

*Oxygen.** All these compounds are readily oxidized by atmospheric air; the lighter, like boron trimethyl and triethyl, are spontaneously inflammable, while boron tributyl catches fire if it is poured on a cloth. The aryl compounds are not spontaneously inflammable, but they oxidize in the air very readily, the tri-α-naphthyl compound far less easily than the rest,[116] perhaps for steric reasons. On the other hand, the tribenzyl is more sensitive to oxidation than the triaryls proper (it gives boron trioxide and dibenzyl), and the tricyclohexyl compound still more so.

It is very remarkable that these compounds are more affected by oxygen when dry than when moist. Thus[114] with dry oxygen boron tributyl takes up 1 molecule to give $Bu—B(O—Bu)_2$ and nothing else. In presence of water the reaction goes just half-way: half a molecule of oxygen is taken up for every boron atom

$$2\,B(Bu)_3 + O_2 = 2\,Bu_2B—O—Bu.$$

A 90 per cent. yield of this ester was obtained. The mechanism of this oxidation is clear up to a point. We may assume that the first stage is the production of the dialkyl-mono-ester $R_2B—O—R$. Then with dry oxygen this is oxidized further to $R \cdot B(OR)_2$, and it is this step which is inhibited by water. In the same way it is found that the mono-alkyl boric acid $Alk \cdot B(OH)_2$ is oxidized to boric acid $B(OH)_3$ by dry oxygen but not by wet. Presumably the condition of the oxidation is the production of another co-ordination compound



and if water is present it co-ordinates itself with the boron and prevents the oxygen from joining up.

With *hydrogen peroxide*, *benzoyl peroxide*, or *perbenzoic acid* the reaction is very energetic and goes the whole way, giving butyl alcohol and boric acid; with hydrogen peroxide this reaction is rapid and quantitative, and affords a good method for estimating boron in organic compounds.

Hydrogen chloride and hydrogen bromide. In hot concentrated aqueous solution these acids react readily with boron tributyl, but only one alkyl is displaced (as with dry oxygen); the product is dibutyl boric acid $Bu_2B—OH$, which easily loses water to form the oxide (anhydride) $Bu_2B—O—BBu_2$. Anhydrous hydrogen bromide reacts readily with boron tributyl at 55–60°, giving a quantitative yield of dibutyl boron bromide, together with one molecular proportion of butane. The stopping of the reaction may be due to an impossibility of the (anyhow very weak) co-ordination with bromine occurring between the boron in $Bu_2B \cdot Br$ and a further HBr (see later, p. 397).

* For a detailed account of the action of oxidizing agents on boron tributyl see Johnson and van Kempen,[114] Bamford and Newitt.[115]

[114] J. R. Johnson and M. G. van Campen, *J.A.C.S.* 1938, 60, 121.

[115] C. H. Bamford and D. M. Newitt, *J.C.S.* 1946, 695.

[116] E. Krause and P. Nobbe, *Ber.* 1930, 63, 934.

Iodine or bromine in cold carbon disulphide solution has no action on tributyl boron, but pure dry bromine gives a mixture of butyl bromide with dibutyl boron bromide and butyl boron dibromide; at the same time some of the alkyl is brominated with the formation of hydrogen bromide and therefore of butane. *t*-Butyl hypochlorite $(CH_3)_3C{-}O{-}Cl$ gave mainly butyl chloride and the oxide $Bu_2B{-}O{-}BBu_2$, indicating that in the formation of the intermediate co-ordination complex it is the bromine that acts as donor with hydrogen bromide, but the oxygen with the hypochlorite.

If the incompleteness of the reaction with hydrogen bromide is due to the stoppage of co-ordination in $Bu_2B{-}Br$, this stoppage must be due to back co-ordination, as in $R_2{=}B\overset{\leftarrow}{-}Br$; but we must suppose that the boron in this state, though it cannot co-ordinate to a second bromine of hydrogen bromide, can do so to a bromine of a Br_2 molecule, or to the oxygen of water.

By various reagents one, two, or all three alkyls can be removed from trialkyl boron. From boron tributyl

Perbenzoic acid or H_2O_2	removes	3 alkyls
Bromine or dry oxygen	,,	2 ,,
HBr or wet oxygen	,,	1 alkyl.

With all these alkyl-boron compounds the B—C link grows steadily stronger as the alkyl groups are replaced by halogens, hydroxyl, or oxy-alkyl. This supports the view that its rupture is due to co-ordination with the boron as acceptor, and that this is weakened by back co-ordination.

Alkali metals. The power of forming addition compounds with alkali metals, such as $K[B(C_6H_5)_3]$ (see below, p. 378), is confined to the triaryls and (curiously) the tribenzyl; the tri-cyclohexyl compound does not possess it, any more than the simpler trialkyls.

The *co-ordination compounds* of the trialkyls and triaryls are of various types: ammines, as $R_3B{\leftarrow}NH_3$, and salts with complex anions, practically all of the form $M[BR_3X]$, where R can be alkyls or aryls, and X can be phenyl, hydroxyl, or fluorine (see later, complex compounds of boron).

2. *Dialkyl and Diaryl Boric Acids* $R_2B{\cdot}OH$ *and their Derivatives*

The dialkyl boric acids are the first stage of oxidation of the trialkyl borons,[117] and as we have seen, can be got from them by treatment with hydrobromic acid in aqueous solution, or with dry gaseous oxygen. They can also be made by alkylating the mono-alkyl boric esters, e.g. with zinc alkyl or the Grignard reagent; or by the hydrolysis of the dialkyl boron monofluorides (see below, p. 377).

Diethyl boric acid and its esters have recently been examined by Meer-

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[117] H. Meerwein, G. Hinz, H. Majert, and H. Sönke, *J. prakt. Chem.* 1936, [2] **147**, 226.

wein and his colleagues,[117-18] who made them by a new method, the action of an aldehyde or ketone on boron triethyl in ether:

$$R\cdot CHO + BEt_3 = R\cdot CH_2O—BEt_2 + C_2H_4.$$

The ester can easily be hydrolysed by water to the free boric acid $Et_2B—OH$. The most convenient ester to use is the *p*-chlorophenate, made from *p*-chlorobenzaldehyde.

Diethyl boric acid $Et_2B—OH$[118] melts at −90° and boils at +36°. If it is distilled at atmospheric pressure it is partly converted into the anhydride or oxide $Et_2B—O—BEt_2$, which boils at 143°. The acid is not spontaneously inflammable.

In addition to the esters which this acid forms with alcohols (e.g. the benzyl ester $Et_2B—O—CH_2\cdot\Phi$, b. pt. 114°/16 mm.; the *p*-chlorophenyl ester, b. pt. 142°/16 mm.) another series is formed with acids, which may be called anhydrides, such as the acetic compound $Et_2B—O—CO—CH_3$, m. pt. 50-2°.

The dialkyl boric acids very readily lose water, to form anhydrides, such as $Et_2B—O—BEt_2$, b. pt. 143°, and $Bu_2B—O—BBu_2$, which boils at 136° under 12 mm. pressure, and by the boiling-point is monomeric in benzene (unlike the anhydrides of the non-alkyl boric acids).

The aromatic derivatives are also known. Diphenyl boric acid

$$(C_6H_5)_2B—OH,$$[109]

made by the hydrolysis of the halide, melts at 264–7°. It is insoluble in water, but easily soluble in organic solvents and in aqueous alkalies. The salts, however, are highly hydrolysed, and the acid can be removed from the alkaline solution by extraction with ether.

3. *Mono-alkyl and Mono-aryl Boric Acids*

The mono-alkyl boric acids $R—B(OH)_2$ and their derivatives have been studied in some detail, especially by J. R. Johnson and his co-workers,[119-20] who have pointed out the remarkable differences between their chemical properties and those of the aryl compounds. The simplest member, methyl boric acid $CH_3—B(OH)_2$, has been prepared by Burg.[121]

The mono-alkyl boric acids can be made by the hydrolysis of their esters, which are formed by the slow oxidation of the trialkyls (Frankland, 1862[106]; Krause[102,122]). Johnson[119] finds the best method to be the action of the Grignard reagent on methyl or ethyl borate[123]; this reaction goes at −70°.

These acids lose water with great ease, and so are difficult to get with sharp melting-points.

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[118] H. Meerwein and H. Sönke, ib. 251.

[119] H. R. Snyder, J. A. Kuck, and J. R. Johnson, *J.A.C.S.* 1938, **60**, 105.

[120] J. R. Johnson, M. G. van Campen, and O. Grummitt, ib. 111.

[121] A. B. Burg, ib. 1940, **62**, 2228.

[122] E. Krause and P. Nobbe, *Ber.* 1931, **64**, 2112.

[123] E. Khotinsky and M. Melamed, ib. 1909, **42**, 3090.

Methyl boric acid, $CH_3 \cdot B(OH)_2$,[121] can be made from methyl magnesium iodide and methyl borate. The free acid formed by the hydrolysis of the ester is first converted completely into the oxide $(CH_3 \cdot BO)_3$ by treatment with anhydrous calcium sulphate, and this after purification is rehydrated with insufficient water, and the unchanged oxide distilled off. $CH_3 \cdot B(OH)_2$ is a solid with a vapour pressure at 25° of 2·5 mm. (that of the oxide at 25° is 79 mm.); its extrapolated boiling-point is about 110°; it loses water so easily on heating that it has no real melting-point. Vapour-density measurements show that there is an equilibrium in the vapour with a constant for loss of water of 0·27 at 100°.

1-propyl-boric acid, $Pr \cdot B(OH)_2$[119]; m. pt. 107°. 1-*n*-butyl boric acid, $Bu \cdot B(OH)_2$[119]; m. pt. 93°; monomeric in acetone solution by the boiling-point; fairly soluble both in water and in organic solvents.

Isobutyl boric acid, m. pt. 106–12°, is more easily oxidized than the previous acids, in which the boron is always attached to a primary carbon.

Tertiary butyl boric acid, $(CH_3)_3C \cdot B(OH)_2$,[120, 122] melts about 110°. Both the acid and its oxide are extremely easily oxidized by air, and must be manipulated in an indifferent gas.

1-*n*-hexyl-boric acid[119]; m. pt. 89°. Benzyl-boric acid,

$$C_6H_5 \cdot CH_2 \cdot B(OH)_2{}^{120};$$

m. pt. 104°; when dry it is oxidized very easily by air, and oxygen must be excluded in its manipulation.

The true *aromatic* derivatives are made from the Grignard reagents in the same way as the aliphatic, using either boron trifluoride[110] or boric esters.[123] Eight different aryl-boric acids were found by the freezing-points to be monomeric in nitrobenzene.[124]

Phenyl boric acid, $C_3H_5 \cdot B(OH)_2$,[107, 126–7] melts about 220°. It can be nitrated at low temperatures without the B—C link breaking, and the orientation of the products depends in a curious way on the conditions; with fuming nitric acid and acetic anhydride at −15°, 95 per cent. of ortho and 5 per cent. of para are produced; in the absence of acetic anhydride only 15 per cent. ortho, but 85 per cent. meta.[127] Branch and his co-workers[125] say that the boron should draw electrons from the phenyl nucleus like a nitro-group, and so the substitution should be in the meta position; that in the presence of acetic anhydride the main product is ortho they attribute to the formation of a co-ordination compound with the anhydride by the boron.

Other examples are: *p*-tolyl,[128] m. pt. 258°; 2-furyl[120]: dimorphic, m. pts. 110° and 122°: not oxidized by air; 2-thienyl-[120] similar.

[124] C. R. Kinney and D. F. Pontz, *J.A.C.S.* 1936, **58**, 196.

[125] D. L. Yabroff, G. E. K. Branch, and H. J. Almquist, ib. 1933, **55**, 2935.

[126] A. D. Ainley and F. Challenger, *J.C.S.* 1930, 2171.

[127] W. Seaman and J. R. Johnson, *J.A.C.S.* 1931, **53**, 711.

[128] F. R. Bean and J. R. Johnson, ib. 1932, **54**, 4415.

Branch and his collaborators have determined the dissociation constants of many of these acids (see later p. 376).

The chemical properties of the mono-alkyl boric acids have been compared in detail with those of their aromatic analogues by Johnson.[119-20] He shows that in almost every particular they are different. (This startling difference, to which there is no parallel among purely organic compounds, is presumably due to interaction of the unsaturated sextet with the aromatic ring.) Practically only two reactions go in the same way with both. (1) The action of heat on the alkaline salt; the sodium salt of butyl-boric acid on heating gives butane, and that of phenyl boric acid benzene. (2) With hydrogen peroxide, both classes of acid split the B—C link, giving boric acid $B(OH)_3$ and the alcohol or phenol. In all their other reactions the alkyl and aryl boric acids behave differently.

Oxidation by air. With the ordinary alkyl boric acids this occurs readily in the absence but not in the presence of water. If the boron is attached to a secondary carbon, the oxidation goes more easily. If to a tertiary, it is so easy that the work must be done in an indifferent gas; the same is true of the benzyl compound, though the carbon there is primary, and of boron tricyclohexyl[132] where it is secondary.

On the other hand, the true aryl compounds, such as the phenyl and tolyl boric acids, including the furane and thiophene derivatives, are not oxidized by gaseous oxygen at all, though of course the carbon attached to the boron is in these molecules tertiary.

Action of alkalies. The mono-alkyl and aryl boric acids are very weak acids (see below, p. 376); they react with aqueous alkalies to give salts such as $Na_2[(Bu\cdot B—O)_2O]$. The alkyl boric acids are not decomposed by aqueous alkalies but only by heating the solid salt. Even prolonged heating with concentrated alkali or with 40 per cent. hydrobromic or hydriodic acid does not break the link from the boron to the alkyl. Here again the benzyl compound is hydrolysed[120] more easily.

Silver nitrate affects both classes of compounds, but in different ways. With alkyl boric acids the silver is quantitatively reduced to the metal thus:*

$$2\ \mathrm{Alk}\cdot B(OH)_2 + 2\ AgOH = \mathrm{Alk}\cdot\mathrm{Alk} + 2\ Ag + 2\ B(OH)_3.$$

By the aryl acids the silver is scarcely reduced, but it seems to act as a catalyst in promoting the hydrolysis:

$$\Phi\cdot B(OH)_2 + H_2O \xrightarrow{AgNO_3} \Phi\cdot H + B(OH)_3.$$

Here, as usual, the furane and thiophene derivatives behave exactly like the simple aromatic compounds.

* An exception to this is the behaviour of the tertiary butyl compound $Me_3C—B(OH)_2$; when treated with silver salts[120] this gives two atoms of metallic silver for every boron atom, the reaction being

$$(CH_3)_3C\cdot B(OH)_2 + 2\ AgOH + H_2O = (CH_3)_3C\cdot OH + 2\ Ag + B(OH)_3.$$

Not more than a trace of the expected hexamethyl ethane is formed; this may perhaps be due to steric reasons.

Ainley and Challenger[126] showed that the B—C link in phenyl boric acid can be broken by a whole series of reagents: by chlorine or bromine water; by a solution of iodine in potassium hydroxide

$$\Phi\cdot B(OH)_2 + Hal_2 + H_2O = \Phi\cdot Hal + H\cdot Hal + B(OH)_3;$$

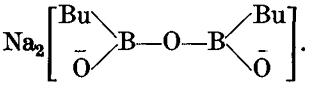
or by mercuric chloride[36] or bromide:

$$\Phi\cdot B(OH)_2 + HgBr_2 + H_2O = \Phi\cdot HgBr + HBr + B(OH)_3.$$

Similar reactions occur with cupric chloride, and zinc and cadmium chlorides, with formation of the aryl halide and in the first case reduction to cuprous chloride. *None* of these reactions occur with the alkyl boric acids.

The esters are known, such as $C_6H_5\cdot B(OEt)_2$, b.pt. 176° (by the action of ethyl alcohol on phenylboron dichloride); it is easily hydrolysed by water to phenyl boric acid and ethyl alcohol. $C_2H_5\cdot B(OC_2H_5)_2$ boils at 125° with some decomposition.

Of the salts a few have been made, but owing to the weakness of the acids (below) only one hydrogen per boron is replaced. Thus butyl boric acid with concentrated sodium hydroxide gives a hydrated salt which dries to the composition $Na_2Bu_2B_2O_3$, no doubt having the structure



This is stable to heat in solution, but the dry salt at a rather high temperature evolves butane.

A few salts of phenyl boric acid $C_6H_5\cdot B(OH)_2$ are known; they all behave like the alkyl derivatives.

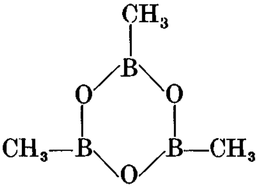
The (thermodynamic) first dissociation constants of a large number of these acids have been determined by Branch and his collaborators.[129–31] (A list of thirty-two is given by Krause and v. Grosse, p. 213.) Most of the acids were too insoluble in water for measurement, and were therefore examined in dilute alcohol; with un-substituted hydrocarbon radicals the value for an alkyl group was much smaller, and for an aryl often larger than that for boric acid. Thus the values $\times 10^{10}$ were: butyl boric acid 0·18, aryl radicals varying from phenyl 13·7 to *o*-tolyl 1·81; benzyl 7·5: boric acid itself has K_1 about 6×10^{-10}.

Alkyl and Aryl Boric Anhydrides

The alkyl compounds[119] can be dried to the anhydrides very easily by standing over phosphorus pentoxide, or by heating *in vacuo* or with thionyl chloride. Many of the alkyl-anhydrides can be distilled, and are trimeric, like paraldehyde, which they resemble in structure and come

[129] G. E. K. Branch, D. L. Yabroff, and B. Bettman, *J.A.C.S.* 1934, **56**, 937.
[130] D. L. Yabroff, G. E. K. Branch, and B. Bettman, ib. 1850.
[131] B. Bettman, G. E. K. Branch, and D. L. Yabroff, ib. 1865.
[132] E. Krause and H. Polack, *Ber.* 1928, **61**, 271.

near in boiling-point. The methyl compound $(CH_3 \cdot BO)_3$[96] has a m. pt. −68° and a b. pt. extrapolated 79° (paraldehyde $(CH_3 \cdot CHO)_3$ boils at 124°); the vapour density at 100° corresponds to the trimeric formula; the structure has been confirmed by electron diffraction by Bauer and Beach[133]; the molecule is planar (apart from the hydrogen atoms) with the distances B—O 1·39±0·02: B—C 1·57±0·03 A.U. (theory B—O 1·54, B=O 1·31, B—C 1·65); but the angles in the ring are of two kinds, B—O—B 112±4° and O—B—O 128±4°; that is, the mean angle of a hexagon, 120°, being larger than the tetrahedral angle, but equal to the natural angle for tricovalent boron, the boron covalencies yield more than those of the oxygen, as we should expect. The planar ring suggests back-co-ordination from the oxygen to the boron, and this resonance would account for the great stability of these compounds and the shortness of the B—O link.



The butyl compound is similar.

4. *Alkyl Boron Halides*

The methyl boron fluorides have been prepared[121] from boron trifluoride and the oxide $(CH_3 \cdot BO)_3$ at −45°;

$$(CH_3 \cdot BO)_3 + 2\,BF_3 = 3\,CH_3 \cdot BF_2 + B_2O_3.$$

The boiling- and melting-points of the methyl fluorides are

	M. pt.	*B. pt.*
$(CH_3)_2BF$	−147·2°	*ca.*—44°
$CH_3 \cdot BF_2$	..	−62·3°

The trialkyl borons give monobromides with hydrogen bromide, and both mono- and dibromides with bromine in the absence of a solvent.[104] Bu_2BBr boils at 65°/4 mm.; it is readily hydrolysed by cold water, but does not react at 20° with molecular silver, or with magnesium or sodium amalgam. $Bu \cdot BBr_2$ boils at 65° at 23 mm.

Aryl Boron Halides

These can be made[103, 107–10] from mercury diaryls and the boron trihalides. The following are some [melting-points] and boiling-points (from Krause and v. Grosse, p. 205).

Monohalides

$(C_6H_5)_2B \cdot Cl$	B. 270°	$(C_6H_5)_2B \cdot Br$	150–160/8 mm. [24°]

Dihalides

	$Ar\cdot BCl_2$	$Ar\cdot BBr_2$
Ar = Phenyl	178° [+7°]	100°/20 m. [33°]
o-Tolyl	193° [+6°]	..
p-Tolyl	.. [17°]	145°/25 m. [44–5°]
β-Naphthyl	.. [116°]	..

The following series of boiling-points is of some interest:

$B(CH_3)_3$	$B(CH_3)_2F$	$B(CH_3)F_2$	BF_3
−20·2°	−44°	−62·3°	−101°
$B(C_6H_5)_3$	$B(C_6H_5)_2Cl$	$B(C_6H_5)Cl_2$	BCl_3
203°/15 mm.	270°	178°	+18°

The electron diffraction of two of these methyl fluorides[134] gives these results:

	B—F	B—C	*Angle* C—B—F
BMe_2F . . .	1·29	1·55	121·5°
$BMeF_2$ . . .	1·30	1·60	121·0°

Both molecules are planar. The theoretical distances are B—F, 1·52, B=F 1·30; B—C 1·65, B=C 1·43.

5. *Alkali Metal Addition Products*

The boron triaryls have the very remarkable property, as was discovered by Krause, of dissolving sodium and the other alkali metals when in ethereal solution to form addition compounds of the type $BAr_3\cdot Na$, which are highly coloured (yellow or green).[111–12, 135–7]

The reaction is reversible; the boron triaryl extracts sodium from a 3 per cent. amalgam but the sodium compound loses its sodium again when treated with pure mercury. The free energy of the reaction by which this compound is formed is, as we should expect, less than for the combination of sodium with triphenyl methyl, the values being boron −11·5, carbon −18 k.cals.[132]

The trialkyl borons (even boron tricyclohexyl) do not possess this property, but it is common to all the triaryls, and is also found, very remarkably, in boron tribenzyl. Boron tri-α-naphthyl is even able to form, in addition to the yellow mono-sodium compound, a dark violet disodium compound, $Na_2\cdot B(C_{10}H_7)_3$.[135–7]

These sodium salts are far more sensitive to oxygen than the triaryls from which they are derived; the colour of the solution vanishes at once on exposure to the air. They dissolve in ether, and the solution conducts electricity, indicating ionization; but conductivities are so low that it would seem that either the substances can assume a covalent structure, or ion pairs can exist in the solution.

[133] S. H. Bauer and J. Y. Beach, *J.A.C.S.* 1941, 63, 1394.

[134] S. H. Bauer and J. M. Hastings, ib. 1942, 64, 2686.

[135] H. E. Bent and M. Dorfman, ib. 1932, 54, 2132.

[136] Id., ib. 1935, 57, 1259.

[137] Id., ib. 1924.

The alkaline compounds are of interest in relation to their carbon analogues the alkaline triaryl methyl compounds. Triphenyl-methyl can form an addition product with sodium, $Na \cdot C(C_6H_5)_3$, which in many ways resembles the boron compound and is also ionized, but it holds the sodium more firmly than the boron compound. A. v. Grosse has pointed[138] out that there is an extraordinarily close similarity between the boron and carbon addition products, as the following description shows.

Boron. $Li \cdot B\Phi_3$: greenish-yellow crystals; forms etherates; much more soluble in ether than the salts of the other metals.

$Na \cdot B\Phi_3$; forms etherates; orange-yellow crystals; soluble in ether.

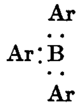
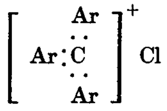
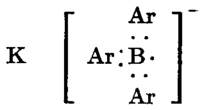
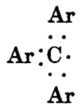
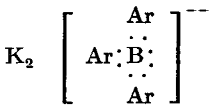
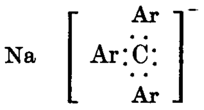
K, Rb, $Cs \cdot B\Phi_3$: all yellow powders, slightly soluble in ether; etherates unstable.

Carbon. $Li \cdot C\Phi_3$: forms etherates; orange-red crystals; much more soluble in ether than the rest.

$Na \cdot C\Phi_3$: red crystals, soluble in ether.

K. Rb, $Cs \cdot C\Phi_3$: blood-red powders, very slightly soluble in ether; forms no etherates.

The analogy extends, however, much farther than this. The triaryl methyl group is remarkable in being able to exist in three forms, as a positive ion, as a neutral free radical, and as a negative ion. This is undoubtedly due to an interaction of the methyl carbon with the aryl groups, by which the strain which would normally exist in such molecules is relieved. There is no reason why a similar interaction should not occur between aryl groups and a boron atom. As a boron atom starts with one electron less than a carbon atom, the boron compounds exactly agree in electronic structure with the triphenyl methyl derivatives.

Boron	*Valency Group*	*Carbon*
 $\mathrm{Ar}\colon\underset{\mathrm{Ar}}{\underset{\cdot\cdot}{\overset{\mathrm{Ar}}{\overset{\cdot\cdot}{\mathrm{B}}}}}$	$6 = \underline{6}$	 $\left[\mathrm{Ar}\colon\underset{\mathrm{Ar}}{\underset{\cdot\cdot}{\overset{\mathrm{Ar}}{\overset{\cdot\cdot}{\mathrm{C}}}}}\right]^{+}\mathrm{Cl}$
 $\mathrm{K}\left[\mathrm{Ar}\colon\underset{\mathrm{Ar}}{\underset{\cdot\cdot}{\overset{\mathrm{Ar}}{\overset{\cdot\cdot}{\mathrm{B}}}}}\cdot\right]^{-}$	$7 = \underline{6}, 1$	 $\mathrm{Ar}\colon\underset{\mathrm{Ar}}{\underset{\cdot\cdot}{\overset{\mathrm{Ar}}{\overset{\cdot\cdot}{\mathrm{C}}}}}\cdot$
 $\mathrm{K}_2\left[\mathrm{Ar}\colon\underset{\mathrm{Ar}}{\underset{\cdot\cdot}{\overset{\mathrm{Ar}}{\overset{\cdot\cdot}{\mathrm{B}}}}}\colon\right]^{--}$	$8 = \underline{6}, 2$	 $\mathrm{Na}\left[\mathrm{Ar}\colon\underset{\mathrm{Ar}}{\underset{\cdot\cdot}{\overset{\mathrm{Ar}}{\overset{\cdot\cdot}{\mathrm{C}}}}}\colon\right]^{-}$

It is natural that these derivatives should not be formed by the trialkyl borons, any more than they are by the trialkyl methyl radical, since this kind of interaction does not occur with an alkyl group; but it is surprising that they should be formed by tribenzyl boron, in which the aromatic

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[138] A. v. Grosse, *Ber.* 1926, 59, 2646.

ring is separated from the boron atom by CH_2; no corresponding compounds of tribenzyl methyl have been observed.

BORON AND NITROGEN

The boron halides react violently with ammonia, and give on heating first the amine $B(NH_2)_3$, then an imine $B_2(NH)_3$, and finally, the nitride BN. Alkyl and aryl derivatives of the amine are known.

The amine B_2NH_7, probably $H_3\overset{-}{B}—\overset{+}{N}H_2—BH_2$, and the benzene-like triborine triamine $B_3N_3H_6$, with its numerous derivatives, have already been described.

Boron Nitride, BN

This can be made by the action of nitrogen, ammonia, nitric oxide, or even atmospheric air on boron at a white heat; if air or nitric oxide is used the oxide B_2O_3 is of course formed as well. It can also be made by igniting borax with ammonium chloride, and in other ways; it is usually the ultimate product of igniting compounds of boron with compounds of nitrogen. It sublimes below 3,000° C., and melts under pressure at that temperature.[139]

Its crystal structure is remarkable.[140-1] It has a graphite lattice, with the B—N distance 1·45 A, practically the same as was subsequently found (1·44 A) for triborine triamine by electron diffraction.* Thus we have the B—N analogues of benzene and of graphite. Boron nitride also occurs in a more reactive and apparently amorphous modification, which can be made by the ignition of the amide $B(NH_2)_3$; on heating, this goes over into the ordinary crystalline form.[142] Douglas and Herzberg[143] find that the spectrum of the discharge in the vapour of BCl_3+N_2 gives bands due to BN; the distances in the upper and lower states are 1·326 and 1·281 A [cf. C—C in Swan Spectrum 1·32 A].

Chemically, the crystalline form of boron nitride is extremely indifferent; it can be heated without change in air, hydrogen, oxygen, iodine, or carbon disulphide; water hydrolyses it to boron trioxide and ammonia, the reactive form rather slowly at 25-100°, the ordinary form only at a red heat. It is decomposed by heating with acids, but not with alkalies.

Boron Imide, $B_2(NH)_3$

This is made by heating the hexammine of boron trisulphide:

$$B_2S_3, 6\,NH_3 = 3\,NH_4SH + B_2(NH)_3;$$

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* Distances: BN 1·45; graphite 1·42 Theory: B—N 1·58; B=N 1·36
$B_3N_3H_6$ 1·44; benzene 1·39 C—C 1·54; C=C 1·33.

[139] E. Friederich and L. Sittig, *Z. Anorg. Chem.* 1925, **143**, 312.

[140] V. M. Goldschmidt and O. Hassel, *Norsk Geologisk Tidskrift*, 1927, **258**, 266.

[141] W. H. Zachariasen, *Z. Krist.* 1931, **80**, 137.

[142] A. Stock and M. Blix, *Ber.* 1901, **34**, 3044.

[143] A. E. Douglas and G. Herzberg, *Canad. J. Res.* 1940, **18 A**, 179.

by the action of ammonia on boron tribromide at - 10°,[145] or by heating the amide $B(NH_2)_3$.[144, 146] It is a white powder, insoluble in all solvents that do not decompose it. It begins to lose ammonia at 125°, and on further heating is converted into boron nitride. It is decomposed by water with much heat into boron trioxide and ammonia; with hydrogen chloride it forms, also with much heat, the salt $B_2(NH)_3$, 3 HCl.

Boron Amine or Amide, $B(NH_2)_3$

This can be made as an inseparable solid mixture with the ammonium salt, by passing the vapour of boron trichloride into liquid ammonia at −50°,[144] or by dropping the tribromide into it.[146]

Various alkyl and aryl derivatives have been made; both the dimethyl-amino- and the ethyl-amino-compounds are volatile liquids. The last of these was made by Kraus and Brown[147] by the action of lithium on a solution of boron trifluoride in ethylamine:

$$BF_3 + 3\,EtNH_2 + 3\,Li = B(NHEt)_2 + 3\,LiF + 3\,H.$$

The dimethylamine derivative was made by Wiberg and Schuster[148-9]; they showed that dimethylamine acts on boron trichloride (like ethyl alcohol, p. 386), replacing the chlorine atoms successively by dimethylamino-groups. The physical properties are:

	M. pt.	*B. pt.*	*Trouton*
BCl_3	−107°	+12·5°	21·6
$(CH_3)_2N \cdot BCl_2$ . .	−46°	111·9°	22·5
$(Me_2N)_2B \cdot Cl$ . .	−54°	146·1°	22·3
$(Me_2N)_3B$ . . .	−40°	147·5°	22·9

The first of these amino-compounds, $(CH_3)_2N—BCl_2$, shows a remarkable dimorphism.[149] It changes in a few days in the cold, or rapidly at 100°, into a solid of the same composition, which melts at 142° (188° higher) and sublimes *in vacuo*. While the liquid form is decomposed at once by water or acids, the solid can be boiled with water or left for days with hydrogen chloride without change. It is insoluble in water, acids, and alkalies, and is scarcely attacked by hot concentrated nitric acid. It is soluble in ether and in benzene; in benzene it is dimeric by the freezing-point, whereas the liquid form is monomeric in the vapour. This isomerism has not been explained.

The phenyl derivative of the triamine $B(NH_2)_3$ was made by Jones and Kinney.[150] Aniline reacts with boron trichloride to give the very reactive ammine $C_6H_5 \cdot NH_2 \rightarrow BCl_3$. If this is heated with excess of aniline in benzene, aniline hydrochloride crystallizes out, and from the mother liquor the

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[144] A. Joannis, *C.R.* 1902, **135**, 1106.
[145] Id., ib. 1904, **139**, 364.
[146] A. Stock and W. Holle, *Ber.* 1908, **41**, 2096.
[147] C. A. Kraus and E. H. Brown, *J.A.C.S.* 1930, **52**, 4414.
[148] E. Wiberg and K. Schuster, *Z. anorg. Chem.* 1933, **213**, 77.
[149] Id., ib. 89.
[150] R. G. Jones and C. R. Kinney, *J.A.C.S.* 1939, **61**, 1378.

phenylamine $B(NHC_6H_5)_3$ separates in white crystals, m. pt. 166–9°, stable when dry, soluble in aniline, readily hydrolysed by water. Hydrogen chloride acts on this in benzene solution to give the triborine derivative tri-N-phenyl tri-B-chloro-triborine triamine $B_3N_3\Phi_3Cl_3$ (see above, p. 359).

COMPOUNDS WITH THE BORON-OXYGEN LINK

These include boron oxide, boric acid, and its numerous derivatives.

Boron monoxide, BO, is said to be got as a light brown sublimate by heating boron with zirconium dioxide *in vacuo* at 1,800°.[151]

Boron Trioxide and Boric Acid

Boron trioxide is formed with the evolution of 349 k.cals. per B_2O_3 solid[152] when boron is heated in air or oxygen; it is usually made by heating boric acid up to its melting-point. It is a white solid of high (but rather uncertain) melting- and boiling-points: it is said to boil above 1,500°.[153] It occurs in a crystalline and a glassy form, the heat of conversion being 4·36 k.cals./mole.[154] It is reduced to elementary boron by the alkali metals, by magnesium, and by aluminium, but not by carbon even at a red heat. Its power of dissolving certain metallic oxides to give characteristically coloured borate 'glasses' is well known. According to Guertler[155] and Foex[156] oxides of the type M_2O (M = Li, Na, K, Rb, Cs, Cu′, Ag, Tl′), as well as the trioxides of As, Sb, and Bi, are completely miscible with boric oxide, while the oxides of the divalent metals Be, Mg, Ca, Sr, Ba, Mn, Co, Zn, and Cd, of the trivalent Al, Y, La, Ce, Er, Cr, and the tetravalent Si, Zr, Sn Th, Mo, W, and U are only partially miscible, or are immiscible. A glass made of the oxides of lithium, beryllium, and boron can be used for the windows of X-ray tubes.[157]

Boric Acid

Boric oxide readily takes up water to form boric acid, evolving 6·2 k.cals. per g.-atom of boron. The solid phases in the system B_2O_3—water are ice, H_3BO_3, three modifications of metaboric acid HBO_2 (monotropic), and B_2O_3.[158] The melting-points of the metaboric acids are 236° (stable), 201°, and 176°. Tensimetric and X-ray measurements of Menzel[159] show that H_3BO_3 occurs only in one crystalline form, which dries to HBO_2 and then to B_2O_3.

The full X-ray analysis of orthoboric acid H_3BO_3 shows that it has a sheet lattice of hexagonal symmetry,[160] in which every boron atom is

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[151] E. Zintl, W. Morawietz, and E. Gastinger, *Z. anorg. Chem.* 1940, **245**, 8.

[152] W. A. Roth and E. Börger, *Ber.* 1937, **70**, 48.

[153] H. v. Wartenberg and O. Bosse, *Z. Chem. Apparatenkd.* 1922, **28**, 384.

[154] J. C. Southard, *J.A.C.S.* 1941, **63**, 3147.

[155] W. E. Guertler, *Z. anorg. Chem.* 1904, **40**, 225.

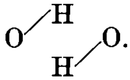
[156] M. Foex, *C.R.* 1938, **206**, 349.

[157] L. J. Mazelev, *J. Appl. Chem. Russ.* 1940, **13**, 1288.

[158] F. C. Kracek, G. W. Morey, and H. E. Merwin, *Amer. J. Sci.* 1938, [v] **35**, A 143.

[159] H. Menzel, H. Schulz, and H. Deckert, *Z. anorg. Chem.* 1934, **220**, 49.

[160] W. H. Zachariasen, *Z. Krist.* 1934, **88**, 150.

joined to three oxygens, and every oxygen to one boron and two oxygens, the distances being B—O 1·38 (theory B—O 1·54: B=O 1·31): O···O in the sheet 2·71 A, and the sheets 3·18 A apart (see diagram in Kahovec[161]). The oxygen atoms must be attached by some kind of hydrogen bond, presumably of the double type  $\mathrm{O}\genfrac{}{}{0pt}{}{\diagup\mathrm{H}}{\mathrm{H}\diagup}\mathrm{O}$. The Raman spectra[161] seem to support this conclusion.

There are three common types of boric acids, ortho- H_3BO_3, pyro- $H_2B_4O_7$, and meta- HBO_2; salts of more highly condensed forms are also known. The various anions such as $[BO_2]^-$ and $[H_3BO_2]^-$ may all exist in solution, but (unlike the phosphate ions) they are permanently in equilibrium with one another. The evidence[162] is that the form or forms present in the solution contain one boron atom per ion. We should expect the form to be the most highly hydrated, $[B(OH)_4]^-$, and this is supported by the occurrence of such derived forms as the complex alkyloxide (p. 407) $M[B(OR)_4]$ and the catechol salts (p. 408).

Boric acid is to some extent volatile in steam. The concentration of boric acid in the vapour of an ordinary aqueous solution boiling under atmospheric pressure[163] is 1/300 of that in the liquid. It is stated[164] that in superheated steam the acid is present as H_3BO_3 below 144° C. and as HBO_2 above.[165]

The steam from the Tuscan fumaroles is at 1·5 to 5 atmospheres pressure and 100-190° C. The condensed water has 0·5 per cent. H_3BO_3; the heat of the steam is also utilized now as a source of power.[166]

Boric acid (this term unqualified always means the ortho-acid $B(OH)_3$ which is much the best known) is a very weak acid. Its acidity is greatly raised by the addition of certain poly-hydroxy-compounds like glycerol, through the formation of complex acids (see p. 388); and also[167] by that of neutral salts, especially those whose cations are highly hydrated; thus if the H_3BO_3 solution is saturated with $CaCl_2, 6\ H_2O$, it can be titrated with methyl orange. In tenth-molar solution the monosodium salt is about 0·76 per cent. hydrolysed.[168] The dissociation constants have all been measured, but owing to their small values the results are not very accurate. The values which have been obtained for K_1 are $5{\cdot}80\times10^{-10}$ at 25°[169]; $5{\cdot}7\times10^{-10}$ at 18°[142]; $6{\cdot}5\times10^{-10}$ [170]; and $5{\cdot}9\times10^{-10}$ [171] at 25°; we may take the value at the ordinary temperature to be 6×10^{-10}. For the second and

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[161] L. Kahovec, *Z. physikal. Chem.* 1938, B **40**, 135.

[162] F. L. Hahn, *Z. anorg. Chem.* 1930, **193**, 316.

[163] P. Jaulmes and A. Gontard, *Bull. Soc.* 1937, [v] **4**, 139.

[164] P. Jaulmes and E. Galhac, ib. 149.

[165] See also S. Bezzi, *Gaz.* 1935, **65**, 766.

[166] Gmelin, *Bor*, p. 72.

[167] H. Schäfer and A. Sieverts, *Z. anorg. Chem.* 1941, **246**, 149.

[168] H. Menzel, H. Schulz, and H. Deckert, ib. 1934, **220**, 49.

[169] B. B. Owen, *J.A.C.S.* 1934, **56**, 1695.

[170] G. E. K. Branch, D. L. Yabroff, and B. Bettman, ib. 1850.

[171] G. G. Manov, N. J. DeLollis, and S. F. Acree, *J. Res. Nat. Bur. Stand.* 1944, **33**, 287.

third constants the values $K_2 = 1{\cdot}8 \times 10^{-13}$ and $K_3 = 3 \times 10^{-14}$ have been obtained.[172]

The solubilities of boric acid in various solvents, in g. to 100 g. solvent, at 25° unless otherwise stated, are (water,[173] other solvents[174]):

Water	3·16	Methyl alcohol	22·7	Ethyl ether	0·0078
		Ethyl alcohol	11·8	Acetic acid	6·72/30°
		Butyl alcohol	5·19	Acetone	0·629/20°

Metallic Borates

A large number of metallic borates have been prepared, either in the dry way by the fusion of their components (when the individuality of the product is sometimes uncertain) or by double decomposition from water.

The soluble borates are almost confined to those of the monovalent metals, and especially the alkalies. They are derived not only from the simple boric acids, but also from a variety of condensed forms containing up to 5 boron atoms in the ion and probably more. Of the alkaline borates the commonest are those with 1, 2, and 5 boron atoms to 1 atom of alkali. Thus from the systems M_2O, B_2O_3, H_2O the following salts will separate at 30°[175-6]:

$LiBO_2$, 8 aq.	$Li_2B_4O_7$, x aq.	LiB_5O_8, 5 aq.
$NaBO_2$, 4 aq[177]	$Na_2B_4O_7$, 10 aq.	NaB_5O_8, 5 aq.
KBO_2, 2·5 aq.	$K_2B_4O_7$, 4 aq.	KB_5O_8, 4 aq.

The crystal structures of some of these salts, especially the ortho- and meta-borates, have been examined. Ortho-borates are formed by the trivalent metals. Goldschmidt has shown[178] that the structures of the anions in $ScBO_3$, YBO_3, and $InBO_3$ are practically identical with those in $M''CO_3$ and $M'NO_3$, being planar and symmetrical. The metaborates are of two types,[179] both with the boron atom attached symmetrically to three oxygens in a plane with it, one of its own two oxygens being also attached to another boron. In calcium metaborate[180-1] $Ca(BO_2)_2$ these groups form endless chains; in potassium metaborate KBO_2[182] they are joined in threes to give B_3O_3 rings (as in the alkyl-boron oxides), the B—O distance being 1·38 A in the ring and 1·33 A outside[183] (theory B—O 1·54, B=O 1·31). Ordinary borax is a hydrated pyroborate, $Na_2B_4O_7$ aq.[184]

[172] F. L. Hahn and R. Klockmann, *Z. physikal. Chem.* 1930, **151**, 80.

[173] W. C. Blasdale and C. M. Slansky, *J.A.C.S.* 1939, **61**, 917.

[174] Gmelin, *Bor*, pp. 78, 79.

[175] M. Dukelski, *Z. anorg. Chem.* 1906, **50**, 38. [176] Id., ib. 1907, **54**, 45.

[177] For the Na salts see farther, H. Menzel and H. Schulz, *Z. anorg. Chem.* 1943, **251**, 167.

[178] V. M. Goldschmidt, *Nachr. Ges. Wiss. Gött.* 1932, 53.

[179] See pictures in Pauling, *Chem. Bond*, p. 196. (Ed. 2, p. 211.)

[180] W. H. Zachariasen, *Proc. Nat. Acad. Sci.* 1931, **17**, 617.

[181] W. H. Zachariasen and G. E. Ziegler, *Z. Krist.* 1932, **83**, 354.

[182] W. H. Zachariasen, *J. Chem. Phys.* 1937, **5**, 919.

[183] A. V. Nikolaev and A. G. Tschelischtscheva, *C. R. Acad. U.R.S.S.* 1940, **28**, 127.

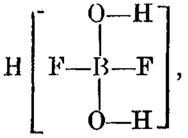
[184] H. Menzel and H. Schulz, *Z. anorg. Chem.* 1940, **245**, 157.

Borotungstates

The large class of hetero-poly-acids is dealt with elsewhere (VI. 1042), but the borotungstates are of special interest in the chemistry of boron. They are mainly[185-6] the salts of an acid which was formerly written $H_9[B(W_2O_7)_6]$, 28 and 22 H_2O, five of the nine hydrogens being replaceable by an alkali metal, an alkaline earth, or NH_4, Ag, Ni, Cu″, or Cd. From the presence in the formula of 6 pairs of tungsten atoms it was assumed that the boron atom must be 6-covalent. But the work of Keggin[187] on the phosphotungstates (which are strictly analogous to the boron compounds) has shown that the unique central atom (phosphorus or boron) is really 4-covalent, being at the centre of a tetrahedron whose points are occupied by 4 oxygens, while the 6 pairs of tungsten atoms lie along the 6 edges, and that the formula should be written $H_5[B(W_3O_{10})_4]$ 30 and 24 H_2O.

Fluoroboric Acids

There are at least two different fluoroboric acids intermediate between $H[B(OH)_4]$ and $H[BF_4]$. The first is the difluoroboric acid $H_3BO_2F_2$, or



$$H\left[\begin{array}{c} \text{O—H} \\ | \\ \text{F—B—F} \\ | \\ \text{O—H} \end{array}\right],$$

isolated by Nieuwland and his colleagues.[188-9] This can be made in several ways as by the action of hydrogen fluoride on boron trioxide (perhaps the best method):

$$B_2O_3 + 9\,HF = 3\,H[BF_2(OH)_2] + BF_3,$$

and also from boron trifluoride and boric acid or water. Difluoroboric acid $H[BF_2(OH)_2]$ is a syrupy liquid rather like chlorsulphonic acid, which boils at 160° and goes to an amorphous glass at $-20°$; it is stable in dry air and does not etch glass. The density of the vapour shows that this is completely dissociated, presumably into $BF_2OH + H_2O$. The pure liquid has a molecular conductivity of 0·988 at 25°, which is of the same order as that of absolute sulphuric acid. It is practically insoluble in carbon tetrachloride, carbon disulphide, or benzene, but it will dissolve in the co-ordination compounds formed by boron trifluoride with ethers, esters, or alcohols.

Difluoroboric acid, very unlike boric acid, is a strong monobasic acid; if powdered sodium chloride is added to its solution in $Et_2O \rightarrow BF_3$ at the b.pt. (121°), practically the whole of the chlorine comes off as hydrogen

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[185] A. Rosenheim and J. Jaenicke, ib. 1912, **77**, 239.

[186] Id., ib. 1917, **101**, 235.

[187] J. F. Keggin, *Nature*, 1933, **131**, 908; *Proc. Roy. Soc.* 1934, **144**, 75.

[188] F. J. Sowa, J. W. Kroeger, and J. A. Nieuwland, *J.A.C.S.* 1935, **57**, 454.

[189] Id., ib. 1937, **59**, 965.

chloride. With nickel chloride it gives a nickel salt (the only salt that seems to have been characterized), which after heating in *in vacuo* has the composition $Ni[BF_2(OH)_2]_2$.

If this acid is dissolved in any of the lower organic acids, alcohols, ethers, esters, aldehydes, or ketones, it is very readily converted into orthoboric acid H_3BO_3 and the boron trifluoride co-ordination compound of the solvent. This reaction is undoubtedly caused by the energy of the co-ordination, for while it occurs with acetic acid it does not with trichloracetic, whose co-ordination compound with boron trifluoride is stable only at low temperatures. Difluoroboric acid has a considerable catalytic power in many organic reactions, though not so great as that of boron trifluoride (see below, p. 392).

With acetyl chloride it forms two compounds, one of the composition $(CH_3 \cdot COCl)_2BF_3$, boiling at 64–6° under 15 mm., and another which is a white solid melting at 206–7° of doubtful composition.[189]

The second fluoroboric acid, *trifluoroboric acid*, $H[BF_3OH]$, has long been known in a hydrated form, but it was regarded as a hydrate of boron trifluoride, $BF_3, 2\,H_2O$. It was discovered by Berzelius. Meerwein and Pannwitz[190-1] have shown that it can easily be made by passing one molecular proportion of boron trifluoride into two of water,[190] or by dissolving boron trioxide in 40 per cent. hydrofluoric acid.[191] It is a colourless liquid melting sharply at 6·0°[192]; it is said[191] to boil undecomposed at 59° under 1·2 mm., but this has been disputed.[192] It is a strong acid which decomposes carbonates and gives alkaline salts; it also forms addition compounds, for example, with dioxane $BF_3, 2\,H_2O, C_4H_8O_2$, melting with decomposition at 128–30°. It will also add on a second molecule of BF_3 to form a solid compound $(BF_3)_2, H_2O$, which will not distil without decomposition.

Klinkenberg and Ketelaar[193] showed by X-ray analysis that the solid $BF_3, 2\,H_2O$ is isomorphous with ammonium perchlorate (and so with $HClO_4, H_2O$) and must be the salt $(H_3O) \cdot [BF_3OH]$.

Alcohols will combine with boron trifluoride in the same way as water; Meerwein obtained as eries of compounds of the type $BF_3, 2\,ROH$, with R = methyl, ethyl, *n*-propyl, and *n*-butyl, all of which distilled at temperatures from 50° to 65° under 2–4 mm. pressure. These alcohol compounds are also strong acids which decompose carbonates and form salts, all of the type BF_3,MOH or BF_3,MOR; for example, $Na[BF_3OH]$, $K[BF_3OH]$, $Na[BF_3O \cdot CH_3]$, and $K[BF_3O \cdot CH_3]$; the structure of the sodium salt was determined by X-ray analysis.[194]

Carboxylic acids in the same way form solutions with boron trifluoride of high acidity,[195] and the compounds $BF_3,R \cdot COOH$ and $BF_3, 2\,R \cdot COOH$

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[190] H. Meerwein, *Ber.* 1933, **66**, 411.

[191] H. Meerwein and W. Pannwitz, *J. prakt. Chem.* 1934, [ii] **141**, 123.

[192] J. S. McGrath, G. G. Stack, and P. A. McCusker, *J.A.C.S.* 1944, **66**, 1263.

[193] L. J. Klinkenberg and J. A. A. Ketelaar, *Rec. Trav.* 1935, **54**, 959.

[194] L. J. Klinkenberg, ib. 1937, **56**, 36.

can be isolated.[190] The latter (1:2) are liquids that can be distilled *in vacuo*; more boron trifluoride converts them into the solid 1:1 compounds which on heating lose half their trifluoride to go over into 1:2. The stability of these complexes falls as the strength of the organic acid increases; the complex formed by acetic acid can be distilled without decomposition: that of monochloracetic loses all its boron trifluoride *in vacuo* at 80°; dichloracetic acid only takes up the trifluoride below −15°, and trichloracetic does not combine with boron trifluoride at all.

Boric Esters

Boric acid or its anhydride reacts with alcohols rapidly even in the absence of a catalyst (tertiary butyl alcohol is an exception) to form the ester $B(OR)_3$[198,198a]; the acetate $B(O \cdot CO \cdot CH_3)_3$ is sometimes better than the oxide.[196-7] The aryl esters are also known. These are some of the boiling-points of $B(OR)_3$[196-7,199]:

R = CH_3	68·5°	R = *n*-Bu	228–9°
Et	118°	*iso*-Bu	211°
n-Pr	179–80°	*tert.* Bu	60°/12 mm.
i-Pr	140°		[M.pt. *ca.* +12°]

Electron diffraction shows[200] that in methyl borate the BO_3 group is plane, with angles of 120°; the distances are B—O 1·38±0·02; O—C 1·43±0·03 A; (theory B—O 1·54, B=O 1·31: C—O 1·43, C=O 1·22); angles B—O—C 113±3°. There is evidence of the rotation of the CH_3 groups round the line of the B—O link, but this must be synchronized, as there is not room for their independent movement.

These esters are not associated, as is shown by their low boiling-points ($Al(OEt)_3$ boils 200° higher than $B(OEt)_3$, at 320°), by their vapour densities, and by the low values (e.g. 22·7) of the Trouton constant. This may be because the double bond which back-co-ordination requires (to complete the octet within the molecule) is more stable with boron as a member of the first short period; but that would not explain the non-association of the boron trialkyls.

The esters of boric acid are formed and hydrolysed as instantaneously as those of nitrous acid.

Methyl borate is remarkable[199] for forming a constant boiling mixture with methyl alcohol, boiling at 55°, or 14° lower than the pure ester, and 11° lower than methyl alcohol. This contains only 30 per cent. by weight

[195] H. Meerwein, *Ann.* 1927, **455**, 227.

[196] L. Kahovec, *Z. physikal. Chem.* 1938, B **40**, 135.

[197] Id., ib. 1939, B **43**, 109.

[198] A. Scattergood, W. H. Miller, and J. Gammon, *J.A.C.S.* 1944, **67**, 2150.

[198a] L. H. Thomas, *J.C.S.* 1946, 820.

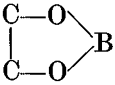
[199] J. J. Etridge and S. Sugden, ib. 1928, 989.

[200] S. H. Bauer and J. Y. Beach, *J.A.C.S.* 1941, **63**, 1394.

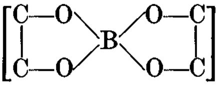
of the ester, or 1 molecule of ester to 7·6 molecules of alcohol. The other esters, including the ethyl ester, do not do this.

Boric Acid and the Poly-alcohols

It has long been known that the very feeble acidity of boric acid can be raised by the addition of certain poly-hydroxy-compounds such as glycerol and mannitol, $CH_2OH(CHOH)_4CH_2OH$, until it can be titrated, using an ordinary indicator. A more delicate test of this change is the conductivity. That of boric acid in water is very small, and that of a poly-alcohol practically zero. But certain poly-alcohols, when added to a boric acid solution, cause an enormous increase in the conductivity, as we should expect from the rise in the acidity. Also when the effective hydroxy-compound is optically active, its rotatory power is greatly increased by the addition of the boric acid. It is evident that these alcohols interact with the boric acid in the solution.

Owing largely to the work of Böeseken, the nature of the reaction has been explained. Only particular hydroxy-compounds behave in this way; glycerol and mannitol will do so, but not mono-hydroxylic alcohols like ethyl alcohol, nor glycol; and of the two cyclo-pentane-1,2-diols the *cis* reacts but not the *trans*. This makes the nature of the reaction clear; it obviously depends on the formation of a ring compound—a cyclic ester—with the group , which is more highly dissociated than boric acid: it is interesting that this structure was suggested by van't Hoff more than sixty years ago.[201]

The complex formed may be monochelate[209] or dichelate (Böeseken[202–3]); this is supported by potentiometric titration (Schäfer[204–5]). This would also explain the increased acidity. The covalent form of an acid with the anion



would involve 3-covalent oxygen and so would be less stable.

Hence a mono-hydroxy-compound cannot react, nor can a di-hydroxy-compound unless the two hydroxyl groups are suitably placed on the same side of the C—C link. This conclusion is supported by the fact that the

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[201] J. H. van't Hoff, *Lagerung der Atome im Raume*, 2nd edn., p. 133.

[202] J. Böeseken and N. Vermaas, *J. Phys. Chem.* 1931, **35**, 1477.

[203] J. Böeseken, N. Vermaas, and A. T. Küchlin, *Rec. Trav.* 1930, **49**, 711.

[204] H. Schafer, *Z. anorg. Chem.* 1941, **247**, 96.

[205] R. E. Rippere and V. K. LaMer, *J. Phys. Chem.* 1943, **47**, 204.

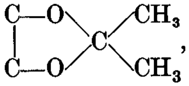
[206] J. Böeseken, *Rec. Trav.* 1921, **40**, 553.

[207] See *Chem. Centr.* 1924, i. 314, 2778.

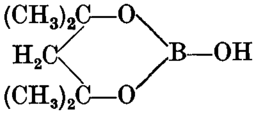
[208] P. H. Hermans, *Z. anorg. Chem.* 1925, **142**, 83.

[209] C. J. Maan, *Rec. Trav.* 1929, **48**, 332.

alcohols which raise the conductivity and the acidity of boric acid in this way are also the alcohols which can condense with acetone[206-7] to form compounds with the grouping

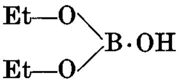


which are much slower to react than the boron compounds (a normal difference between boron and carbon, due probably to the boron not having a complete octet, and therefore readily co-ordinating), and so can be isolated and their structures determined. Sometimes the boron compounds and their salts can be isolated. Thus Hermans[208] has isolated the diacetone-alcohol derivative (m. pt. +7°, b. pt. 228°) of this structure



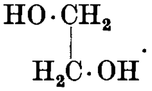
as well as the similar derivative of 2,4-dimethyl-cyclo-hexane-2,4-diol (these form 6-rings); and those of cyclo-pentane-1,2-diol and cyclo-hexane-1,2-diol along with its potassium salt $C_6H_{10}BO_3K$ (the 1,2-diol compounds have of course 5-rings).

That these cyclic compounds are so readily formed when open chain esters like



are not, is an example of the great stability of ring-compounds as such, as is shown in chelate complexes generally.

This reaction has been shown by Böeseken to be of the greatest value as an instrument in stereochemical investigation. Thus the inactivity of glycol with boric acid must be due to the two hydroxyl groups repelling one another and assuming preferentially the *trans*-position



$$\begin{array}{c} HO\cdot CH_2 \\ | \\ H_2C\cdot OH \end{array}.$$

In the same way Böeseken has[210] used this reaction to determine the orientation of the 1,2-diols formed by the oxidation of compounds with a $C=C$ double link. Some singular results have been got; thus ortho-hydroxy-benzyl alcohol raises the conductivity of half-molar boric acid from 29 to 304 gemmhos, but if a methyl group is inserted on the ring in position 5 this effect disappears.[211] So too[212] 1,8-dihydroxynaphthalene has a much greater effect on the conductivity of boric acid than the 1,2

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[210] J. Böeseken, ib. 1928, 47, 683.

[211] J. Böeseken, J. H. Gonggrijp, and A. E. A. van Rhijn, ib. 1938, 57, 1356.

[212] J. Böeseken, J. A. de Bruin, and W. E. van Rijswijk, ib. 1939, 58, 3.

or the 2,3 isomer, perhaps owing to the varying distances between the oxygen atoms.

Boron Compounds of Oxy-acids

Several compounds of this kind have been made which are sometimes called salts, or boryl compounds, or mixed anhydrides. Examples are the phosphate BPO_4 and the arsenate $BAsO_4$. These can be made[213] by evaporating down an aqueous solution of the two acids; they are ultimately hydrolysed by excess of water. Schultze[214] found that they have the same lattice, which is like that of crystobalite; both the boron and the phosphorus or arsenic atoms are surrounded by four oxygens at the points of a tetrahedron, each oxygen belonging both to a boron and to a phosphorus or arsenic tetrahedron.

These are obviously highly associated covalent compounds; in water they are presumably hydrolysed, and in the solid they must be essentially giant molecules of the structures described; they do not seem to dissolve in organic solvents.

In the same way boron trioxide dissolves in sulphuric acid, and various solids have been obtained from the solution.

A number of compounds of the type of $B(O\cdot CO\cdot R)_3$ have been made[216] from boron trioxide and organic acid anhydrides. The best known is the acetate $B(O\cdot CO\cdot CH_3)_3$, made by heating the trioxide with acetic anhydride (though not with acetic acid). It melts at 147-8°[217]; it is soluble in chloroform and in acetone but only slightly in benzene. It dissociates completely into its components in the vapour state. It has all the reactions of a mixed anhydride; with alcohols it gives the boric esters. Similar compounds of other carboxylic acids have been prepared by Pictet.[215-16] The supposed boro-acetic anhydride of Pictet and Geleznoff[216] has been shown by Dimroth[218] to be the pyroboric derivative $(AcO)_2B—O—B(OAc)_2$; it begins to decompose at 146°, melts at 150–2°, and by heating in a vacuum at 150-6° is converted into metaboric acetate $O{=}B—O—CO—CH_3$.

BORON SULPHIDES

The trisulphide B_2S_3 is the only binary sulphide of boron whose existence is proved. This can be made by melting the components together (Berzelius, 1824), or by passing sulphur vapour over boron at 1200°,[219] or by heating the compound $H_2B_2S_4$ described below.

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[213] E. Gruner, *Z. anorg. Chem.* 1934, **219**, 181.

[214] G. E. R. Schultze, *Z. physikal. Chem.* 1934, B **24**, 215.

[215] A. Pictet and G. Karl, *Bull. Soc.* 1908, [4] **3**, 1121.

[216] A. Pictet and A. Geleznoff, *Ber.* 1903, **36**, 2219.

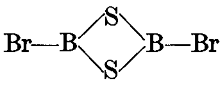
[217] L. Kavohec, *Z. physikal. Chem.* 1939, B **43**, 109.

[218] O. Dimroth, *Ann.* 1925, **446**, 97.

[219] H. Moissan, *Ann. Chem. Phys.* 1895, [7] **6**, 312.

Boron trisulphide B_2S_3 forms colourless crystals which begin to melt at 310°; it has some vapour pressure at the ordinary temperature and sublimes completely at 200°. It burns if it is heated in air or chlorine. It is at once hydrolysed by water to boric acid and hydrogen sulphide; with hydroxylic compounds it reacts in the same way, but it is insoluble in carbon bisulphide and in benzene.

The hydrogen compound B_2S_3,H_2S, or $H_2B_2S_4$, was discovered by Stock and Poppenberg.[220] Hydrogen sulphide will not react with boron trichloride, but it will with the tribromide, because the latter reaction is exothermic but the former endothermic. If hydrogen sulphide is passed into a solution of boron tribromide in carbon bisulphide or benzene at the ordinary temperature, hydrogen bromide is evolved. It can be shown[221] that there is first formed a compound B_2S_3,BBr_3 or $B_2S_2Br_2$, which can be isolated; this reacts much more slowly, but after some days all the bromine is removed as hydrogen bromide, and on evaporation of the solvent white crystals of $H_2B_2S_4$ separate. This is soluble (unlike boron trisulphide) in carbon disulphide and in benzene (about 20 per cent. in warm benzene), and its molecular weight as determined by freezing-point in benzene is that of $H_2B_2S_4$. The structures of these compounds which do not seem to have the boron atoms attached to one another or to the hydrogen in the latter are presumably



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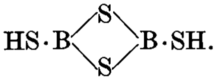

Boron selenide B_2Se_3 was made from its elements by Sabatier[222] and by Moissan.[219] It behaves just like the sulphide, but is less volatile.

According to Moissan[219] fused tellurium does not combine with boron.

BORON HALIDES

All four halogens form tri-halides with boron, and there is a second chloride B_2Cl_4. Also a variety of compounds are known in which the valencies of the boron are partly satisfied by halogens, such as the alkylboron halides already described (p. 377), and others to be discussed later. The halides have the following melting- and boiling-points:

	BF_3	BCl_3	B_2Cl_4	BBr_3	BI_3
B. pt. . . .	−101°	+12·5°	*ca.* +55° 0°/40 mm.	91°	210°
M. pt. . . .	−130·7°	−107°	−100°	−46°	+43°

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[220] A. Stock and O. Poppenberg, *Ber.* 1901, **34**, 399.

[221] A. Stock and M. Blix, ib. 3039.

[222] P. Sabatier, *Bull. Soc.* 1891, [3] **6**, 219.

Boron Trifluoride, BF_3

This can be made by heating calcium fluoride with boron trioxide or potassium borofluoride[223] in concentrated sulphuric acid. Unless the materials used are quite free from silicon the product contains silicon tetrafluoride, which cannot be separated by fractional distillation (SiF_4 subl. −95·7°), but only by passing the vapours over boron trioxide at 800°, when the silicon tetrafluoride gives boron trifluoride and silica[224]; but a really pure boron trifluoride can only be got from materials free from silicon.

Boron trifluoride boils at −101°[224] and melts at −130·7°. The Trouton constant of 26·1 is very high for a non-associated liquid (but that of SiF_4 is 25·1); the vapour density of boron trifluoride gives no indication of double molecules down to −75°.[225] Electron diffraction shows that the molecule in the vapour has a plane structure with angles of 120°, the B—F distance being 1·31 A[226] (1·30 A[227]) (theory for B—F 1·52: perhaps there is back-co-ordination). This structure is supported by the infra-red spectrum[228-9] and the Raman spectrum[230]; Gage and Barker[229] calculate from the infra-red spectrum a B—F distance of 1·29 A.

Boron trifluoride is very soluble in water, and like silicon tetrafluoride is only partially hydrolysed, forming a good deal of fluoroboric acid HBF_4; if the solution is distilled the trifluoride comes off first and the complex acid afterwards. It is soluble in most organic liquids; its solubility in *n*-pentane is about 30 g. per litre at 55° under 3 atm. pressure[232]; but it is remarkable that it is quite insoluble below its boiling-point in CF_2Cl_2, and only partially miscible at —130° with CF_3Cl or CF_4.[231] It forms co-ordination compounds with a very large number of organic nitrogen and oxygen compounds such as ammonia, amines, hydrocyanic acid, ethers, aldehydes, and ketones. (See further under boron complexes.) It is no doubt owing to this power of co-ordination that boron trifluoride is so effective a catalyst for a great variety of organic reactions; these may be briefly discussed.

Catalytic Power of Boron Trifluoride

Our knowledge of this is mainly due to the work of Meerwein[233] in Germany and of Sowa and Nieuwland in America.

[223] E. Krause and R. Nitsche, *Ber.* 1921, **54**, 2784.

[224] O. Ruff and O. Bretschneider, *Z. anorg. Chem.* 1932, **206**, 59.

[225] W. Fischer and W. Weidemann, ib. 1933, **213**, 106.

[226] H. A. Lévy and L. O. Brockway, *J.A.C.S.* 1937, **59**, 2085.

[227] H. Braune and P. Pinnow, *Z. physikal. Chem.* 1937, B **35**, 239.

[228] C. R. Bailey, J. B. Hale, and J. W. Thompson, *Proc. Roy. Soc.* 1937, **161**, 107.

[229] D. M. Gage and E. F. Barker, *J. Chem. Phys.* 1939, **7**, 455.

[230] D. M. Yost, D. de Vault, T. F. Anderson, and E. N. Lassettre, ib. 1938, **6**, 424.

[231] H. S. Booth and J. H. Walkup, *J.A.C.S.* 1943, **65**, 2334.

[232] G. N. Cade, R. E. Dunn, and H. J. Hopp, ib. 1946, **68**, 2454.

[233] H. Meerwein, *Ann.* 1927, **455**, 227.

As Meerwein has pointed out,[238] its behaviour is very like that of aluminium chloride in the Friedel-Crafts reaction, except that in place of organic halides it involves the use of oxygen compounds—alcohols, ethers, acids, esters—and it splits off water, with which it co-ordinates, instead of hydrogen chloride. The resemblance between the actions of the two halides undoubtedly goes very far; with both the catalytic power is primarily due to the loosening of atomic linkages in the organic molecule through co-ordination with the halide. Boron trichloride, which seems to have a much smaller catalytic power than the trifluoride, is also less ready to form co-ordination compounds in general, perhaps because the chlorine is less reluctant than the fluorine to form 'back-co-ordination' links; aluminium fluoride cannot be used as it is a high-melting salt.

Examples of the catalytic power of boron trifluoride are very numerous,* and may be divided into a series of groups.

A. *Formation of esters.* Boron trifluoride promotes their formation from alcohols + acids[234,242] from ethers + acids[237]; and from alcohols + amides.[240]

B. *Reactions in which an alkyl or an acyl group passes from oxygen to carbon.* Acetic anhydride is converted by the trifluoride into the BF_3 compound of diacetoacetic anhydride $(Ac_2CH \cdot CO)_2O$[238]; with acetone it forms β-diketones[262]; alkyl-phenyl ethers give alkyl phenols[235,239,251]; alkyl ethers with esters of salicylic acid and similar compounds give alkyl-phenyl derivatives[248,259,264,261]; acids and anhydrides react with benzene to give acyl-benzenes and water[243,256a]; alcohols react with benzene[247,254,257,263] or naphthalene[250,260,262] to give alkyl benzenes and alkyl naphthalenes.

* A summary of the subject has been given by Kästner.[253]

[234] H. D. Hinton and J. A. Nieuwland, *J.A.C.S.* 1932, **54**, 2017.
[235] F. W. Sowa, H. D. Hinton, and J. A. Nieuwland, ib. 2019.
[236] Id., ib. 3694.
[237] G. F. Hennion, H. D. Hinton, and J. A. Nieuwland, ib. 1933, **55**, 2857.
[238] H. Meerwein, *Ber.* 1933, **66**, 411.
[239] F. J. Sowa, H. D. Hinton, and J. A. Nieuwland, *J.A.C.S.* 1933, **55**, 3402.
[240] F. J. Sowa and J. A. Nieuwland, ib. 5052.
[241] W. J. Croxall, F. J. Sowa, and J. A. Nieuwland, ib. 1934, **56**, 2054.
[242] T. B. Dorris, F. J. Sowa, and J. A. Nieuwland, ib. 2689.
[243] H. Meerwein and D. Vossen, *J. prakt. Chem.* 1934 [ii] **141**, 149.
[244] S. J. Slanina, F. J. Sowa, and J. A. Nieuwland, *J.A.C.S.* 1935, **57**, 1547.
[245] W. Croxall, F. J. Sowa, and J. A. Nieuwland, ib. 1549.
[246] V. N. Ipatiev and A. v. Grosse, ib. 1936, **58**, 2339.
[247] J. F. McKenna and F. J. Sowa, ib. 1937, **59**, 470.
[248] W. J. Croxall, F. J. Sowa, and J. A. Nieuwland, *J. Org. Chem.* 1937, **2**, 253.
[249] T. B. Dorris, F. J. Sowa, and J. A. Nieuwland, *J.A.C.S.* 1938, **60**, 656.
[250] C. C. Price, J. M. Ciskowski, ib. 2499.
[251] A. J. Kolka and R. R. Vogt, ib. 1939, **61**, 1463.
[252] C. C. Price and M. Meister, ib. 1595.
[253] D. Kästner, *Angew. Chem.* 1941, **54**, 273, 296.
[254] R. L. Burwell and S. Archer, *J.A.C.S.* 1942, **64**, 1032.
[255] C. R. Hauser and D. S. Breslow, ib. 1940, **62**, 2389.
[256] C. R. Hauser and J. T. Adams, ib. 1942, **64**, 728.
[256a] H. G. Walker and C. R. Hauser, ib. 1946, **68**, 2742.

BF_3 will also catalyse the introduction of alkyl into an acidic CH_2, as in acetoacetic ester+alcohols or ethers.[255] Even a tertiary alkyl (with tertiary butyl alcohol or ether) can be put into aceto-acetic ester with BF_3, though it is usually very difficult to introduce it into an active methylene group.[256,258]

C. *Direct addition of olefines* to form alkyl derivatives as in:

$$H_2C{=}CH_2 + H{-}\overset{|}{\underset{|}{C}}{-}R = H_3C{-}CH_2{-}\overset{|}{\underset{|}{C}}{-}R$$

or

$$H_2C{=}CH_2 + H{-}O{-}R = H_3C{-}CH_2{-}O{-}R.$$

Propylene can be added to acids to form their isopropyl esters[241,264]; ethylene[246] and propylene[244,215] react with benzene to give ethyl and isopropyl benzene; in the same way propylene can be added to phenol to form the ether.[236.245] It will also catalyse the polymerization of olefines,[265] and the addition of hydrogen fluoride to the C=C link.[256b]

D. Boron trifluoride also resembles aluminium chloride in its power of *catalysing isomeric change*. It has been shown to hasten the Beckmann reaction, the benzidine transformation, the change from diazoamino to aminoazo, that of phenyl acetate to *p*-hydroxyacetophenone[238] and the equilibrium of *cis* and *trans* stilbene[252] (93·1 per cent. *trans*); it is interesting to notice that boron trifluoride does not promote the change in ethyl maleate, presumably because the fluoride attaches itself to an oxygen of the carboxyl group rather than to the double carbon link (see further, ref. [266]).

It has been shown[249] that difluoroboric acid $H[BF_2(OH)_2]$ has a similar but much weaker catalytic power, for example, in changing a mixture of phenol and ethylene to anisole.

Boron Trichloride, BCl_3

Boron trichloride can be made by passing chlorine over heated boron (Davy, 1809) or over various alloys of boron; or by heating boron with a metallic chloride, etc.; or by the action of phosphorus pentachloride or oxychloride on boric oxide: the first method is probably the best. The crude product is freed from chlorine by prolonged shaking with mercury and from hydrogen chloride and silicon tetrachloride by repeated fractionation[267-8]; it has been used, as has also the bromide, for determining

[256b] A. L. Henne and R. C. Arnold, *J.A.C.S.* 1948, **70**, 758.
[257] G. F. Hennion and V. R. Pieronek, ib. 1942, **64**, 2751.
[258] J. T. Adams, B. Abramovitch, and C. R. Hauser, ib. 1943, **65**, 552.
[259] G. F. Hennion and R. A. Kurtz, ib. 1001.
[260] G. F. Hennion and L. A. Auspos, ib. 1603.
[261] C. E. Welsh and G. F. Hennion, ib. 1941, **63**, 2603.
[262] J. T. Adams and C. R. Hauser, ib. 1945, **67**, 284.
[263] G. Vermillion and M. A. Hill, ib. 2209.
[264] S. F. Zavgorodni, *J. Gen. Chem. Russ.* 1944, **14**, 270.
[265] A. G. Evans, G. W. Meadows, and M. Polanyi, *Nature*, 1946, **158**, 94.
[266] W. J. Monacelli and G. F. Hennion, *J.A.C.S.* 1941, **63**, 1722.
[267] A. Stock and O. Priess, *Ber.* 1914, **47**, 3109.
[268] A. Stock and E. Kuss, ib. 1923, **56**, 1463.

the atomic weight of boron.[269] It boils at 12·5° and freezes at 107°. Its vapour density is normal, and it is practically a non-conductor of electricity.

The structure of the molecule has been shown by electron diffraction[226] to be the same as that of the trifluoride (p. 392), with the B—Cl distance 1·73 A (theory 1·87). The Raman spectrum supports this.[270]

Boron trichloride is very readily hydrolysed by water to boric acid, and by alcohols to boric chloro-esters. It forms addition compounds with great ease, though not quite so easily as the fluoride. It dissolves chlorine, but it does not react with it, nor with ozone.

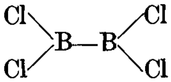
If it is heated with calcium fluoride to 200°, or treated with antimony trifluoride and pentachloride at any temperature down to −78°, it is converted wholly into the trifluoride without the production of any mixed compounds; also if a mixture of boron trifluoride and trichloride is heated or subjected to the electrical discharge no rearrangement takes place.[271]

Boron Subchloride, B_2Cl_4

This, the only known binary halide of boron that is not of the BX_3 type, was obtained by Stock[272] by the action of an electric arc with a zinc anode in boron trichloride vapour; the product (a very small yield) is purified by fractionation.

B_2Cl_4 melts at −98°, and has a vapour pressure of 75 mm. at +10° (extrapolated b. pt. +55°). The vapour density is normal. In the absence of air it slowly decomposes to boron and boron trichloride. It dissolves in water with a minute evolution of hydrogen to give a solution which has strong reducing properties but does not give the black precipitate with a nickel salt which is characteristic of the hypoborates.

It is clear that this substance has the structure



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it is the 'acid chloride' of the sub-boric acid already described, whose structure has been established by synthesis. It obviously forms this acid when it is dissolved in water.

Boron Tribromide, BBr_3

This is very similar to the chloride, and is made in the same way by passing bromine vapour over boron, but at a rather higher temperature, a dull red heat.[273] M. pt. −46°, b. pt. +91°; crit. T. 300°[277]: molecular weight normal, not only in the vapour but also by the freezing-point in benzene.[273]

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[269] O. Honigschmid and L. Birckenbach, ib. 1467.

[270] T. F. Anderson, E. N. Lassettre, and D. M. Yost, *J. Chem. Phys.* 1936, 4, 703.

[271] H. S. Booth and S. G. Frary, *J.A.C.S.* 1943, 65, 1836.

[272] A. Stock, A. Brandt, and H. Fischer, *Ber.* 1925, 58, 653.

[273] A. Stock and E. Kuss, ib. 1914, 47, 3113.

Electron diffraction[226] shows it to be of the same type as the fluoride and chloride (p. 395), with the B—Br distance 1·87 A.U. (theory B—Br 2·02 B=Br 1·80).

F. L. Benton and T. E. Dillon[278] find that ethers react with BBr_3 to give good yields of Alk·OH+Alk·Br. Ar—O—Alk gives good yields of Ar·OH+Alk·Br.

Boron Tri-iodide, BI_3, is similar; it can be got by passing hydrogen iodide mixed with boron trichloride[274] or tribromide[275] vapour through a red-hot tube.

It forms colourless needles, which melt at 43° and boil undecomposed at 210°; it is a non-conductor.[274] It is soluble in carbon bisulphide and tetrachloride, and in benzene. It is decomposed by light, and violently hydrolysed by water.

Mixed Trihalides

According to Besson,[275] if hydrogen iodide acts on boron tribromide at 300-400°, a mixture of the trihalides BBr_2I (b. pt. 125°), $BBrI_2$ (b. pt. 180°) and BI_3 is formed.

Mixed Halide Derivatives

Many of these compounds have already been discussed: the halo-hydrides (B—H, p. 363); the alkyl and aryl boron halides (B—C, p. 377); and the hydroxyhalides, i.e. the fluoroborates (B—O, p. 385). The 3-covalent oxyhalides and their esters remain to be discussed.

Oxyhalides. No simple oxyhalides of boron have been isolated but there is reason to think that they exist. Baumgarten and Bruns[279] found that boron trifluoride acts on boron trioxide to produce a volatile oxyfluoride $(BOF)_n$, probably trimeric, with a B_3O_3 6-ring; they confirmed this later,[284] showing that it is formed quantitatively from alumina and boron trifluoride at 450°. Wiberg and his co-workers[280-1] have obtained an oxychloride, though not in a pure state, from the dichloro-boron alkyloxides $Cl_2B{\cdot}OCH_3$ and $Cl_2B{\cdot}OC_2H_5$ by heating them for some time to 50-70°, when they break up into the alkyl halide and the oxyhalide Cl·BO, which, however, at this temperature changes largely into the trichloride (which evaporates) and boron trioxide, so that the actual product was a white solid which contained by analysis about 50 per cent. each of ClBO and BCl_3, and was at once hydrolysed by water.

Halide Esters

A better known series is that of the alkyloxyhalides $hal_2B{\cdot}O{\cdot}Alk$ and $hal{\cdot}B(O{\cdot}Alk)_2$, of which the fluorides were examined by Gasselin[282]

[274] H. Moissan, *C.R.* 1891, **112**, 717; 1892, **115**, 204.

[275] J. A. Besson, ib. 1891, **112**, 1001; 1892, **114**, 543.

[277] K. Höjendahl, 5 *Nordiske Kemikermöde*, 1939, 209.

[278] *J.A.C.S.* 1942, **64**, 1128.

[279] P. Baumgarten and W. Bruns, *Ber.* 1939, **72**, 1753.

[280] H. Ramser and E. Wiberg, ib. 1930, **63**, 1136.

[281] E. Wiberg and W. Sütterlin, *Z. anorg. Chem.* 1931, **202**, 1.

and the chlorides especially by Wiberg and Sütterlin.[281,283] Both kinds can be made by the action of the trihalide on the necessary alcohol, or by heating the compound of the halide with ether.

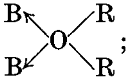
The boiling-points and [melting-points] of these compounds[281-2] are:

Boiling-points and [melting-points]

BF_3	−101° [−130·7°]	BCl_3	12·5° [−107°]
BF_2OCH_3	+87° [41·5°]	BCl_2OCH_3	58·0° [−15°]
$BF(OCH_3)_2$	+53°	$BCl(OCH_3)_2$	74·7° [−87·7]
BF_2OEt	82° [23°]	BCl_2OEt	77·9°
$BF(OEt)_2$	78°	$BCl(OEt)_2$	112·3°
$B(OCH_3)_3$	68·7°		
$B(OEt)_3$	117·4°		

All these are monomeric in the vapour, and readily hydrolysed by water to boric acid, hydrofluoric or hydrochloric acid, and alcohol; the Trouton constants of the chlorides are from 21·6 to 22·9.

Not very much is known of the fluorides (the boiling-points seem unusual); but the formation and decomposition of the chlorides have been shown by Wiberg and Sütterlin[281,283] to be determined by the co-ordination, which depends on what the three groups already attached to the boron are. With ether, for example, the dichloro-alkylate like the trichloride can co-ordinate, but the monochloro-dialkylate like the trialkylate (the boric ester) cannot. The ether compound of the dichloro-compound has the unusual composition of $(BCl_2OR)_2,OR_2$, suggesting that the (ether) oxygen is 4-covalent



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it is very unstable, melts below 0°, and even at this temperature rapidly redistributes itself to the monochloro-dialkylate $BCl(OR)_2$ and the etherate of the trichloride BCl_3,OR_2.

Though the reaction of boron trichloride with an alcohol is quite violent, it is subject to two curious limitations. (1) If one mole of alcohol is used for one mole of boron trichloride, there is complete conversion into the dichloro-compound Cl_2BOR and HCl, instead of a mixture of products being formed, as we might have expected. This might mean that the first chlorine is very much more easily replaced than the second, but there is much greater support for the alternative view that what reacts is the complex BCl_3,ROH (which in fact reacts so readily that it cannot be isolated) and so there is in this mixture no free alcohol to react with the BCl_2OR which is formed from the addition compound by loss of hydrogen chloride; this is supported by the fact that the very strong co-ordination compound $Cl_3B{\leftarrow}N(CH_3)_3$, which cannot co-ordinate with alcohol, does not react with it.

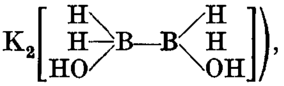
[282] V. Gasselin, *Ann. Chim. Phys.* 1894, [7] 3, 5 (*J.C.S. Abstr.* 1895, **1**, 451).
[283] E. Wiberg and W. Sütterlin, *Z. anorg. Chem.* 1931, **202**, 22, 31, 37.
[284] P. Baumgarten and W. Bruns, *Ber.* 1941, **74**, 1232.

(2) The other restriction on these changes is that in the energetic reaction of alcohol with boron trichloride not more than two of the chlorine atoms are replaced by alkyloxy-groups. The reason is evidently that the trichloride can co-ordinate with alcohol, and so can the dichloro-compound BCl_2OR; its co-ordination product with the alcohol accordingly goes to the monochloro-derivative $ClB(OR)_2$; but this as we know *cannot* (above, p. 397) any longer co-ordinate, and so no further reaction takes place, and no boric ester is formed.

BORON COMPLEXES

One of the strongest tendencies of boron is to make up the sextet which its three normal covalencies give it to an octet, the maximum valency group of a first-period element.

Strictly speaking, the complexes of boron include those complex anions which are formed by the addition of electrons either to the abnormal 4-covalent hydrides and their derivatives (for example, $Na_2[H_3B—BH_3]$ (p. 348), or the hypoborates as



or to the triaryls, as in $Na[B(C_6H_5)_3]$. In all these the co-ordination (if we can call it so) does not alter the number of covalent links formed by the boron, though it may alter their character. These have already been discussed.

In more normal types of complex the boron atom gains two electrons by co-ordination, and at the same time increases its covalency from 3 to 4. These can be classified according to the nature of the donor atom, which can be (1) hydrogen, (2) carbon, (3) nitrogen or phosphorus, (4) oxygen (and possibly sulphur), (5) halogens.

The formation of chelate rings seems to occur only with oxygen.

1. *Hydrogen*

There can be little doubt that lithium borohydride (p. 366) is an ionized compound, $Li[BH_4]$, and so has a complex anion in which hydrogen acts as a donor, completing the series

$$[BH_4]^- \qquad CH_4 \qquad [NH_4]^+$$

2. *Carbon*

Attempts to isolate complexes of the type of $M[BR_4]$ (where R is a hydrocarbon radical) analogous to the compounds $M[AlR_4]$ (p. 429) have failed. But Johnson and his colleagues[285] have obtained definite evidence of the occurrence of such complexes in solution. If one mole of boron tributyl is added to an ethereal solution of one mole of phenyl magnesium bromide, heat is evolved, and the liquid separates into two layers, the

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[285] J. R. Johnson, H. R. Snyder, and M. G. van Campen, *J.A.C.S.* 1938, 60, 115.

upper (ethereal) layer containing half the boron tributyl; if magnesium diphenyl is used instead, the whole of the boron is found in the lower layer. This lower layer must contain the complex anion $[C_6H_5 \cdot B(C_4H_9)_3]^-$, for it is slowly hydrolysed by water, while the Grignard reagent is hydrolysed at once, and the tributyl boron not at all. Moreover, the cation must be $[Mg \cdot C_6H_5]^+$ the reactions being

$$BBu_3 + 2\,C_6H_5MgBr = [Mg \cdot C_6H_5][C_6H_5 \cdot BBu_3] + MgBr_2$$

$$BBu_3 + Mg(C_6H_5)_2 = [Mg \cdot C_6H_5][C_6H_5 \cdot BBu_3].$$

Lithium phenyl also reacts with the borine very vigorously, lithium butyl and butyl magnesium bromide less so, and zinc dibutyl not at all. The failure of Thomson and Stevens[286] to get evidence of the occurrence of this reaction is due to their having used ligroin as the solvent, and not ether.

A tetra-alkyl complex of this type has been isolated by Schlesinger and Brown[287]; they found that lithium ethyl absorbs gaseous boron trimethyl to give a solid of the composition of $Li[BMe_3Et]$, which is unexpectedly soluble in benzene and can be recrystallized from it; it dissolves in water and the solution slowly evolves a gas.

A co-ordination compound with carbon of a different kind is the carbonyl $H_3B \leftarrow C \equiv O$, already described (p. 350), among the B—H compounds.

3. *Nitrogen*

In co-ordination with boron the strongest donor is nitrogen, which is followed by oxygen and this by the halogens beginning with fluorine (which is perhaps as strong as oxygen). Phosphorus and arsenic will also co-ordinate, but much less strongly than nitrogen.

The nitrogen complexes are nearly all ammines. The derivatives of tertiary amines are especially well known, since ammines with hydrogen on the nitrogen often decompose within the molecule and cannot be isolated. The replacement of the hydrogen in ammonia by alkyls weakens the co-ordination to boron as it does to other acceptors; thus, when ammonia is passed into a solution of boron trifluoride in trimethylamine the compound $F_3B \leftarrow NH_3$ separates, in spite of the excess of trimethylamine present.[288] Aniline, dimethylaniline, pyridine, and other amines will also co-ordinate with boron. The nitrogen complexes other than the ammines are practically confined to a few derivatives of hydrocyanic acid and certain nitriles.

The strength of the co-ordination also depends on the groups already attached to the boron. In general it is strongest with the hydride, the trialkyls, and the trifluorides, weaker with the chlorides, and weakest or non-existent with the boric esters. This is to be expected, since it is in this order that the back-co-ordination of the attached atoms increases.

[286] T. Thomson and T. S. Stevens, *J.C.S.* 1933, 556.

[287] H. I. Schlesinger and H. C. Brown, *J.A.C.S.* 1939, 61, 3429.

[288] C. A. Kraus and E. H. Brown, ib. 1929, 51, 2690.

The reactivity of boron compounds is greatly diminished by conversion into co-ordination complexes. In fact it is clear that the ordinary reactions of compounds of boron are due to co-ordination with the reactants (as happens with other elements too), and if the boron octet is already made up by a strong donor which does not itself react further, the reactivity of the molecule is destroyed. Thus the ammines of the spontaneously inflammable boron trialkyls $AlK_3B \leftarrow NH_3$ are not oxidized by air (Frankland), nor is the ammine of boron triphenyl[289]; and we have seen that the reactivity of the alkyloxy-halides of boron is wholly determined by the co-ordination.

The ammines can be classified according to the boron compounds from which they are derived; a change in the donor molecule from ammonia to a tertiary amine has a much smaller effect on the properties, apart from the intra-molecular reactions which can occur with unreplaced hydrogen.

Ammines of Trialkyl Boron

The boron trialkyls form ammines with great ease. The trimethyl boron compound $Me_3B \leftarrow NH_3$ was discovered by Frankland, and re-examined by Stock[290]; it is formed readily and quantitatively from its components at low temperatures; it melts at 56° and boils at 110°. At low temperatures (25-35°) the vapour, whose pressure is very small, is not more than 90 per cent. dissociated; freezing-points in benzene indicate that there it is practically undissociated. It is not oxidized by air, even in benzene.

The ethyl compound seems to be similar, but it is a liquid (Frankland).

H. C. Brown and his colleagues[293] have examined the relations between the nature of the base and the stability of the ammine, which are complicated; for example, trimethylamine forms a more stable complex than pyridine with diborane and with boron trifluoride (as it does with hydrogen bromide), but a less stable one with boron trimethyl. Later[294] they found a remarkable relation between the degree of dissociation of the boron trimethyl complex in the vapour at 90° (this is 71 per cent. for the trimethylamine complex at 150 mm.) and K_{ion} the thermodynamic dissociation constant of the base in water. The following are the values of K_{vap}, the dissociation constant in the vapour, and K_{ion}[295]:

Base	K_{vap} *at* 90°	$\left.\begin{matrix}K_{\text{ion}}/25° \\ \textit{in water}\end{matrix}\right\} \times 10^5$
NH_3	2·7	1·79
NMe_3	0·197	6·31
NH_2Me	0·0176	42·5
$NHMe_2$	0·0099	59·9

For further confirmatory work see references [296-8].

[289] E. Krause, *Ber.* 1924, **57**, 813.

[290] A. Stock and F. Zeidler, ib. 1921, **54**, 531.

[291] E. Krause and H. Polack, ib. 1928, **61**, 271.

[292] E. Krause and P. Nobbe, ib. 1930, **63**, 934.

Boron tricyclohexyl and tribenzyl have a curious behaviour in their ammines. Boron tricyclohexyl forms the usual 1 : 1 ammines with ammonia, pyridine, and piperidine, but they are exceptionally highly dissociated; the ammonia complex (m. pt. 100°) loses all its ammonia *in vacuo* at 100°, and all the ammines are rapidly oxidized by air. The ammines of tribenzyl boron[292] are similar, but here there is a marked gradation as we go from ammonia to a tertiary amine; the ammonia compound is only slowly oxidized by air, the methylamine compound fairly easily, the trimethylamine compound very rapidly. This shows that, as usual, the replacement of hydrogen by alkyl weakens the donor power of the ammonia.

Ammines of the boron triaryls are very similar to the trialkyl derivatives. Boron triphenyl[289] forms the ammine if its ethereal solution is treated with ammonia gas, which incidentally is a proof that the co-ordination is stronger to nitrogen than to oxygen; the compounds with methylamine, ethylamine, dimethylamine (m. pt. 186°) and trimethylamine (m. pt. 136°) are made in the same way, which is a stronger proof of the same thing. They are all stable to air. Similar compounds with aniline, pyridine, quinoline, piperidine, &c., are known, and other triaryls behave in the same way.[291-2]

Ammines of the Boron Trihalides

Boron trifluoride and trichloride give much more stable ammines than the trialkyls or triaryls. The trifluoride complexes are best made in ether[299]; $F_3B \leftarrow NH_3$ is a solid soluble in liquid ammonia and in all the ethylamines; if its solution in triethylamine is evaporated, the original $F_3B \leftarrow NH_3$ remains, showing that ammonia is much more firmly attached than triethylamine. Similarly Burg and Green have shown[300] that the replacement of one fluorine in $Me_3N \rightarrow BF_3$ by CH_3 greatly weakens the $N \rightarrow B$ link; at 230° the dissociation of $Me_3N \rightarrow BF_3$ is immeasurably small, while that of $Me_3N \rightarrow BMeF_2$ is 90 per cent. A second methyl has a smaller effect and a third a still smaller (but still perceptible) one. The heat of formation of the $N \rightarrow B$ link in the trimethylamine complex is 23·1 k.cals. for BF_2Me, and 18·3 for $BFMe_2$, and about 14 k.cals. for BMe_3.[301]

The simple compound $F_3B \leftarrow NH_3$ sublimes at 180° with some decomposition; it is in many ways unstable, owing to the tendency for the ammonia to react with the fluorine to give such amino-compounds as BF_2NH_2. Thus in liquid ammonia sodium causes some evolution of

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[293] H. C. Brown, H. I. Schlesinger, and S. Z. Cardon, *J.A.C.S.* 1942, **64**, 325.

[294] H. C. Brown and H. Bartholomay, *J. Chem. Phys.* 1943, **11**, 43.

[295] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* 1941, **177**, 499.

[296] H. C. Brown, M. D. Taylor, and M. Gerstein, *J.A.C.S.* 1944, **66**, 431.

[297] H. C. Brown, H. Bartholomay, and M. D. Taylor, ib. 435.

[298] H. C. Brown and M. D. Taylor, ib. 846.

[299] C. A. Kraus and E. H. Brown, ib. 1929, **51**, 2690.

[300] A. B. Burg and A. A. Green, ib. 1943, **65**, 1838.

[301] H. I. Schlesinger, N. W. Flodin, and A. B. Burg, ib. 1939, **61**, 1078.

hydrogen, indicating the presence of ammonium fluoride; the behaviour with lithium of the ethylamine compound $F_3B \leftarrow NH_2Et$ in ethylamine solution shows that here the ammonolysis is complete. But the solid which we have called $F_3B \leftarrow NH_3$ must really have this constitution, and cannot be $BF_2NH_2 + NH_4[BF_4]$ since it is wholly soluble in triethylamine, which does not dissolve ammonium salts.

$F_3B \leftarrow NH_3$: subl. 180° with some decomposition. $F_3B \leftarrow NH_2Et$: m. pt. 89°; the boiling-point in ether indicates some slight association. $F_3B \leftarrow NHEt_2$: m. pt. 160° (the melting-points are curious); $F_3B \leftarrow NEt_3$: m. pt. 29·5°; b. pt. 80°/3 mm.

In benzene the freezing-points indicate, according to earlier measurements, that it is monomeric; but lately[306] Bright and Fernelius have found cryoscopically that both $Me_3N \cdot BF_3$ and $Me_2\Phi N \cdot BF_3$ are dimeric in 1 per cent. solution in benzene. It is slowly decomposed by air.

Pyridine combines with boron trifluoride in benzene solution with evolution of heat to give $F_3B \leftarrow py$[302], m. pt. 45°, b. pt. about 300°; monomeric in benzene by the f. pt. The vapour density shows 18 per cent. dissociation at 313° and 63 per cent. at 356°, corresponding to a heat of formation of 50·6 k.cals. It is soluble in benzene, pyridine, and hot absolute alcohol; if it is heated with 95 per cent. alcohol it is converted into the borofluoride $(pyH) \cdot [BF_4]$. Other amines will co-ordinate with BF_3 in the same way.[307]

Boron trichloride forms similar ammines. $Cl_3B \leftarrow NMe_3$ was made by Wiberg and Sütterlin[303] from the components at $-40°$; much heat is evolved, and the product is always 1:1 whatever proportions are used. It is extremely stable; it melts at 243° and sublimes in a high vacuum. Water and alcohol, which react with the trichloride in ether, have no action on the ammine.

Aniline reacts violently with boron trichloride, and in benzene solution at $-15°$ gives $\Phi NH_2 \cdot BCl_3$[304]; it melts at about 100°, and decomposes at 120°. It is less stable than most ammines of the trihalides—much less stable than $Cl_3B \leftarrow NMe_3$—and reacts violently with water. $\Phi NMe_2 \cdot BCl_3$ melts at 145°; it is stable when dry, but rapidly hydrolysed by water.

Boron tribromide combines with ammonia, but only at temperatures at which the reaction goes farther to give amides. Hence no simple ammines of the tribromide have been isolated.[305] The trioxy-compounds, the boric esters, on the other hand, will not co-ordinate at all. Intermediate compounds have of course an intermediate behaviour (see refs.[308-9]).

[302] P. A. van der Meulen and H. A. Heller, *J.A.C.S.* 1932, **54**, 4404.

[303] E. Wiberg and W. Sütterlin, *Z. anorg. Chem.* 1931, **202**, 35.

[304] R. G. Jones and C. R. Kinney, *J.A.C.S.* 1939, **61**, 1378.

[305] E. Pohland, *Z. anorg. Chem.* 1931, **201**, 285.

[306] J. R. Bright and W. C. Fernelius, *J.A.C.S.* 1943, **65**, 735.

[307] A. B. Burg and La V. L. Martin, ib. 1635.

[308] D. L. Yabroff and G. E. K. Branch, ib. 1933, **55**, 1663.

[309] A. B. Burg, ib. 1940, **62**, 2228.

[310] E. Pohland and W. Harlos, *Z. anorg. Chem.* 1932, **207**, 242.

Methyl boric acid, $CH_3\cdot B(OH)_2$,[309] has not itself been found to give ammines, but the trimeric anhydride $(CH_3\cdot BO)_3$, which contains the B_3O_3 6-ring, combines with trimethylamine to give $(CH_3\cdot BO)_3NMe_3$, a white solid melting at 67° and with an extrapolated b.pt. of 131°, whose vapour is 85 per cent. dissociated at 100°. A corresponding ammonia compound occurs, and also a less stable one with two, $(CH_3BO)_3(NH_3)_2$, but none with 3 NH_3 or 2 NMe_3, the reaction going farther with ammonia than with trimethylamine. Thus in these B—O compounds, so long as one carbon is attached to the boron, the latter can act as an acceptor.

The trioxy-derivatives, the boric esters, do not combine with amines or ethers, nor are they oxidized by oxygen. The boron in these compounds, owing no doubt to the strong back-co-ordination of the oxygen, does not seem to have any acceptor power left.

Cyanide Complexes

Boron trifluoride combines with hydrogen cyanide at low temperatures to give $HCN\cdot BF_3$ (b. pt. extrapolated +27°; m. pt. 40° under pressure), but the vapour is completely dissociated.[310]

Boron tribromide forms a similar compound[311] $HCN\cdot BBr_3$, white crystals which sublime easily and melt with some decomposition at 70°.

Organic nitriles will also combine readily with boron trifluoride, giving, for example, $CH_3\cdot CN\rightarrow BF_3$,[312-13] m. pt. 87°, b. pt. 101°; it is stable when dry, but at once decomposed by water. This compound is not dissociated in benzene solution according to the freezing-point, but is so wholly in the vapour, as is also the trichloro-compound. The heats of formation of the solids from their vapours are 26·5 and 33·8 k.cals.[314] The dipole moment of $CH_3CN\rightarrow BF_3$ is 5·8 D.[314]

Phosphorus and Arsenic Complexes

Phosphine and even arsine can to some extent co-ordinate with the boron trihalides, but not with the trialkyls or triaryls. The trifluoride, trichloride, and tribromide will all form addition products with phosphine[315]; they are not very stable, are easily decomposed by warming and hydrolysed by water with the loss of the phosphine, and have the phosphine expelled by ammonia. The bromide on heating is converted into boron phosphide BP and hydrogen bromide. At a low enough temperature the composition of the trifluoride complex is $H_3P\rightarrow BF_3$, whatever excess of the trifluoride is used.[316] At higher temperatures secondary reactions occur.

For the phosphine compound of diborane,[317] $(PH_4)[H_3\overset{-}{B}—\overset{+}{P}H_2—\overset{-}{B}H_3]$, see p. 355.

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[311] E. Pohland, ib. 1931, **201**, 285.

[312] G. Patein, *C.R.* 1891, **113**, 85.

[313] H. Bowlus and J. A. Nieuwland, *J.A.C.S.* 1931, **53**, 3835.

[314] A. W. Laubengayer and D. S. Sears, ib. 1945, **67**, 164.

[315] J. A. Besson, *C.R.* 1890, **110**, 80.

[316] E. Wiberg and U. Heubaum, *Z. anorg. Chem.* 1935, **225**, 270.

[317] E. L. Gamble and P. Gilmont, *J.A.C.S.* 1940, **62**, 717.

Arsine forms a similar compound $H_3As{\rightarrow}BBr_3$[318] with the tribromide at —100° in complete absence of air and water.[318] It is colourless, crystalline, and very unstable; it decomposes on heating without melting, but can be sublimed. On standing it loses arsine, and after some weeks in a sealed tube, much sooner if it is warmed, is converted into boron tribromide, arsenic, and hydrogen. Unlike arsine itself if it is exposed to air at any temperature above —30° it oxidizes at once, usually catching fire; with a slow supply of oxygen it goes to boron trioxide, hydrogen bromide, and arsenic, with some arsenic tribromide. Ammonia expels the arsine and leaves a white mass of the composition $2\ BBr_3$, $9\ NH_3$.

Various compounds of the boron trihalides with the tri- and penta-halides of phosphorus have been described, for example, $2\ BBr_3,PCl_5$, $BBr_3,POCl_3$[319], BBr_3,PBr_5, BBr_3,PBr_3, and BBr_3,PCl_3[320-1]; the last of these has a vapour pressure of 21·5 mm. at 20°, fumes in air, and is at once decomposed by water.

4. *Oxygen Complexes*

A. *Open-chain Complexes*

The acceptor powers of boron are less in the trialkyls and triaryls than in the trihalides, and this is more apparent with oxygen than with nitrogen since the complexes with oxygen are always weaker. For example, unlike the trihalides and some of their derivatives, and unlike the aluminium trialkyls,[322] the trialkyls and triaryls of boron will not co-ordinate with ether: this is remarkable because in the trihalide the back-co-ordination is at a maximum, but there are parallel cases: thus stannic chloride has its strong acceptor power for oxygen greatly reduced if one chlorine is replaced by alkyl, and destroyed if a second is so replaced.

Almost, if not quite, the only oxygen complexes formed by the boron trialkyls or triaryls are with the hydroxyl or alkyl-oxy-groups. Frankland and Duppa[323] found that gaseous boron trimethyl is absorbed by concentrated potassium hydroxide solution, and on evaporation a gummy mass of the approximate composition $KBMe_3OH$ remains; sodium, calcium, and barium hydroxides give similar complexes. None of these salts have been obtained in the crystalline state, but they show the insensitiveness to oxygen characteristic of the co-ordination compounds of boron. The aryl compounds were prepared as crystalline solids by Fowler and Kraus,[324] with tetra-alkyl ammonium cations. Thus triphenyl boron in alcoholic solution reacts with tetramethyl ammonium hydroxide to give the salt $(Me_4N)\cdot[(C_6H_5)_3B\cdot OH]$, EtOH; the ethyl alcohol is replaceable by water, the resulting salt melting at 185–7°. The tetrabutyl compound is similar.

[318] A. Stock, *Ber.* 1901, **34**, 949.
[319] G. Oddo and M. Tealdi, *Gaz.* 1903, **33**, ii. 431.
[320] J. Tarible, *Z. anorg. Chem.* 1894, **5**, 240.
[321] E. Wiberg and K. Shuster, ib. 1933, **213**, 94.
[322] E. Krause, *Ber.* 1924, **57**, 814.
[323] E. Frankland and D. Duppa, *Ann.* 1862, **124**, 129.
[324] D. L. Fowler and C. A. Kraus, *J.A.C.S.* 1940, **62**, 1143.

The *trihalides* of boron are much more ready to co-ordinate; the oxygen in almost any organic compound—alcohol, ether, acid, ester, aldehyde, ketone—can act as the donor.

The hydroxyl compounds, alcohols and acids, do not merely add, but react farther, as water does: they form compounds of the compositions $BF_3,2ROH$ and BF_3,ROH,[325] clearly ethers of trifluoroboric acid $H[BF_3OH]$, the second alcohol molecule solvating the hydrogen ion (see p. 386). The formation of compounds of this kind is proved by the fact that the vapour pressure of the system BF_3—MeOH is at a minimum (9 mm./25°) for a 1 : 1 mixture, which also has a high conductivity.[326]

The *trihalides* readily co-ordinate with the ethers; thus we have BF_3,Me_2O, boiling at 126-7°,[327] and BF_3,Et_2O, readily formed from its components at a low temperature, m.pt. −60·4°,[328] b.pt. 128°.[329]

Boron trichloride also combines readily at low temperatures with methyl and ethyl ether. The products have the composition BCl_3,R_2O whatever proportions are taken.[330] They are beautifully crystalline substances, the methyl compound melting at +76° and the ethyl at +56°; they have no perceptible vapour pressure at the ordinary temperature, but they sublime without decomposition in a high vacuum. Laubengayer *et al.* have shown by electron diffraction[331,333] that in $Me_2O \rightarrow BF_3$ the valencies of the boron are tetrahedral, the distances being B—F 1·43, B—O 1·50, O—C 1·45 (theory 1·52, 1·54, 1·43). The following properties were measured[332]:

	$Me_2O \rightarrow BF_3$	$MeEtO \rightarrow BF_3$	$Et_2O \rightarrow BF_3$
M. pt.	—14°	—98°	—60·4°
B. pt.	126·6°	127°	125·7°
Association factor cry. in benzene	1·05	1·07	. .
Dipole moment in benzene .	4·35	5·07	4·92
Ht. formation (all gas) . .	13·9 k.cals.	. .	12·5 k.cals.

The last was measured calorimetrically.

The dissociation of $Me_2O \rightarrow BF_3$ in the vapour is considerable,[334] and in the electron diffraction experiments is assumed to be 50 per cent. Brown and Adams found it to be much larger than this. The Raman spectra of liquid $Me_2O \rightarrow BF_3$[337] suggest, however, that the amount of dissociation is small. The co-ordinating power of the ethers falls off in the order[335]

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[325] H. Meerwein, *Ber.* 1933, **66**, 411.
[326] L. A. O'Leary and H. H. Wenzke, *J.A.C.S.* 1933, **55**, 2117.
[327] V. Gasselin, *Ann. Chim. Phys.* 1894, [7] **3**, 5.
[328] E. Wiberg and W. Mathing, *Ber.* 1937, **70**, 690.
[329] S. Sugden and M. Waloff, *J.C.S.* 1932, 1492.
[330] E. Wiberg and W. Sütterlin, *Z. anorg. Chem.* 1931, **202**, 22.
[331] S. H. Bauer, G. R. Finlay, and A. W. Laubengayer, *J.A.C.S.* 1945, **67**, 339.
[332] A. W. Laubengayer and G. R. Finlay, ib. 1943, **65**, 884.
[333] S. H. Bauer, G. R. Finlay, and A. W. Laubengayer, ib. 889.
[334] H. C. Brown and R. M. Adams, ib. 2253.
[335] Id., ib. 1942, **64**, 2557.

tetrahydrofurfuryl > methyl > ethyl. In dioxane solution boron trichloride has a dipole moment of 4·86,[336] showing that the co-ordination is practically complete.

They are very sensitive to water and to alcohol, which at once convert them into boric acid or its ester. Above 50° (best at 80°) they decompose thus:

$$Cl_3B \leftarrow OR_2 = Cl_2B \cdot O \cdot R + RCl.$$

The dichloro-product can still co-ordinate with ether, giving

$$(Cl_2B \cdot OR)_2,\ R_2O,$$

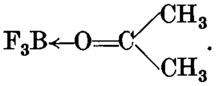
presumably with 4-covalent oxygen. This is very unstable, and even below 0° disproportionates to $Cl \cdot B(OR)_2 + Cl_3B \leftarrow OR_2$. This mono-chloro-compound has no longer any power of co-ordination with ether, and so the reaction stops.

Boron trifluoride will also co-ordinate with esters; the following boiling-points [and melting-points] are given[338-9]

BF_3+Me formate	94°	[+23·5°]
Et formate	102°	[+3°]
Me acetate	123°	[31°]
Et acetate	120°	[26°]
n-Pr acetate	127°	
Et propionate	116°	[33°]

All these are completely split up into their components in the vapour. Similar compounds are formed by methyl benzoate and glycollate.[340]

Boron trifluoride also combines with aldehydes and ketones. Benzaldehyde gives a 1:1 compound[341] and acetone reacts in the same way to give the solid[327, 342]



$$F_3B \leftarrow O{=}C\begin{matrix}CH_3\\CH_3\end{matrix}.$$

Finally, we have those open-chain compounds in which the boron is attached to four oxygen atoms. How far boric acid and its salts give in water the ions $[B(OH)_4]^-$ is uncertain, but the tetra-alkyl derivatives of this form were discovered by Copaux,[343] and subsequently examined by Cambi.[344] They are made by the action of the alkali metals or their alkylates on the boric esters, usually dissolved in their own alcohols. They are undoubtedly salts, and are not affected by atmospheric oxygen. They nearly all crystallize with alcohol of crystallization. Examples are

[336] T. J. Lane, P. A. McKusker, and B. C. Curran, *J.A.C.S.* 1942, **64**, 2076.

[337] F. V. Dunderman and S. H. Bauer, *J. Phys. Chem.* 1946, **50**, 32.

[338] H. Bowlus and J. A. Nieuwland, *J.A.C.S.* 1931, **53**, 3835.

[339] G. T. Morgan and R. Taylor, *Chem. and Ind.* 1931, 869.

[340] Id., *J.C.S.* 1932, 1497.

[341] F. Landolph, *Ber.* 1877, **10**, 1313.

[342] V. Gasselin, *Bull. Soc. Chim.* 1893, [3] 9, 483.

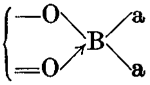
[343] H. Copaux, *C.R.* 1898, **127**, 721.

[344] L. Cambi, *Atti. R.* 1914, [5] **23**, i. 244.

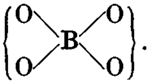
$Li[B(OCH_3)_4]$, 2·5 MeOH; Na, 1·5; K 1·5; $Ca[B(OCH_3)_4]_2$; and the ethyl compounds $Na[B(OC_2H_5)_4]$, EtOH; K, 1·5 EtOH and Tl′, not solvated. There is also $Na[B(O\text{-}n\text{-}Pr)_4]$, PrOH. The number of half-molecules in alcohol is remarkable; the salt molecules obviously fit into the crystal in pairs.

B. *Chelate Oxygen Complexes*

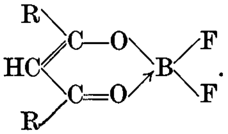
The only known chelate complexes of boron have the ring joined through two oxygen atoms. Since the maximum covalency of boron in its normal compounds is 4, the compounds can be either monochelate type



or dichelate type



Boron trifluoride reacts very readily with β-diketones in benzene solution; one-third of the fluorine is given off as hydrogen fluoride, and a chelate derivative of this structure is formed[345]



The acetylacetone (m.pt. 43°), benzoylacetone (155°), and dibenzoyl methane (191°) compounds were made. They are obviously covalent; they are soluble in benzene and monomeric in it by the freezing-point (with up to 12 per cent. association).

Similar compounds were prepared by Dimroth[346] from certain hydroxy-anthraquinones, by adding the latter to a solution of boron triacetate in acetic anhydride. Thus 1-hydroxy-anthraquinone gives the boric diacetate compound I below, which on warming *in vacuo* loses acetic anhydride and goes to the metaboric derivative II. But 2-hydroxy-anthraquinone does not combine with boric acetate at all, and under this treatment is merely acetylated. This difference is quite general; if the anthraquinone derivative used has an α-(1-) hydroxyl group it forms a chelate compound with the boron; if not, the boron is not taken up at all.

The naphthalene and phenanthrene compounds behave in the same way.[347]

These complexes are sometimes coloured, and can then be used as tests for traces of boron; 1 microgram of boron can be detected by the colour produced with quinizarine and sulphuric acid.[349]

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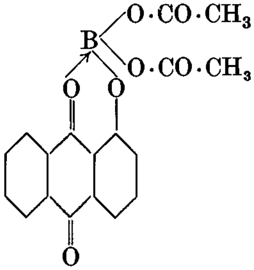
[345] G. T. Morgan and R. B. Tunstall, *J.C.S.* 1924, **125**, 1963.

[346] O. Dimroth and T. Faust, *Ber.* 1921, **54**, 3020.

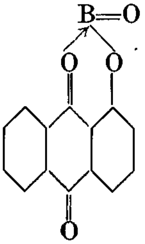
[347] O. Dimroth, *Ann.* 1925, **446**, 97.

[348] W. Dilthey and F. J. Schumacher, ib. 1906, **344**, 300, 326.

[349] P. W. Maunsell, *N. Zealand J. Sci. Techn.* 1940, **22**, B, 100.



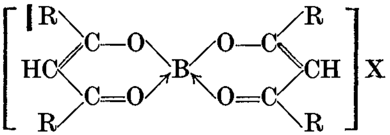
(I)



(II)

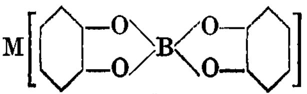
Dichelate Complexes

β-diketone compounds. If a β-diketone such as acetylacetone is treated with boron trichloride instead of the trifluoride, the reaction goes farther, since the B—Cl link is weaker than B—F, and two chelate groups are introduced. This completes the covalency maximum of the boron, while it satisfied only two of its valencies (the enol having in combination a valency of 1 and a covalency of 2), so that the salt of a monovalent cation is formed. These so-called boronium salts were discovered by Dilthey.[348] They are readily formed in ethereal solution by acetylacetone and benzoylacetone. The simple salts, such as the chloride $[A_2B]Cl$, the iodide, and the sulphate are usually too unstable to purify, but the salts of numerous complex anions, I_3', $FeCl_4'$, $AuCl_4'$, $ZnCl_3'$, $SnCl_6''$, and $PtCl_6''$, have been prepared. They nearly all dissolve readily in chloroform and can be precipitated with ether; they are decomposed by water. In many ways, even in solubility, they are surprisingly like the trichelate siliconium salts $[A_3Si]X$ (see below, under Silicon, IV. 613). Some melting-points are: acetylacetone salts $-FeCl_4$ 137°; $-AuCl_4$ 135°; $_2-PtCl_6$ 180°; $_2-SnCl_6$ 210°. Benzoylacetone derivatives, $[A_2B]I$ (the only simple salt of the whole series that was purified) 210°; $[A_2B]ZnCl_3$ 208°.

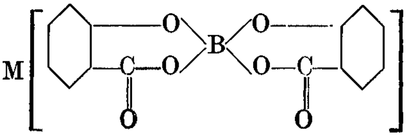


Catechol and Salicylic Complexes

Where the chelate group has two replaceable hydrogens, the boron will form dichelate anions, as with catechol[356] (I) and salicylic acid (II):



(I)



(II)

A variety of salts of these and similar acids have been prepared largely by Boeseken and his colleagues.[350-5] They are readily formed and stable; indeed, if potassium chloride is added to an aqueous solution of catechol and boric acid, hydrochloric acid is liberated, as can be shown by titration with Congo red.[351] The free acid of the catechol salt, $H[B(cat)_2]$, has been isolated by heating the aniline or pyridine salt *in vacuo* at 100°, and subliming the residue at 180° to 200° under 1-2 mm. pressure.

The tetrahedral arrangement of the 4 covalencies of the boron has been established by resolving the brucine and strychnine salts of the 4-chloro-catechol derivative[354] and the salicylate.[353] The active salts racemize rather easily, especially in presence of moisture, and it was not found possible to obtain active salts of inactive cations.

A sulphide complex $H_2S \rightarrow BCl_3$, f. pt. $-35°$, has been prepared.[358]

5. *Complex Halides*

These are almost confined to the fluorides, which are numerous and stable, as might be expected from the great affinity of boron for fluorine. Complex anions of 4-covalent boron in which only part of the covalencies are occupied by halogen have already been dealt with, except for one group.

Fowler and Kraus[359] showed that boron triphenyl $B(C_6H_5)_3$ will co-ordinate with alkaline fluorides, as it does with hydroxides, and form the complexes $M[B(C_6H_5)_3F]$; with the tetra-alkyl ammonium fluorides they got $(NMe_4)\cdot[B\Phi_3F]$, m. pt. 176°, and $(NBu_4)\cdot[B\Phi_3F]$, m. pt. 161-2°, stable in air.

The borofluorides proper, $M[BF_4]$, are the last term of the series:

$$H[B(OH)_4] \quad (H[BF(OH)_3]) \quad H[BF_2(OH)_2] \quad H[BF_3OH] \quad H[BF_4],$$

of which all but the second member are known and only the last remains for us to discuss.

This borofluoric or tetrafluoroboric acid and its salts were discovered by Berzelius, who observed the remarkable reaction of ammonium fluoride with boric acid, in which ammonia is eliminated and ammonium borofluoride $NH_4[BF_4]$ produced. The subject has recently been investigated by Wilke-Dörfurt and Balz.[360]

Borofluoric acid, HBF_4, is formed when boron trifluoride is dissolved in water; part of the trifluoride is hydrolysed (boric acid crystallizes out when the solution is concentrated), and the rest combines with the hydrogen fluoride produced to form borofluoric acid. The acid is usually prepared by adding slight excess of boric acid to 40 per cent. aqueous

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[350] A. Rosenheim and H. Vermehren, *Ber.* 1924, **57**, 1337.

[351] H. Weil and M. Adler, ib. 2091.

[352] P. H. Hermans, *Z. anorg. Chem.* 1925, **142**, 83.

[353] J. Meuelenhoff, ib. 373.

[354] J. Boeseken and J. A. Mijs, *Rec. Trav.* 1925, **44**, 758.

[355] J. Meulenhoff, ib. 150.

[356] H. Schäfer, *Z. anorg. Chem.* 1942, **250**, 82.

[357] Id., ib. 127.

[358] D. R. Martin, *J.A.C.S.* 1945, **67**, 1088.

[359] D. L. Fowler and C. A. Kraus, ib. 1940, **62**, 1143.

[360] E. Wilke-Dörfurt and G. Balz, *Z. anorg. Chem.* 1927, **159**, 197.

hydrofluoric acid; the solution contains up to 30 per cent. of HBF_4.[361] The equilibrium constant for the reaction

$$BF_4^- + 3\,H_2O = H_3BO_3 + 4\,F^- + 3\,H^+$$

is $2{\cdot}5 \times 10^{-19}$ at 18°.[362] Borofluoric acid does not attack glass in the cold, but only when hot.

HBF_4 is a strong acid; its salts are not electrolytically hydrolysed in water when they are freshly dissolved. A quantitative estimation of the strength is difficult, because the BF_4 ion undergoes slow chemical hydrolysis in water on standing. Thus the alkaline salts assume an acid reaction, and gradually, especially on warming, concentration of the fluorine ion increases, as can be shown with the lanthanum acetate test[363] or with calcium chloride; the calcium salt $Ca[BF_4]_2$ itself gives at first a clear solution in water, but this soon becomes turbid and calcium fluoride separates.

The crystal structure of the BF_4 anion shows that it is tetrahedral.[364-6] The salts of the alkali metals, of monovalent thallium, and of ammonium all have essentially the same crystal lattice as barium sulphate. It has been shown[367] that in the cubic high-temperature form of the potassium and ammonium salts the BF_4 ion is rotating, like the ClO_4 ion in potassium perchlorate. There is a remarkable resemblance between these two ions: both are the anions of strong acids; both are monovalent; both have on their outsides the very undeformable atoms of oxygen or fluorine; both are tetrahedral, and they are of about the same size: the Cl—O distance in ClO_4' is 1·63, and the B—F in BF_4' 1·53 A.U. They are in general isomorphous[364]; the alkaline borofluorides are isodimorphous with the perchlorates.[369] The solubilities of the two classes are also very similar; the borofluorides resemble the perchlorates in the enormous solubilities of many of the salts of uni- and divalent metals, and also in the much smaller solubilities of those of the hexammines of divalent nickel, manganese, and cadmium, and of trivalent cobalt.[360] The following are some of the values in milli-moles per litre at the ordinary temperature:

	$[Cd,6NH_3]''$	$[Ni,6NH_3]''$	$[Co,6NH_3]'''$
Perchlorate	23	6·9	13
Borofluoride	8·5	6·0	16

They also resemble one another in the great insolubility of many of their amine salts, such as those of tetramethyl and tetraethyl ammonium, of pyridine, of strychnine, and of the diazonium bases[368]: these last also

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[361] H. Funk and F. Binder, ib. 1926, **155**, 327.

[362] J. G. Ryss and N. P. Bakina, *C.R. U.R.S.S.* 1936, **2**, 107.

[363] R. J. Meyer and W. Schulz, *Z. angew. Chem.* 1925, **38**, 203.

[364] J. L. Hoard and V. Blair, *J.A.C.S.* 1935, **57**, 1985.

[365] L. J. Klinkenberg, *Rec. Trav.* 1937, **56**, 36.

[366] O. Hassel and G. Bödtke-Naess, *Norske. Vid. Akad. Oslo*, 1933, **7**, 1.

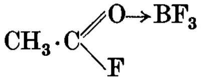
[367] C. Finbak and O. Hassel, *Z. physikal. Chem.* 1936, B **32**, 433.

[368] E. Wilke-Dörfurt and G. Balz, *Ber.* 1927, **60**, 115.

agree in not being explosive. Again, both acids form salts of the peculiar nitrosyl cation $[N\overset{\leftarrow}{=}O]^+$.[369-70] $(NO)\cdot[BF_4]$, which is hygroscopic and excessively soluble in water, crystallizes out when a highly concentrated solution of fluoroboric acid is saturated with nitrous fumes. Like the perchlorate it has one molecule of water of crystallization, which is easily lost over phosphorus pentoxide. It can be purified, like the ammonium salt, by sublimation at 200-50° under 0·01 mm. pressure. Like nitrosyl perchlorate $(NO)\cdot[ClO_4]$ it is decomposed by water with the evolution of nitrous fumes. It converts methyl alcohol at once into methyl nitrite.

Acyl Borofluorides

Boron trifluoride (or trichloride) will combine with acyl halides: thus Meerwein[372] obtained solids of the compositions $CH_3\cdot CO\cdot Cl,BF_3$ and $CH_3\cdot CO\cdot Cl,BCl_3$ existing only below −70°. Boron trifluoride gives a more stable compound with acetyl fluoride at −50°.[373] This might be either a covalent compound



or a salt $[CH_3\cdot\overset{+}{C}=O]\cdot(BF_4)$ or $[CH_3\cdot C\equiv\overset{+}{O}]\cdot(BF_4)$, with a cation formed by the basic dissociation of the acid. It is partly dissociated in the cold, and wholly at +20°. But in sulphur dioxide solution at about N/25 (and about −8°) its molecular conductivity is roughly a third of that of potassium iodide at the same concentration; with a rise of temperature the conductivity falls off rapidly, suggesting that a salt form is present at low temperatures. The substance is hydrolysed by water with a large evolution of heat.

Since the heat of linkage of boron is much greater to fluorine than to the other halogens, the fluoroborates are naturally the most stable of the complex halides. Indeed, the others seem hardly to exist at all. The only indications of even a chloride are in the unstable acetyl-chloride compound mentioned above, and in the fact that nitrogen peroxide N_2O_4 will combine[371] with boron trichloride with evolution of oxygen to give a compound of the composition $NOCl,BCl_3$, which may well be the nitrosyl salt $[NO]BCl_4$. It forms crystals which melt at 23–4° forming two liquid layers, apparently chiefly of NOCl and BCl_3 respectively. It is decomposed by water. Co-ordination compounds with organic and other chlorides are also known.[373a]

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[369] D. Vortländer, J. Hollatz, and J. Fischer, ib. 1932, **65**, 535.

[370] G. Balz and R. Mailänder, *Z. anorg. Chem.* 1934, **217**, 161.

[371] A. Geuther, *J. prakt. Chem.* 1873, [ii] **8**, 357.

[372] H. Meerwein and H. Maier-Hüser, *J. prakt. Chem.* 1932, [2] **134**, 67.

[373] F. Seel, *Z. anorg. Chem.* 1943, **250**, 331.

[373a] D. R. Martin, *J. Phys. and Colloid Chem.* 1947, **51**, 1400.

ALUMINIUM

WHEN we pass from boron to aluminium, the size, both of the atom and of the ions, is almost doubled (atomic radii B 0·88, Al 1·26; ratio 1·43; ionic radii B^{+++} calculated 0·24 (there is no actual B^{+++} ion); Al^{+++} 0·83 A.U.; ratio 3·46). Accordingly the ionization is much less completely repressed in aluminium. While boron is invariably covalent, aluminium is on the line between ionization and covalency; in this it resembles beryllium,[374] by the usual diagonal relationship, but on the whole the covalent side is more important in aluminium than in beryllium; thus the conductivities of the fused chlorides at their melting-points are:

$$BeCl_2\ 3{\cdot}2 \times 10^{-3},\ AlCl_3\ 0{\cdot}6 \times 10^{-6}.$$

The increase of charge from 2 to 3 is more effective than the increase in ionic radius from 0·34 to 0·83.

Another very important difference as we go from boron to aluminium is that the covalency limit rises from 4 to 6. This is evident in the complex compounds. Both elements being trivalent, boron can form only one additional covalency by co-ordination, as in $Et_3B \leftarrow NH_3$ or $K[BF_4]$, while aluminium can not only do this, but can go farther and form 3 extra links, as in $Na_3[AlF_6]$.

Aluminium is the third commonest element, and the commonest metal, in the earth's crust, of which it forms 7·5 per cent. by weight.

From its large affinity for oxygen it always occurs in the oxidized form, and usually as complex silicates, such as felspars and micas, and the products of their weathering, the clays.

Metallic Aluminium

This is made practically entirely by the electrolysis of bauxite Al_2O_3 dissolved in molten cryolite Na_3AlF_6, at 800–1,000°. The production in Germany alone in 1938 was 180,000 tons, which involved the consumption of $3{\cdot}6 \times 10^9$ kilowatt hours.[375] Owing to its low specific gravity (2·7) its mechanical strength and electrical conductivity as referred to the weight are very large: an aluminium wire has only half the weight of a copper wire of the same conductivity. It is especially valuable for aeroplanes, but usually as an alloy with other metals; for example, duralumin is an alloy of 93-5 per cent. Al, 3·5-5·5 Cu, 0·5 Mg, and 0·5 Mn.

From its great affinity for oxygen we should expect the metal to oxidize very readily, but its oxidation is stopped by the formation of a protective layer of oxide[376] on the surface, which renders it in fact indifferent in the

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[374] According to Pauling (*Chem. Bond.* 2nd ed., 74) Al and Be have the same electronegativity value 1·5, and the Al bonds have the same ionic percentage as Be: these are

Be—F	—O	—Cl	—Br	—I
79	63	44	35	22.

[375] See *Nature*, 1940, **146**, 565.

[376] The fundamental physics of this layer is discussed by N. F. Mott, *Trans. Far. Soc.* 1939, **35**, 1175.

cold to air, water, and hydrogen sulphide, and to nitric acid of any concentration. If this layer is broken down the natural activity of the metal becomes evident. Amalgamation of the surface with mercury makes it oxidize at once, with the formation of a mossy growth of oxide which may be 1 or 2 cm. high, and which continues to grow until the metal is used up. In the same way sodium chloride solution removes the layer, and the metal is attacked by air. This oxidation by moist air is prevented by the presence of 0·2 per cent. copper, 1 per cent. iron, or 5 per cent. silicon.[377]

Aluminium is soluble in alkaline solutions with evolution of hydrogen and production of an aluminate such as $Na[AlO_2]$.

Aluminium Hydride

If aluminium is vaporized in hydrogen at high temperatures a 'spectroscopic' hydride is formed, shown by its spectrum to be AlH. With 1 atmosphere of hydrogen at 1,500° there is 0·35 mm. of AlH present. The volumes of hydrogen at N.T.P. absorbed by 100 g. (38·7 c.c.) Al at various temperatures are:[378]

700°	800°	900°	1000° C.
0·23	0·89	1·87	3·86 c.c.

(AlH would have 41 litres H_2 to 100 g. Al.)

A mixed alkyl-hydride $Al_2Me_4H_2$ and perhaps also a pure hydride Al_2H_6 are described by Wiberg and Stecher (1939: p. 415 below).

A series of *aluminohydrides*, analogous to the borohydrides (p. 364), have recently been described.[379] Lithium hydride reacts with aluminium chloride in ether to give $LiCl+LiAlH_4$; more $AlCl_3$ converts this into AlH_3 (perhaps Al_2H_6), which cannot be separated from its ether compound, and soon decomposes; the lithium aluminohydride can be got by evaporating off the ether. A similar gallium compound $LiGaH_4$ can be made, but little is known of it. The sodium and calcium aluminohydrides were also made but were not isolated. $LiAlH_4$ is a powerful reducing agent, converting $SiCl_4$ into silane, Me_2SnCl_2 into Me_2SnH_2, and $ZnMe_2$ into ZnH_2; it will also reduce organic compounds. A comparison of $LiAlH_4$ (*al*) and $LiBH_4$ (*b*) shows that both are white solids, stable in cold air; *b* begins to decompose at 250–75°, *al* at 125-50°. Both dissolve in ether, *al* 7-8 times as much as *b*; *al* hydrolyses more readily; it reacts (to form obscure products) with ammonia, which *b* does not.

Aluminium and Carbon: Aluminium Carbide

Apart from the acetylide Al_2C_6 (made by passing acetylene over aluminium at 450-500°[380]) the only certain carbide is Al_4C_3 (Moissan, 1894), formed from the elements slowly at 1,000°, in 20′ at 2,000°,[381] with

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[377] H. Lichtenberg, *Z. anorg. Chem.* 1938, **239**, 189.

[378] L. L. Bircumshaw, *Trans. Far. Soc.* 1935, **31**, 1439.

[379] A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J.A.C.S.* 1947, **69**, 1199.

[380] J. F. Durand, *Bull. Soc.* 1924, [iv] **35**, 1141.

[381] O. Ruff and E. Jellinek, *Z. anorg. Chem.* 1916, **97**, 315.

a heat evolution (calculated for the solids at 22°) of 50 k.cals. per mole.[382] Pale yellow crystals, m. pt. 2,200°, subliming *in vacuo* at 1,800°.[384] In the lattice[383] the shortest C··C distance in 3·16 A, so that the carbon atoms are not united. Hence when it is attacked by water (slowly in the cold, quickly when hot or acidified) it gives methane with less than 10 per cent. of hydrogen.[381]

Aluminium Alkyls

The aluminium alkyls were first made by G. B. Buckton and W. Odling in 1865, by the action of aluminium on mercury alkyls. They can also be prepared[385] by the action of 'electron metal', an alloy of aluminium and magnesium, on a solution of the alkyl halide in ether; the metal dissolves, and after evaporation an etherate AlR_3,Et_2O remains, volatile without decomposition, and for many purposes behaving just like the trialkyl itself.

The trialkyls are volatile liquids[386-7]:

	M. pt.	*B. pt.*	*Trouton*	BR_3*, b. pt.*
$AlMe_3$	+15·0°[394a]	126·1°	24·1	−20°
$AlEt_3$	−52·5°	185·6°	36·2	+95°
$Al(n\text{-}Pr)_3$ . . .	−107°	*ca.* 250°	..	..

The dielectric constant of $AlEt_3$ at 25° is 2·87.[390]

These compounds are all considerably associated.

Wiswall and Smyth[395] find the following approximate values of the dipole moments in the vapour at −13° to +140°, and that of $AlMeCl_2$ in solution: $AlMe_3$ 1·34–1·46 D; $AlMe_2Cl$ 1·61–1·73; $AlMeCl_2$ 1·96 D. But the strong association (indicated by the b. pts.) obviously interferes.

The latest vapour-density measurements show[387] that $AlMe_3$ is dimeric in the vapour at 70°, and its heat of monomerization at 100–55° is 20·2 k.cals.; $AlEt_3$ is 12 per cent. dimeric at 150°. So, too, in ethylene dibromide[388-9] melting-points show the association factors to be 2·1 for the triethyl and 2·6 for the tripropyl. Similar though slightly lower values have been found in benzene.[394a]

The structures of the dimeric molecules Al_2Me_6 have been examined by electron diffraction by Davidson, Hugill, Skinner, and Sutton,[391] and by

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[382] W. Roth, U. Wolf, and O. Fritz, *Z. Elektrochem.*, 1940, **46**, 42.

[383] M. V. Stackelberg and E. Schnorrenberg, *Z. physikal. Chem.* 1934, B **27**, 37.

[384] E. Tiede and E. Birnbräuer, *Z. anorg. Chem.* 1914, **87**, 167.

[385] E. Krause and B. Wendt, *Ber.* 1923, **56**, 466.

[386] A. V. Grosse and J. M. Mavity, *J. Org. Chem.* 1940, **5**, 106.

[387] A. W. Laubengayer and W. F. Gilliam, *J.A.C.S.* 1941, **63**, 477.

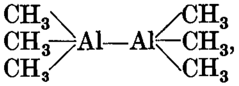
[388] E. Louise and L. Roux, *C.R.* 1888, **107**, 600.

[389] Abegg, *Aluminium*, p. 71.

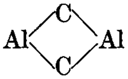
[390] F. Hein and H. Schramm, *Z. physikal. Chem.* 1930, **149**, 408.

[391] N. R. Davidson, J. A. C. Hugill, H. A. Skinner, and L. E. Sutton, *Trans. Far. Soc.* 1940, **36**, 1212.

Brockway and Davidson[392]; they find them to have an ethane-like structure



with the distances Al—Al 2·20±0·06 A, Al—C 2·05±0·05, and the C—Al—Al angle 105±10°. As there are no electrons available, on the ordinary principles, for the Al—Al linkage, various other models were tried, especially one with the



ring; but they did not agree with the observed maxima. The remarkable shortness of the Al—Al (theory 2·52) link rather suggests that the wrong model was adopted; the lack of electrons would be expected to lengthen the link. See further, Kohlrausch.[396] For an explanation by the formation of C—H··Al bridges, see Pitzer.[394a] The aluminium alkyls are relatively ineffective metallating agents.[347]

Aluminium trimethyl decomposes gradually at 300°, the principal product being methane; for the kinetics of this reaction see ref. [398]. The aluminium alkyls are violently attacked by air or water. The first three are spontaneously inflammable in air, and they all go at once with water to the hydroxide and the saturated hydrocarbon.

$$Al(C_2H_5)_3 + 3\,H_2O = Al(OH)_3 + 3\,C_2H_6.$$

They all readily form addition compounds with many organic substances, especially ethers; with these last the products, such as $AlEt_3,Et_2O$, are so stable that they can be distilled without decomposition, and the ether usually cannot be removed except by reagents that decompose the whole molecule (see further, p. 432). The aluminium alkyls have strong reducing properties and will, for example, reduce ketones to secondary alcohols even more readily than the boron alkyls.[393]

Like zinc ethyl, aluminium ethyl will dissolve alkaline alkyls to give conducting solutions, presumably forming complex salts $M[AlR_4]$; see p. 429.

A mixed alkyl-hydride of aluminium has been briefly described[399]; it is got as a viscous liquid volatile *in vacuo* in the cold, by the action of an electric discharge on a mixture of aluminium trimethyl and hydrogen. It

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[392] L. O. Brockway and N. R. Davidson, *J.A.C.S.* 1941, **63**, 3287.

[393] E. Krause and P. Dittmar, *Ber.* 1930, **63**, 2401.

[394] V. Grignard and R. L. Jenkins, *Bull. Soc.* 1925, [4] **37**, 1376.

[394a] K. S. Pitzer and H. S. Gutowski, *J.A.C.S.* 1946, **68**, 2204.

[395] R. H. Wiswall and C. P. Smyth, *J. Chem. Phys.* 1941, **9**, 352.

[396] K. W. F. Kohlrausch and J. Wagner, *Z. physikal. Chem.* 1942, B **52**, 185.

[397] H. Gilman and A. H. Haubein, *J.A.C.S.* 1945, **67**, 1083.

[398] L. M. Yeddanapalli and C. C. Schubert, *J. Chem. Phys.* 1946, **14**, 1.

[399] W. E. Wiberg and O. Stecher, *Angew. Chem.* 1939, **52**, 372; preliminary note.

burns explosively in air, and is at once hydrolysed by water. Above 160° it decomposes, giving aluminium trimethyl; no hydride Al_2H_6 could be isolated from this reaction, but only metallic aluminium and hydrogen.

It was, however, found[400] that by treating the mixed alkyl-hydride $Al_2Alk_3H_3$ with trimethylamine an addition product $(AlH_3)_n,NMe_3$ was formed, and this on distillation at 100-35° gave a hydride $(AlH_3)_n$, white, amorphous, non-volatile, stable up to 100°, but above that temperature decomposing to give aluminium and hydrogen.[400]

Aluminium triphenyl (Friedel and Crafts, 1886) and aluminium tri-*p*-tolyl[393] can be made from the metal and mercury diaryl; on extraction with ether and evaporation the etherate (m. pt. triphenyl 112°, tritolyl 125°) separates, which on heating *in vacuo* does not distil but loses its ether with some decomposition. The pure triaryl (m. pt. triphenyl 230°) is got by working in benzene; the association factor for the tritolyl in benzene is 1·19–1·71 in 0·01-0·04 molar solution by the freezing-point and 1·55 in 0·04 molar solution by boiling-point. The triaryls are easily soluble in benzene; they are oxidized by air in solution and slowly in the solid state, but much less readily than the trialkyls; unlike the boron trialkyls they react at once with iodine. In general they react in the usual ways. but much more slowly than the zinc or magnesium compounds; aluminium replaces magnesium in its aryls more rapidly than zinc does.[401]

A variety of compounds of the type $Alk_2Al{\cdot}X$ are known, where X can be NMe_2, OMe, halogens, etc.

The halides are further discussed below (p. 417); the others were made by Davidson and Brown[402] by heating aluminium trimethyl with dimethylamine, dimethyl phosphine, methyl alcohol, and methyl mercaptan; for example,

$$Me_3Al + NHMe_2 = Me_2Al{-}NMe_2 + CH_4.$$

The relative stability and the degree of polymerization from the vapour density of these compounds have recently been examined in detail by Davidson and Brown.[402]

Polymerization is very common among the covalent compounds of aluminium; the trialkyls and the trihalides are dimeric: so also are the $Me_2Al{-}X$ compounds mentioned above, when $X = NMe_2$, S·Me, Cl, or Br; but $Me_2Al{-}PMe_2$ and $Me_2Al{-}OMe$ are trimeric, and the aluminic esters $Al(O{\cdot}Alk)_3$ are roughly tetrameric (see p. 421).* Though the heats of association to the dimeric form are much the same for $AlMe_3$ (20·0 k.cals.[403]) as for $AlCl_3$ (29·0 k.cals.[406]) the mechanisms are obviously different; as electron diffraction shows, the halides have the ring struc-

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* It should be noticed that none of the corresponding boron compounds are associated.

[400] O. Stecher and E. Wiberg, *Ber.* 1942, **75**, 2003.

[401] H. Gilman and K. E. Marple, *Rec. Trav.* 1936, **55**, 133.

[402] N. R. Davidson and H. C. Brown, *J.A.C.S.* 1942, **64**, 316.

[403] A. W. Laubengayer and W. F. Gillam, ib. 1941, **63**, 477.

[404] A. Smits and J. Meyering, *Z. physikal. Chem.* 1938, B **41**, 98.

ture,[405] while the trialkyls[406] have a structure like that of ethane. The co-ordination compounds formed by all these substances $R_3Al \leftarrow B$ (where $B = NMe_3$, OMe_2, etc.) are invariably monomeric.

These substituted alkyl compounds Me_2AlX are remarkably stable; neither the dimeric nor the trimeric forms (except to some extent $Me_2Al—S\cdot Me$) are appreciably dissociated at 150° and 30 mm., at which Al_2Me_6 is 50 per cent. monomeric; their physical properties are given in the following table:

	Compound	*M.pt.*	*B.pt.*	*Ht. of evapn.*	*Trouton*
Dimeric	$Me_2Al—NMe_2$	154–6° C.	. .	13·22 k.cals.	. .
	$Me_2Al—S\cdot Me$	103°	228°	14·1	28
	$Me_2Al—Cl$*	−21° −45°	119·4°	9·84	25·0
	$Me_2Al—Br$	. .	150°	10·44	24·6
Trimeric	$Me_2Al—OMe$	. .	[ca. 140°]	13·9	. .
	$Me_2Al—PMe_2$	220°	[ca. 250°]	. .	. .

* Dimorphic.

These compounds form co-ordinated addition compounds, for example with amines and ethers, and depolymerize in doing so, thus:

$$(Me_2Al\cdot Cl)_2 + 2\,NMe_3 = 2\,Me_2ClAl \leftarrow NMe_3$$

but only of course if the heat of co-ordination is greater than that of polymerization. $(Me_2AlCl)_2$ forms in this way stable compounds with trimethylamine and with dimethyl ether; $(Me_2Al\cdot SMe)_2$ co-ordinates with trimethylamine but not with ether; while $(Me_2Al\cdot NMe_2)_2$ and the two trimers $(Me_2Al\cdot PMe_2)_3$ and $(Me_2Al\cdot OMe)_3$ (which seem to be exceptionally stable) will not co-ordinate with either. It would therefore appear that the energy of polymerization of $Me_2Al—X$ increases in the order

$$X = Cl < SMe < NMe_2,\ PMe_2,\ OMe.$$

The cause of the difference in the size of the polymers is quite unknown. They presumably have rings with alternate Al atoms, of 4 and 6 members respectively.

As regards the energy of co-ordination of $AlMe_3$ and its substitution products, displacement measurements[402] show that this falls off in the order $NMe_3 > PMe_3 > OMe_2 > SMe_2 > MeCl$ (this last having none).

Halides

H. Hallwachs and A. Scharfarik in 1859 found that aluminium dissolves in ethyl iodide to give an inflammable oil. Grignard[394] isolated from this

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[405] K. J. Palmer and N. Elliott, *J.A.C.S.* 1938, **60**, 1852.

[406] N. R. Davidson, J. A. C. Hugill, H. A. Skinner, and L. E. Sutton, *Trans. Far. Soc.* 1940, **36**, 1212; L. O. Brockway and N. R. Davidson, *J.A.C.S.* 1941, **63**, 3287.

$EtAlI_2$ (m.pt. 35–7°, b.pt. 158-60°/4 mm.) and Et_2AlI (b.pt. 118–20°/4 mm.). v. Grosse and Mavity[386] showed that the reaction

$$2\,Al + 3\,RX = AlRX_2 + AlR_2X$$

works with many alkyl and aryl chlorides, bromides, and iodides, though with the higher alkyls it sometimes fails through decomposition. The products can be separated by fractionation, or the mixture converted into R_2AlX by heating with AlR_3, or into $RAlX_2$ with AlX_3. Both $AlMeBr_2$ and $AlMeI_2$ on distillation give marked disproportionation to $Me_2AlX + AlX_3$.

These mixed alkyl or aryl halides are very like the trialkyls or triaryls; they are dimeric in solution; they easily catch fire; they react violently with water, and they form mono-etherates. They do not react with carbon monoxide.

The table gives the [melting-] and boiling-points of some of these compounds, from v. Grosse and Mavity.[386]

X =	Cl	Br	I
$CH_3 \cdot AlX_2$	[72·7°] 100°/100 mm.	[79°]	[68–72°]
$(CH_3)_2AlX$	[—] 83°/200 mm.	[0°] 75°/50 mm.	110°/50 mm.
$Et \cdot AlX_2$	[32°] 115°/50 mm.	..	[39°]
Et_2AlX	[—] 125°/50 mm.	180°/760 mm. 121°/10 mm.	.. ..
$C_6H_5 \cdot AlX_2$	[94°]	..	..

v. Grosse and Mavity,[386] by heating the Me—Al chlorides with sodium, get $Al(CH_3)_3$; if this is heated to 100-35° with $Al(O \cdot CH_3)_3$ it gives $CH_3 \cdot Al(O \cdot CH_3)_2$, which is infusible and non-volatile, and $(CH_3)_2Al \cdot O \cdot CH_3$ [31°], 87°/10 mm. In the same way they get $EtAl(O \cdot Et)_2$, 137°/0·1 mm. and $Et_2Al \cdot O \cdot Et$, 108°/10 mm.

Aluminium Nitride

At 800° aluminium absorbs nitrogen rapidly with emission of heat and formation of the nitride AlN (for details see ref. [407]); this is formed by heating aluminium in air (along with alumina) or in other nitrogen compounds such as ammonia, or by heating alumina with carbon in nitrogen in the electric furnace. It melts under 4 atmospheres pressure at 2,200°[409] and begins to decompose into its elements below this. The crystal lattice is that of wurtzite[408,410–11] (Al—N 1·87 A; theory 1·96), and it obviously forms giant molecules similar to diamond, with $\overset{-}{\text{Al}}$—$\overset{+}{\text{N}}$ replacing C—C. It is hydrolysed by water in the cold to alumina and ammonia; it can thus be used to get ammonia from air ('Serpek Process').

[407] F. Fichter, *Z. anorg. Chem.* 1907, **54**, 322.

[408] A. F. Wells, *S.I.C.* 427.

[409] J. Wolf, *Z. anorg. Chem.* 1914, **87**, 125.

[410] H. Ott, *Z. Phys.* 1924, **22**, 201.

[411] V. M. Goldschmidt, *Trans. Far. Soc.* 1929, **25**, 253.

A kind of intermediate between aluminium carbide and nitride is the 'carbonitride' Al_5C_3N made by the action of ammonia on aluminium carbide Al_4C_3 or on a mixture of the metal and carbon at 1800°; it resembles the carbide in appearance and properties[412]; its rather complicated crystal structure has been determined.[413]

The *phosphide* AlP, which is formed from its elements with evolution of heat, seems to be the only phosphide of aluminium. It forms yellow or dark grey crystals, not melting or decomposing up to 1,000°, but readily hydrolysing to give phosphine.[414]

Aluminium Oxide and Hydroxide

Apart from a spectroscopic suboxide AlO, aluminium forms only one oxide, Al_2O_3, corundum. This is the material of various precious stones; ruby is Al_2O_3 with a trace of chromium, and sapphire is Al_2O_3 with a trace of cobalt. It is the hardest natural substance after diamond and carborundum SiC. In addition to the usual α-form (corundum), alumina occurs in two others, though the so-called β-alumina has been shown to contain alkali metal.[415–18]

Corundum melts at $2015 \pm 15°$[419], and its extrapolated boiling-point is $2980 \pm 60°$[420]; about 1 mg. dissolves in a litre of water at 29°.[421] Plates of 'white sapphire' cut from crystals of pure synthetic corundum transmit excellently from the visible down to 1,435 A, and are not attacked by liquid and gaseous hydrogen fluoride in 15 hours.[422] The heat of formation of corundum is 402·9 k.cals./mole,[423] or 7·2 k.cals. per gramme of aluminium, a higher value per gramme than that of any other metal: compare

Al	Si	Mg	K	Mn
7·2	6·6	6	1·25	1·7

This reaction is the basis of the use of thermite, a mixture of aluminium powder with ferric oxide or some other metallic compound of high oxygen content, which is said to give temperatures approaching 3,000°; v. Wartenberg and Wehner[424] found spectroscopically that the temperature of a thermite containing Fe_3O_4 was $2,400° \pm 50°$. With excess of aluminium this mixture will reduce even the most refractory metals, such as chromium,

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[412] M. v. Stackelberg, E. Schnorrenberg, R. Paulus, and K. F. Spiess, *Z. physikal. Chem.* 1935, **175**, 127.

[413] M. v. Stackelberg and K. F. Spiess, ib. 140.

[414] W. E. White and A. H. Bushey, *J.A.C.S.* 1944, **66**, 1666.

[415] C. W. Stillwell, *J. Phys. Chem.* 1926, **30**, 1445.

[416] J. Gallup, *Amer. Ceramic Soc.* 1935, **18**, 144.

[417] H. Kraut, E. Flake, W. Schmidt, and H. Volmer, *Ber.* 1942, **75**, 1357.

[418] Wells, *S.I.C.* 335.

[419] R. F. Geller and P. J. Yavorsky, *J. Res. Nat. Bur. Stand.* 1945, **34**, 395.

[420] O. Ruff and M. Konschak, *Z. Elektrochem.* 1926, **32**, 518.

[421] W. Busch, *Z. anorg. Chem.* 1927, **161**, 169.

[422] S. Freed, H. L. McMurray, and E. J. Rosenbaum, *J. Chem. Phys.* 1939, **7**, 853.

[423] W. Roth, U. Wolf, and O. Fritz, *Z. Elektrochem.* 1940, **46**, 421.

[424] H. v. Wartenberg and G. Wehner, ib. 1936, **42**, 293.

manganese, cobalt, and vanadium. It was by this method that metallic chromium and manganese were first obtained free from carbon.

Alumina catalyses various organic reactions on heating, especially the loss of water by alcohols to form olefines (as ethylene from ethyl alcohol); but an alcohol can also be split off, as with an acetal in the reaction[430]

$$CH_3(CH_2)_5CH(O\cdot Pr)_2 = CH_3(CH_2)_4\cdot C{\equiv}CH + 2\,HO\cdot Pr$$

and even a molecule of ether, as when ethyl orthoacetate $CH_3\cdot C(O\cdot Et)_3$ passed over it at 250° gives $CH_3\cdot CO\cdot OEt + Et_2O$.

Aluminium Hydroxide

Alumina can take up as much as 3 H_2O per Al_2O_3, but no more.[429] There are two definite hydrates, $AlO\cdot OH$ and $Al(OH)_3$.[427-8] The first is diaspore,[425] which is almost certainly the same as bauxite (the main source of aluminium; the name is derived from Baux in France), though this may contain $Al(OH)_3$. For making aluminium bauxite is freed from ferric oxide by digestion with sodium hydroxide, when it dissolves as the aluminate $Na[Al(OH)_4]$, which is then decomposed by carbon dioxide. For the crystal structure of α-$AlO\cdot OH$ see refs. [425-6].

Forms of α-$(OH)_3$ are hydrargyllite (laterite is mainly this), Gibbsite, and Bayerite.

Chemically aluminium hydroxide can react in three ways:

1. As an acid giving aluminate ions, as in $H[AlO(OH)_2]$ or $H_3[Al(OH)_6]$, or $H[AlO_2]$, from which the metallic aluminates are derived.
2. As a base $Al[OH]_3$, giving rise to ionized salts such as the nitrate $Al[NO_3]_3$ and the sulphate $Al_2[SO_4]_3$.
3. It can form covalent derivatives, with the OH groups replaced by others, as in $AlBr_3$, $Al(C_2H_5)_3$, and $Al(O\cdot CH_3)_3$.

These three classes of derivatives cover practically the whole chemistry of aluminium, with the exception of the complex compounds, in which the aluminium has the covalencies of 4 and 6.

Aluminates

These are formed when aluminium dissolves in alkalies with evolution of hydrogen. The aluminates correspond to the borates, but aluminium hydroxide is as we should expect an even weaker acid than boric: its first dissociation constant is estimated to be 6×10^{-12},[434] whereas that of boric acid is 6×10^{-10}, a hundred times as great. Hence the salts in solution are highly hydrolysed, and even carbon dioxide is able to precipitate alumina from

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[425] W. Hoppe, *Z. Krist.* 1942, **104**, 11.

[426] P. P. Reichertz and W. J. Yost, *J. Chem. Phys.* 1946, **14**, 495.

[427] R. Fricke, *Z. anorg. Chem.* 1928, **175**, 250; 1929, **179**, 287.

[428] G. F. Hüttig and O. Kostelitz, ib. 1930, **187**, 1.

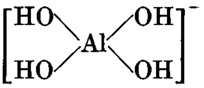
[429] C. F. Prutton, S. H. Maron, and E. D. Unger, *J.A.C.S.* 1935, **57**, 407.

[430] F. Sigmund and S. Herschdörfer, *Mon.* 1931, **58**, 268. [431] Id., ib. 280.

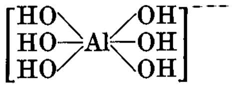
[432] R. Fricke and P. Jucaitis, *Z. anorg. Chem.* 1930, **191**, 129.

[433] P. Jucaitis, ib. 1934, **220**, 257. [434] A. Maffei, *Gaz.* 1934, **64**, 149.

them. The alkaline salts are all soluble, and of two types, $M[AlO_2]$aq. and $M_3[AlO_3]$aq. In solution the ions are no doubt hydrated, and should presumably be written



and



The solid phases of the sodium and potassium salts have been found[432-3] to be $Na[AlO_2]$, 5/4 and 3 H_2O: $K[AlO_2]$, 3/2 H_2O; equilibrium with the solutions (which are up to 20-normal, and then very viscous) is only established very slowly.

The large mineral class of the spinels have compositions of the type $M''[AlO_2]_2$, where M'' can be Mg, Zn, Fe'', etc., and Al can be replaced by Cr''', Fe''', and other trivalent metals; an example is chrysoberyl $Be[AlO_2]_2$. The crystal structures[435] suggest that the lattice is made up of M''' and $M''O_4$ ions, tetrahedral as in MoO_4; in fact the lattice is very like that of silver molybdate $Ag_2[MoO_4]$.

Aluminic Esters or Alkyloxides, $Al(O \cdot R)_3$

These covalent derivatives of aluminium hydroxide, formed by replacing the hydrogen atoms by alkyl or aryl groups, are usually called alkyloxides (ethoxide, etc.), but they are exactly analogous to the boric esters in structure and largely in behaviour. They were discovered by Gladstone and Tribe in 1881.[438] They are readily formed with evolution of hydrogen when aluminium (usually as powder) is warmed with anhydrous alcohol; a trace of water stops the reaction, presumably by forming a protective layer on the metal. They are solids which melt and then distil at rather high temperatures without decomposition:[439-41]

	M. pt.	*B. pt.*	$B(OR)_3$ *b. pt.*
$Al(OCH_3)_3$	..	..	..
$Al(OEt)_3$	139°	320°/760	118°/760
$Al(OisoPr)_3$	125°	242°/10 mm.	176°/760
$Al(OCH_3\Phi)_3$	81°	..	..

They are almost insoluble in alcohol, easily soluble in benzene, and at once hydrolysed by water. They have even less power of co-ordination than the boric esters, only forming such complexes as the alkylates $M[Al(O \cdot Alk)_4]$[436]; not only have all attempts to isolate other such compounds failed, but the polarization (which is always greatly increased by co-ordination) of a benzene solution of the ester is not raised by the addition of such powerful donors as ketones and nitriles.

On the other hand, unlike the boric esters, they are highly associated.

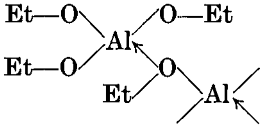
[435] Wells, *S.I.C.* 332.

[436] H. Meerwein and T. Bersin, *Ann.* 1929, **476**, 113.

The association factors determined cryoscopically in benzene at various concentrations and the dipole moments in benzene at 25° are[437];

	Assn. factor	*Dip. mom.*
$Al(OEt)_3$	4·4–4·6	1·35 D
$Al(OisoPr)_3$	3·8–4·0	1·4
$Al(OCH_2\Phi)_3$	3·0–3·1	1·8

A co-ordinate link must be formed between the aluminium atom of one molecule and the oxygen of another, as in



The dipole moments seem remarkably small for open-chain polymers of this kind, and Ulich and Nespital suggest 6 and 8 rings with alternate Al and O atoms. In thus polymerizing, the aluminium esters (like the alkyls and the halides) are in sharp contrast to their boron analogues; this has not been satisfactorily explained.

The aluminic esters will combine with the halides to form complexes which polymerize farther; their molecular weights can be determined by the freezing-points in benzene[436]; they include such compounds as $Al_4Cl_6(O \cdot Et)_6$ and $Al_3Cl_5(O \cdot Pr)_4$; their structures are unknown.

They react on warming with alcohols and esters exchanging the alkyloxy-groups, the lighter expelling the heavier from the aluminium, the primary the secondary, and the latter the tertiary alkyls.[431, 441-3]

These alkyloxides or aluminates have recently been found valuable for reducing aldehydes and ketones to their alcohols. Such a reduction is in general not easy; other groups in the molecule, for example C=C, may be reduced at the same time, or the reduction may go too far (to the hydrocarbon) or pinacones may be formed (Meerwein[444-5]). With the aluminium compound the reaction goes to equilibrium:

$$R \cdot CHO + CH_3CH_2 \cdot O \cdot al \rightleftharpoons R \cdot CH_2 \cdot O \cdot al + CH_3CHO.$$

As no hydrogen is produced, other reducible groups in the molecule remain untouched. This goes better with aldehydes than with ketones, which are harder to reduce. Much better yields are got[446] with ketones (as well as

[437] H. Ulich and W. Nespital, *Z. physikal. Chem.* 1933, **165**, 294.

[438] J. H. Gladstone and A. Tribe, *J.C.S.* 1881, **39**, 4.

[439] W. Tischtschenko, *J. Russ. Phys.-Chem. Ges.* 1899, **31**, 694, 784 (Chem. Centr. 00, I. 10, 585).

[440] R. A. Robinson and D. A. Peak, *J. Phys. Chem.* 1935, **39**, 1125.

[441] H. Meerwein and T. Bersin, *Ann.* 1929, **476**, 113.

[442] P. R. Fehland and H. Adkins, *J.A.C.S.* 1935, **57**, 193.

[443] R. H. Bakor, ib. 1938, **60**, 2673.

[444] H. Meerwein and H. Schmidt, *Ann.* 1925, **444**, 221.

[445] H. Meerwein, *J. prakt. Chem.* 1936, ii. **147**, 211.

[446] W. G. Young, W. H. Hartung, and F. S. Crossley, *J.A.C.S.* 1936, **58**, 100.

with aldehydes) by using aluminium isopropylate, as a secondary alcohol then appears on both sides of the equation.[447-8] The reagent is almost ideal: from its nature the reaction cannot go too far, and it is found experimentally that pinacones are not formed. The reagent is made by heating aluminium with isopropyl alcohol and a tenth of a per cent. of mercuric chloride; the solution is then boiled with the aldehyde or ketone, using a reflux with warm water, so that the acetone distills off as it is formed, and the reaction goes to completion. Lund[447] gives sixteen examples of dialkyl, alkyl-aryl, and diaryl ketones reduced in this way, the yields being mostly 90-100 per cent.

Aluminium Halides

Aluminium is obviously on the line between ionization and covalency formation, and will form compounds of one or the other type according to the conditions, and in particular to the deformability of the atoms to which it is attached. Of the halides the fluoride should be most readily ionized, and the others increasingly tend to go into the covalent form. This is so, as is seen from the following table, the evidence for which is discussed later.

	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
Solid . . .	ion.	ion.	cov.	cov.
Liquid . . .	ion.	cov.	cov.	cov.
Vapour . . .	(ion.)	cov.	cov.	cov.
Aq. solution . .	ion.	ion.	ion.	ion.
Bz. solution . .	. .	cov.	cov.	cov.

The salt character of the fluoride is obvious from the high melting- and boiling-points, and from its insolubility in non-dissociating solvents; the stannic and mercuric fluorides occupy the same exceptional position.

Physical properties

	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
M. pt. . . .	1,290°	192·6°/1,700 mm.[a]	97·5°[b]	179·5°[c]
B. pt. . . .	Sbl. 1,291°	Sbl. 180°[d]	255°[e]	381°[e]
Ht. of formation[e] .	. .	167	121	71 k.cals.
Crit. temp.[f] . .	. .	356·4°	499°	682°

a = [450]; *b* = [452]; *c* = [454]; *d* = [451]; *e* = [453]; *f* = [455].

Aluminium Fluorides

Aluminium subfluoride, AlF. Klemm and Voss[460] have shown that this probably exists in the vapour. When metallic aluminium and its trifluoride are heated together *in vacuo* at 650-850° a white sublimate is formed, whose composition on repeated redistillation from excess of aluminium approaches AlF (found Al: F 1 to 1·36, 1·22, 1·09, 1·06, 1·05).

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[447] H. Lund, *Ber.* 1937, **70**, 1520.

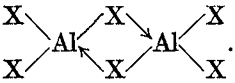
[448] P. G. Stevens and O. C. W. Allenby, *J.A.C.S.* 1940, **62**, 3264.

The solid gives the X-ray lines for Al and for AlF_3, but no others. Hence there must be a volatile subfluoride of the composition AlF, which breaks up on solidification into the metal and the trifluoride.

Aluminium fluoride, AlF_3,[449] which can be made from its elements, sublimes without melting at 1291°, and has a sol^y in water of 0·56/25°.[459] It forms numerous hydrates, probably at least with 1/2, 3, and 9 H_2O, but their nature is obscure[456-8]; the trihydrate is dimorphic.[461] Chemically it is extremely inert, especially as compared with the other trihalides; boiling sulphuric acid has no action on it, and water at 400° or fusion with potassium hydroxide only decomposes it very slowly.

Aluminium Chloride, $AlCl_3$

The other three trihalides resemble one another in most ways. In the vapour near the boiling-points they are largely dimeric (Nilson and Pettersson, 1887); according to Fischer and Rahlfs[451] the percentage of the monomeric form near the boiling-point is $AlCl_3$ (180°) 0·02; $AlBr_3$ (255°) 0·7; AlI_3 (380°) 24. The heat of evaporation of aluminium chloride is that of a normal dimeric covalent liquid, giving for Al_2Cl_6 a Trouton constant of 21·1.[465] Dimeric molecules are also found in non-co-ordinating solvents like benzene, though not in donor solvents such as ether and pyridine.[469] The dimeric structures have been determined in the vapour by electron diffraction[470]; all three are formed of two AlX_4 tetrahedra with one edge (and two halogen atoms) in common,



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[449] O. Ruff, *Z. angew. Chem.* 1928, **41**, 738.

[450] A. Smits, J. L. Meyering, and M. A. Kamermans, *Proc. Akad. Amst.* 1932, **35**, 194.

[451] W. Fischer and O. Rahlfs, *Z. anorg. Chem.* 1932, **205**, 37.

[452] W. Biltz and A. Voigt, ib. 1923, **126**, 39.

[453] W. Klemm and H. Jacobi, ib. 1932, **207**, 186.

[454] A. Vian and E. Moles, *Anal. Fis. Quim.* 1936, **34**, 81.

[455] L. Rotinjanz and W. Suchodski, *Z. physikal. Chem.* 1914, **87**, 635.

[456] E. Birk, *Z. anorg. Chem.* 1927, **166**, 286.

[457] V. S. Jatlov and A. I. Zelinskaja, *J. Gen. Chem. Russ.* 1937, **7**, 1787.

[458] I. Tananaev, ib. 1938, **8**, 1120.

[459] R. H. Carter, *Ind. Eng. Chem.* 1928, **20**, 1195.

[460] W. Klemm and E. Voss, *Z. anorg. Chem.* 1943, **251**, 233.

[461] W. F. Ehret and F. J. Frere, *J.A.C.S.* 1945, **67**, 64.

[462] W. Biltz and W. Wien, *Z. anorg. Chem.* 1922, **121**, 257.

[463] W. Biltz and W. Klemm, ib. 1926, **152**, 267.

[464] W. E. Laschkarew, ib. 1930, **193**, 270.

[465] A. Smits, J. L. Meyering, and M. A. Kamermans, *Proc. K. Akad. Amst.* 1931, **34**, 1327.

[466] W. A. Roth and E. Börger, *Z. Electrochem.* 1938, **44**, 540.

[467] W. Fischer, *Z. anorg. Chem.* 1931, **200**, 332.

[468] H. Gerding and E. Smit, *Z. physikal. Chem.* 1942, **B 51**, 217.

[469] A. Werner, *Z. anorg. Chem.* 1897, **15**, 1.

[470] K. J. Palmer and N. Elliott, *J.A.C.S.* 1938, **60**, 1852.

The Al—X distance is rather longer when X is a linking halogen (Al—X_s) than when it is not co-ordinated (Al—X_p). The results are:

	$AlCl_3$	$AlBr_3$	AlI_3
Al—X_p	2·06	2·21	2·53 A
Al—X_s	2·21	2·33	2·58
Theory for Al—X	2·25	2·40	2·59

This structure is supported by the Raman spectra of the liquids,[404, 468] whose whole behaviour shows them to be covalent. The bromide and iodide are clearly covalent in the solid state as well. But it is remarkable that the solid chloride is ionized; this is established by the molecular volumes (Biltz[462]), and supported by the conductivities.[452, 463]

TABLE

	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
Mol. vol. solid[a]	27·1	54·7	88·7	102·5 c.c.
„ liqu./T°[b]	. .	100/90°	118/265°	147/382°
Ratio	.	0·55	0·75	0·70
Sp. condy. × 10^6 liqu./m. pt.		0·45/194°	0·09/97·5°	1·2/191°
Ht. of fusion	.	8·9[c]	2·7[d]	3·8 k.cals.[d]

a = [462]; *b* = [452]; *c* = [485]; *d* = [487].

As the table shows, solid aluminium chloride has an abnormally small molecular volume, while the expansion on heating and the heat of fusion are abnormally large. So too the specific conductivity of solid aluminium chloride, which is zero at the ordinary temperature, increases very steeply[452] just below the melting-point, reaching about 5 × 10^6; and then as it melts drops almost to zero, rising slowly to about 1 × 10^6 some 50° higher. The bromide and iodide show no such anomaly; their conductivity in the solid state is zero, and in the liquid just above the melting-point is of the same order of magnitude as that of the liquid chloride. The crystal structure of the chloride, which has a layer lattice of an ionic type,[464] supports this (the lattices of the bromide and iodide are unknown).

Aluminium chloride dissolves in water with evolution of 79·4 k.cals./$AlCl_3$,[466] and the solution is highly hydrolysed (2 per cent. at $V = 10$).

Aluminium Bromide, $AlBr_3$

This also is made from its elements (for details see ref. [471]). As would be expected from its lower melting-point and covalency in the solid, it is more soluble in non-ionizing solvents than the chloride. In bromine[472] it gives a conducting solution in which boiling-point and freezing-point show

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[471] P. K. Winter and P. L. Cramer, *J. Ind. Eng. Chem.* 1940, **32**, 856.

[472] W. Finkelstein, *Z. physikal. Chem.* 1923, **105**, 15.

it to be Al_2Br_6.[477] Sol^y 168/25° in chloroform,[473] 33/25° in *n*-hexane.[476] The dipole moments of the bromide and iodide (the chloride is too insoluble) have been measured in benzene and carbon bisulphide[474]; the results (extrapolated as usual to infinite dilution) are:

	In benzene	*In* CS_2
$AlBr_3$	5·2	*ca.* 0 (0·55)
AlI_3	2·5	0

In concentrated benzene solution the value for the bromide is nearly zero. This shows that there is solvation in benzene, and further that it is the monomeric and not the dimeric form that is solvated.

Solutions of aluminium bromide in hydrocarbons do not conduct, but those in other solvents often do, especially in phenyl and methyl cyanide, and in nitrobenzene. The better the conductivity the poorer the yield in the Friedel-Crafts reaction when that solvent is used as a reactant.[475]

Aluminium iodide, AlI_3, is best made by the action of iodine vapour in hydrogen on the metal at 420°.[454] The molecular weight in iodine solution by the boiling-point is that of Al_2I_6.

The Friedel-Crafts reaction, which is the most important property of aluminium chloride, is discussed later (p. 436).

Aluminium oxyhalides, AlOX. The compounds AlOCl and AlOBr can be got[478] by heating the etherates of the trihalides; they have not been purified; they are soluble only in donor solvents like nitrobenzene and acetone, in which they give brown and red solutions.

Aluminium Salts of Oxy-acids

Aluminium hydroxide is a weak but not a very weak base; its salts with strong acids are not more highly hydrolysed than those of beryllium (about 1-2 per cent. at $V = 10$). As with beryllium, weak acid salts, such as the nitrite, cyanide, and acetate, cannot be prepared, or are at once hydrolysed by water. The strong acid salts are quite stable; they include the halides, all of which behave in water as salts, the chlorate, perchlorate, nitrate, and sulphate. All except the fluoride (sol^y 0·56/25°) are extremely soluble in water, and all are highly hydrated: AlF_3, 9 and 3 H_2O; $AlCl_3$, $AlBr_3$ all 6 H_2O; $Al(ClO_3)_3$ 9 and 6; $Al(ClO_4)_3$ 9, 8, and 6; $Al_2(SO_4)_3$ 27, 18, 16, and 10 (18 at ordinary temperatures).

O—C salts. The carbonate is not known[479]; the formate is doubtful;

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[473] H. H. Kavaler and C. J. Monroe, *J.A.C.S.* 1928, **50**, 2423.

[474] W. Nespital, *Z. physikal. Chem.* 1932, B **16**, 176.

[475] E. Wertyporoch and B. Adamus, ib. 1934, **168**, 31.

[476] E. R. Boedeker and A. G. Oblad, *J.A.C.S.* 1947, **69**, 2036.

[477] E. Beckmann, *Z. anorg. Chem.* 1912, **77**, 275.

[478] W. Menzel and M. Froehlich, *Ber.* 1942, **75**, 1055.

[479] F. K. Cameron and W. O. Robinson, *J. Phys. Chem.* 1908, **12**, 572.

the acetate can only be made in the absence of water (as from acetic anhydride and aluminium chloride at 180°),[480] and is 40 per cent. hydrolysed in water at $V = 10$ and 25°; it readily gives basic salts.

No definite neutral oxalate is known.[481]

O—N salts. $Al(NO_3)_3$ is stable from $-27°$ to $+73°$; very soluble in water (63·7/25°), and also in alcohol.

Aluminium sulphate is the most technically valuable salt of aluminium. It is used for purifying water, as a size for paper (when it must be free from iron), and as a mordant, especially for dyeing cotton. The production of the sulphate in the U.S.A. in 1930 was 320,000 tons, of which 17,000 were iron-free.[482]

The anhydrous salt begins to lose sulphur trioxide at 605°. Tensimeter measurements show[483] that it forms hydrates with 27, 18, 16, 10, and 6 H_2O; the 18-hydrate (sol^y 38·3/25°) is stable to above 100°. The anhydrous salt forms no compound with ammonia even down to $-20°$,[484] which suggests complexity.

Aluminium sulphate is a constituent of the most famous of all series of double salts, the alums $M'M'''(SO_4)_2, 12\,H_2O$; it is doubtful whether aluminium forms any double sulphates except of this class. These salts, though extremely stable—potassium alum separates out from solutions of all mixtures of potassium and aluminium sulphates with an $Al/(Al+K)$ ratio greater than 0·10 and less than 0·93—have none of the characteristics of true complex salts: the properties of the solutions are those to be expected from a mixture of the component sulphates in these proportions. The final test of crystal structure proved unexpectedly difficult, but it has now been shown[485–6] that the alums are not complex salts, since the 12 molecules of water are found to be divided into two groups of 6, one surrounding the univalent cation and the other the aluminium, which latter must therefore be present as a cation, and not as part of a complex anion.

The latest work on the crystal structures of the alums[486–8] has shown that there are three slightly different but distinct types of alum structure, α, β, and γ, and that large cations give the β, middle-sized the α, and the smallest the γ. Clug[493] has shown that of the chrome alums the ammonium

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[480] W. Tischtschenko and W. Kisselew, *J. Russ. Chem. Ges.* 1899, **31**, 793.

[481] Gmelin, *Aluminium*, [B] 302 (1933).

[482] C. L. Mantell, *Min. Ind.* 1931, **39**, 27.

[483] F. Kraus and A. Fricke, *Z. anorg. Chem.* 1927, **166**, 170.

[484] F. Ephraim and S. Millmann, *Ber.* 1917, **50**, 534.

[485] H. Lipson and C. A. Beevers, *Proc. Roy. Soc.* 1935, **148**, 664.

[486] H. Lipson, ib. 1935, **151**, 347.

[487] Id., *Nature*, 1935, **135**, 912.

[488] Id., *Phil. Mag.* 1935, [vii] **19**, 887.

[489] A. E. Hill and N. Kaplan, *J.A.C.S.* 1938, **60**, 550.

[490] F. A. H. Schreinemakers and A. J. C. de Waal, *Chem. Weekblad*, 1906, **3**, 539.

[491] J. P. Sanders and J. T. Dobbin, *J. Phys. Chem.* 1931, **35**, 3086.

[492] J. F. Spencer and G. T. Oddie, *Nature*, 1936, **138**, 169.

[493] H. P. Clug, *J.A.C.S.* 1940, **62**, 2992.

and potassium are α: the rubidium, caesium, thallous, and methylammonium are β. Double sulphates of the alum type can be made with at least eleven different trivalent metals,* but not all of these will combine with every monovalent cation; this seems to depend on the size. Thus lithium probably forms no alums (see below); sodium only two, with Al and Cr; potassium with these elements and also with Fe, Ga, V, Rh, and Ir; rubidium and caesium with all these trivalent elements and with Co, In, Ti, and Mn as well. The limits of formation of solid solutions by different alums have been examined by Clug and Alexander[494] and by Hill and Kaplan[489]; the latter find among the Al alums an unbroken series for K and NH_4, and for NH_4,Al and NH_4,Fe, but not for NH_4,Al and Na,Al (this must be related to the type of lattice).

The existence of a true lithium alum is very doubtful. Vain efforts to make one go back as far as C. G. Gmelin in 1819. The system

$$Li_2SO_4,\ Al_2(SO_4)_3,\ H_2O$$

was examined at 30° by Schreinemakers[490] and at 0°, 25°, and 50° by Sanders and Dobbin,[491] all of whom failed to find any double salt. J. F. Spencer[492] and Horan and Duane,[495] who examined the solubility curves of the system Li_2SO_4, $Al_2(SO_4)_3$, H_2O at 0° C., got evidence of the formation of a solid phase $LiAl(SO_4)_2$, 12 H_2O over a very narrow range (the wt. per cent. Li_2SO_4 at the three points where it was got was 14·11, 13·94, 13·28[495]); the crystalline form could not be observed. If lithium alum exists, the Li^+ ion must be surrounded by 6 H_2O, whereas the covalency maximum of lithium is normally 4.

O-halogen Salts

Aluminium chlorate, $Al(ClO_3)_3$, is known only as a 9- and a 6-hydrate, and not in the anhydrous state. It is extremely soluble in water and in alcohol; the aqueous solution on evaporation evolves chlorine dioxide and ultimately explodes.

Aluminium perchlorate, $Al(ClO_4)_3$. The anhydrous salt[496] can only be made by treating the chloride with anhydrous perchloric acid and evaporating off the excess first of acid and then of aluminium chloride; the perchlorate remains, with 5–15 per cent. of chloride as an impurity. The salt crystallizes with 15, 9, and 6 H_2O; the solubilities in water are 121·6/0°, 131·0/14·3°, 149·8/96°.[497]

Aluminium periodate: the salt $Al(IO_4)_3$, 12 H_2O can be obtained[498] by treating the hydroxide with a solution of periodic acid.

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* Al, Ti, V, Cr, Mn, Fe, Co, Ga, In, Rh, Ir.

[494] H. P. Clug and L. Alexander, *J.A.C.S.* 1940, **62**, 2993.
[495] H. A. Horan and A. J. Duane, ib. 1941, **63**, 3533.
[496] E. G. Hackenberg and H. Ulich, *Z. anorg. Chem.* 1939, **243**, 99.
[497] D. Dobrosserdov, *Ukraine Chem. J.* 1926, **2**, 109, 119.
[498] V. Biber, A. Vnukova, and N. Konschin, *J. Gen. Chem. Russ.* 1936, **6**, 873.

ALUMINIUM COMPLEXES

Aluminium, like boron, readily acts as acceptor; its covalency in complexes is often 4, but unlike that of boron can rise to 6. The chief donors are:

1. Alkali metals (i.e. electrons).
2. Carbon.
3. Nitrogen. 3 A. Phosphorus.
4. Oxygen. (*a*) Open chain; (*b*) Chelate.

4 A. Sulphur.

5. Halogens: (*a*) Fluorine; (*b*) Chlorine; (*c*) Bromine; (*d*) Iodine.

1. *Addition Compounds of Alkali Metals*

In these the aluminium compound takes an electron from the metal and becomes an anion (with a valency group of 7). They are little known, but sodium dissolves in an ethereal solution of aluminium triphenyl[499] to give a reddish-brown solution, decolorized by air, which leaves on evaporation a brown powder; this must be the salt $Na[Al(C_6H_5)_3]$, like $Na[B(C_6H_5)_3]$.

2. *Carbon*

These are of the types:

A. Addition compounds of alkyls and aryls, such as $M[AlR_4]$.

B. Addition compounds of unsaturated hydrocarbons, such as ethylene, and benzene.

C. [? Carbonyl compounds.]

A. $M[AlAlk_4]$. These are only known in solution; they are similar to the zinc compounds already described (II. 278), and are made[500] by dissolving lithium or sodium ethyl in aluminium triethyl; their formation requires a temperature of 110-15°, while the zinc complexes are formed at 35–40°. A liquid layer separates, containing most of the alkali metal, and having considerable conductivity.

B. Aluminium halides undoubtedly form co-ordination complexes with aromatic, ethylenic, and acetylenic hydrocarbons,[501] though scarcely any (and no simple ones) have been isolated. Solutions of aluminium chloride in alcohol absorb ethylene, butylene, amylene, and acetylene, and solids of such compositions as $AlCl_3, C_2H_2, 2\,EtOH$ separate out.[503] Benzene solutions of the chloride absorb olefines in the same way, and by a further reaction alkyl benzenes are produced.[504-5] With benzene itself no compounds have been isolated,[502] but the large dipole moments of the halides

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[499] E. Krause and H. Polack, *Ber.* 1926, **59**, 1428. (No further papers on it have appeared.)

[500] F. Hein, E. Petschner, K. Wagler, and F. A. Segitz, *Z. anorg. Chem.* 1924, **141**, 171.

[501] W. E. Henderson and W. C. Gangloff, *J.A.C.S.* 1916, **38**, 1382 (C. 17, i. 561); 1917, **39**, 1420, (C. 18, i. 10).

[502] B. Menschutkin, C. 10, i. 167.

[503] W. Nespital, *Z. physikal. Chem.* 1932, B **16**, 176.

[504] T. M. Berry and E. E. Reid, *J.A.C.S.* 1927, **49**, 3142.

[505] M. B. Turova-Pollak and Z. Makaeva, *J. Gen. Chem. Russ.* 1939, **9**, 1279.

in benzene[503] (see above,[508] p. 426) show that co-ordination must take place, since both monomeric and dimeric aluminium halides must from their symmetry be non-polar. The fall of these dipole values to zero with increase of concentration is to be expected for an equilibrium of the type

$$AlBr_3, C_6H_6 \rightleftharpoons AlBr_3 \rightleftharpoons Al_2Br_6.$$

C. *Carbonyls.* It is doubtful if they exist. When alumina is reduced by carbon at 1,500-2,000°, a white sublimate is formed, which is generally thought to be the carbide Al_4C_3, but may possibly be the carbonyl $Al_4(CO)_3$.[506,507]

3. *Nitrogen*

Co-ordination compounds with ammonia and organic amines are formed with great ease by the aluminium halides (excluding as usual the fluoride), with less ease by the aryl compounds, and not at all by the esters.

The halides readily absorb ammonia, and the most stable compounds produced are the monammines and triammines.[510,511] The latter are presumably salts; the monammines are covalent compounds of the type of $Cl_3Al \leftarrow NH_3$.

	Cl_3	Br_3	I_3
M. pt. AlX_3 . . .	192°	98°	191°
„ AlX_3,NH_3 . .	125°	124°	126°
B. pt. AlX_3 . . .	160°	255°	381°
„ AlX_3,NH_3 . .	422°	429°	..

They boil without decomposition at rather high temperatures, and the vapour density near the boiling-point corresponds to the simple but undissociated molecule AlX_3,NH_3; but the high values of the Trouton constant (Cl 25; Br 27) suggest association in the liquid. The change from the solid ionized $AlCl_3$ to the covalent ammine is clearly indicated in the regularity of the melting-points as compared with those of the simple halides. The fused monammines have considerable conductivity (0·01 to 0·02, while $AlCl_3$ is about 10^{-5}).[510]

Many similar compounds with organic amines are known. Mixtures of aluminium halides with amines (as also with organic compounds of oxygen) have in benzene large dipole moments, indicating co-ordination (see p. 433).

The aluminium triaryls form monammines if their ethereal solutions are treated with ammonia, but these are much less stable than the halide complexes.[509] Thus the triphenyl compound $\Phi_3Al \leftarrow NH_3$ melts at 112° with some decomposition, and the tritolyl begins to lose ammonia when

[506] C. H. Prescott and H. B. Hinke, *J.A.C.S.* 1927, **49**, 2756.

[507] R. Brunner, *Z. Elch.* 1932, **38**, 68.

[508] H. Ulich and W. Nespital, *Z. Elektrochem.* 1931, **37**, 559.

[509] E. Krause and P. Dittmar, *Ber.* 1930, **63**, 2401.

[510] W. Klemm and E. Tanke, *Z. anorg. Chem.* 1931, **200**, 343–66.

[511] W. Klemm, E. Clausen, and H. Jacobi, ib. 367–84.

its benzene solution is boiled. This ammine is at once oxidized by air, which the corresponding boron compounds $BAlk_3,NH_3$ are not. This is no doubt because the 4-covalent boron compound, but not its aluminium analogue, is covalently saturated; so that the aluminium atom, but not the boron atom, can form a co-ordinate link with the oxygen.

Cyanide complexes. Aluminium chloride forms a compound $AlCl_3$, 2 HCN[512] (presumably linked through the nitrogen), and a series of complexes with organic nitriles have been prepared.[513]

Phosphine Compounds

Aluminium chloride bromide and iodide all absorb phosphine at 70° or above (implying an unexpected heat of activation) to give compounds AlX_3,PH_3 analogous to the monammines, but less stable.[514] The melting-points and the temperatures at which the dissociation pressure of phosphine is 10 mm. are:

	$AlCl_3,PH_3$	$AlBr_3,PH_3$	AlI_3,PH_3
M. pt.	82°	116°	149°
T°./10 mm. . . .	10°	85°	93°

The last row of figures involves the solid phase of the halide, and so the chloride value is abnormal.

4. *Oxygen*

The oxygen complexes of aluminium are more numerous than any other class. They can be divided into the open-chain and the chelate compounds.

(*a*) *Open-chain*

The most obvious of these is the hexahydrated cation $[Al(OH_2)_6]^{+++}$, the existence of which is evident from the hydration of the salts. Brönsted[515] has determined its 'acid dissociation', i.e. its tendency to go over into $[Al(OH_2)_5OH]^{++}+H^+$. At 25° he finds these values for the corresponding Al, Cr, and Fe ions:

Al	Cr‴	Fe‴
$0{\cdot}13\times10^{-4}$	$1{\cdot}26\times10^{-4}$	63×10^{-4}

Meerwein and Bersin[516] have made a series of alkylates such as $K[Al(OR)_4]$, mostly by dissolving aluminium in a solution of the alkali metal in the alcohol.

Other salts (e.g. Li, Tl′, Mg, Cu″, Ni) were made.

The aluminium trihalides (and sometimes also the trialkyls and triaryls) form addition compounds with water, alcohols, ethers, aldehydes, and

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[512] L. E. Hinkel and R. T. Dunn, *J.C.S.* 1931, 3343.
[513] Gmelin, *Aluminium*, B. 215, 234.
[514] R. Höltje and F. Meyer, *Z. anorg. Chem.* 1931, **197**, 95.
[515] J. N. Brönsted and K. Volqvartz, *Z. physikal Chem.* 1928, **134**, 97.
[516] H. Meerwein and T. Bersin, *Ann.* 1929, **476**, 113.

ketones. The water compounds no doubt contain hydrated cations and are described under the salts. The alcoholates are not very numerous, but aluminium chloride crystallizes[517] with 4, 5, and 6 molecules of methyl alcohol and 4 of ethyl.

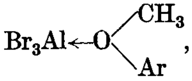
The *ether* complexes are exceptionally stable, and are formed by both the trialkyls and the trihalides.

The *trialkyl* complexes, all of the type AlR_3,R'_2O, were fully examined by Krause and Wendt.[518] They can be made directly from the components, from the action of $AlCl_3$ on the Grignard reagent in ether, or by dissolving 'electron metal' (an alloy of aluminium and magnesium) in the ethereal solution of an alkyl iodide, as in making the Grignard reagent; after driving off the ether, the etherate can be distilled over *in vacuo.*

These etherates are so stable that they can be distilled without decomposition a little below the boiling-points of the trialkyls (e.g. $Et_3Al \leftarrow OEt_2$, b. pt. 217°/760 mm.); but they are as sensitive to air and to water as the trialkyls themselves. The triaryls (Krause and Polack[519]) behave in the same way, but the ether is less firmly held, and is split off *in vacuo* at about 150°. They are monomeric in benzene.

Halide compounds. The trihalides also form 1:1 compounds with ether which are rarely found to distil, but are very stable in the cold; thus $Cl_3Al \leftarrow OEt_2$ (m. pt. 35°[521]) distills unchanged at 147°/11 mm.[523]; and the corresponding bromides show in benzene by their melting- and boiling-points[520] an association factor from 1·1 to 1·5; as they have very high dipole moments[524] (p. 433), this may be due to dipole association, as with nitrobenzene. See further, reference [525].

Compounds of the aryl-alkyl ethers, of the type



$$Br_3Al \leftarrow O\begin{matrix} CH_3 \\ Ar \end{matrix},$$

when boiled in benzene solution split off alkyl halides to form non-complex ester-halide compounds $Ar—O—AlBr_2$ (a further example of the way in which the hydrolysis of halides proceeds through a co-ordination compound), which are hydrolysed by water to give the phenol Ar—OH. This explains the mechanism of the well-known reaction for hydrolysing phenol ethers with aluminium chloride.

The trichlorides and tribromides co-ordinate with many other organic compounds of oxygen, as is shown by the isolation of the complexes,[522] by molecular weight determinations through the freezing- and boiling-

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[517] Gmelin, *Aluminium*, B. 214.

[518] E. Krause and B. Wendt, *Ber.* 1923, **56**, 466.

[519] E. Krause and H. Polack, ib. 1926, **59**, 777.

[520] H. Ulich, *Z. physikal. Chem.* 1931, Bodenstein Festband, 428.

[521] W. Menzel and M. Froehlich, *Ber.* 1942, **75**, 1055.

[522] Gmelin, *Aluminium* B; $AlCl_3$ 213–16, $AlBr_3$ 232–5.

[523] P. Urech and R. Sulzberger, *Helv. Chim. Acta*, 1944, **27**, 1328.

[524] W. Nespital, *Z. physikal Chem.* 1932, B **16**, 178.

points (especially in benzene),[520] by the dipole moments in solution,[524] and in other ways. Such compounds (nearly always 1:1) are formed by aldehydes (few), ketones (many and stable),[526] esters, acid chlorides, nitro-compounds,[529–30] and even sulphones.

Ulich and Nespital[527–8] have shown that both these and the nitrogen complexes have very large dipole moments in benzene or carbon disulphide, as is to be expected from the large moment of the co-ordinate link; but it is remarkable that the moments seem always to exceed those of the donor molecules by the same amount; the same is true of the boron complexes; the values are given in the following table:

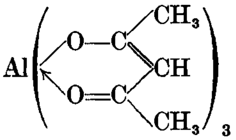
Dipole moments

Complex	*Moment of*		*Difference*
	Complex	*Donor*	
$AlCl_3$, $EtNH_2$	6·9	1·3	5·6
$AlCl_3$, Et_2O	6·7	1·2	5·5
$AlBr_3$, Et_2O	6·5	1·2	5·3
$AlCl_3$, $\Phi \cdot NO_2$	9·2	3·9	5·3
$AlBr_3$, $\Phi \cdot NO_2$	9·2	3·9	5·3
$AlCl_3$, Φ_2CO	8·3	3·0	5·3
BCl_3, CH_3CN	7·7	3·2	4·5
BCl_3, $EtCN$	7·8	3·4	4·4
BCl_3, Et_2O	6·0	1·2	4·8

Scheka[530] finds the same for a series of aluminium chloride complexes of Cl—, CH_3— and CH_3—O— substituted nitrobenzenes; the difference is always about 5·3 D.

(*b*) *Chelate Oxygen Complexes*

These are numerous, and owing to the greater stability of the chelate ring are nearly all 6-covalent (trichelate).



β-diketone derivatives, etc.[535–40] The best known is the acetylacetone compound, melting at 192°, boiling undecomposed at 315°, monomeric by vapour density and in benzene solution, almost insoluble in water but easily soluble in alcohol, ether, and benzene. Similar derivatives are

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[525] E. P. Kohler, *Am. Chem. J.* 1902, **27**, 249.

[526] H. Ulich and G. Heyne, *Z. Elektrochem.* 1935, **41**, 509.

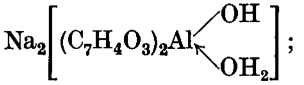
[527] H. Ulich and W. Nespital, *Angew. Chem.* 1931, **44**, 750.

[528] Id., *Z. Elektrochem.* 1931, **37**, 559.

[529] V. A. Plotnikov and E. J. Gorenbein, *Mem. Inst. Chem. Ukrain. Acad. Sci.* 1936, **3**, 471.

[530] V. A. Plotnikov, Z. A. Jankelovitsch, and I. A. Scheka, *J. Gen. Chem. Russ.* 1933, **3**, 802.

formed of acetoacetic ester (m.pt.78°), of diethyl malonate (95°), and of salicylic ester.[542] Salicylic acid gives a peculiar salt which must have the structure

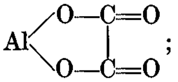


$$Na_2\left[(C_7H_4O_3)_2Al\begin{matrix}OH\\ OH_2\end{matrix}\right];$$

the salts all have enough water for this. The corresponding aluminioxalates $M_2[(C_2O_4)_2Al(OH)(OH_2)]$ are known, as well as the chromisalicylates.

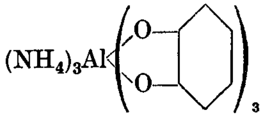
The other O-chelate aluminium complexes are derivatives of dibasic acids ('ato' complexes).

Carbonato-compounds (described by Dittmar in 1893) are very doubtful. *Oxalato* are numerous, containing the ring



two types, a dichelate $M[Al(C_2O_4)_2]aq.$ and a trichelate $M_3[Al(C_2O_4)_3]aq.$, are known,[533-4] in addition to the basic salt mentioned above. The trichelate complex is very stable and has been resolved[535]; it racemizes easily, with a half-life of 42 hours at 25°. Long has shown[541] by the use of radioactive carbon that the interchange of oxalate ions is negligibly small at 35°, so that the mechanism of the racemization must be one which does not involve a dissociation of the complex anion. See further, refs.[531-2]; nearly all the oxalato-salts, including those of potassium, rubidium, and ammonium, are hydrated.

The catechol derivatives are similar; catechol is a dibasic acid, though a very weak one. The stability of the derivatives is due to the ring structure. Treadwell *et al.*[545] have prepared the ammonium salt



and resolved it with strychnine, obtaining an active potassium salt.

[531] A. Rosenheim and L. Cohn, *Z. anorg. Chem.* 1896, **11**, 192.

[532] G. Wyrouboff, *Bull. Soc. Min.* 1900, **23**, 89.

[533] G. J. Burrows and G. Walker, *J.C.S.* 1923, **123**, 2738.

[534] G. J. Burrows and K. H. Lander, *J.A.C.S.* 1931, **53**, 3600.

[535] W. Wahl and M. Andersin, *Ber.* 1927, **60**, 399.

[536] A. Combes, *Ann. Chim. Phys.* 1887, [vi] **12**, 199, 253; *C.R.* 1887, **105**, 870.

[537] A. Hantzsch and C. H. Desch, *Ann.* 1902, **323**, 18.

[538] G. T. Morgan and H. D. K. Drew, *J.C.S.* 1921, **119**, 1060.

[539] W. T. Astbury, *Proc. Roy. Soc.* 1926, **112**, 449.

[540] R. A. Robinson and D. A. Peak, *J. Phys. Chem.* 1935, **39**, 1125.

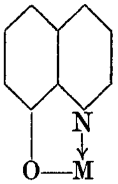
[541] F. A. Long, *J.A.C.S.* 1939, **61**, 570.

[542] G. J. Burrows and I. W. Wark, *J.C.S.* 1928, 222.

[543] R. Berg, *Z. anal. Chem.* 1927, **71**, 361.

[544] G. E. F. Lundell and H. B. Knowles, *Bur. Stand. J. Res.* 1929, **3**, 91.

The 8-hydroxy-quinoline complexes used in analysis are O—N-chelate compounds; under suitable conditions the aluminium derivative can be precipitated alone from a solution containing various metals.[543-4]



4 A. *Sulphur Complexes*

Not many of these are known. Rather obscure complexes were got by Plotnikow[546] and by Ruff[547]; a more definite series was made from the trihalides and hydrogen sulphide by Biltz[548]: their heats of formation and the temperatures T.° at which the dissociation pressure reaches 100 mm. are:

	$AlCl_3,H_2S$	$AlBr_3,H_2S$	AlI_3, 2 H_2S	AlI_3, 4 H_2S
Ht. of formation .	9·22	9·72	9·13	6·30 k.cals./mole.
T.°	+14°	+30°	+11°	−79°

$AlBr_3,H_2S$ is monomeric in benzene solution by the freezing-point,[549] and in this solution at 25° has a dipole moment of 5·1 D,[550] 4·2 D greater than that of hydrogen sulphide.

5. *Complex Halides*

The covalent link Al—F, like Si—F, is obviously very strong, and aluminium forms numerous stable complex fluorides; but its affinity for halogens falls off very rapidly: none but fluorine give it a covalency of more than 4; complex chlorides and bromides are rare, and complex iodides are almost unknown.

The fluorides are nearly all of the type $M_3[AlF_6]$; a few $M[AlF_4]$ are known, and a few $M_2[AlF_5]$; these last, however, are almost always hydrated, and so should probably be written $M_2[F_5Al \leftarrow OH_2]$. The free acid of the first type seems to occur, as solid phases of the compositions $H_3[AlF_6]$ 3 and 6 H_2O have been prepared.[551]

The best known of these salts is cryolite, $Na_3[AlF_6]$ (m.pt. 1,000°), which is almost confined to one locality in Greenland, where there are large deposits of it. Other salts of this type are the lithium salt, m.pt. 790°,

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[545] W. D. Treadwell, G. Szabados, and E. Haiman, *Helv. Chem. Acta*, 1932, **15**, 1049.

[546] W. Plotnikow, *J. Russ. Phys.-Chem. Soc.* 1913, **45**, 1163.

[547] O. Ruff and H. Golla, *Z. anorg. Chem.* 1924, **138**, 17.

[548] W. Biltz and E. Keunicke, ib. 1925, **147**, 171.

[549] H. Ulich, *Z. physikal. Chem.* 1931, Bod. Festbd. p. 423.

[550] W. Nespital, ib. 1932, B **16**, 153.

[551] I. Tananaev, *J. Gen. Chem. Russ.* 1938, **8**, 1120.

and the potassium, 1025°[552–3] (these high m. pts. show how stable the compounds are). The ammonium salt goes at 350° to ammonium fluoride and $NH_4[AlF_4]$, and the latter above this to NH_4F+aluminium fluoride.[554] The crystal lattices of $NH_4[AlF_4]$, $Tl[AlF_4]$ (which are isomorphous) and Tl_2AlF_5 contain[555] octahedral AlF_6 groups with more or fewer fluorine atoms common to 2; the structure of cryolite[556] is similar; it is made up of sodium ions and somewhat distorted AlF_6 octahedra.

The *chlorides* are much less stable; all are probably of the type $M[AlCl_4]$[558] and these cannot be made from water,[558] but only from the melt,[557, 565] or from a solution of the trihalide in benzene.[564] The alkaline salts $M[AlCl_4]$ have the m. pts.[557,565] Li 143·5°, K 257°, NH_4 304°.

The solid *bromides* again seem all to be $M[AlBr_4]$; they can be made in the dry way, and have m. pts. Li 197°, Na 201°, NH_4 232°; they seem to form solid solutions with excess of the trihalide.[557] The lithium and the cuprous salt $Cu[AlBr_4]$ (m. pt. 241°) were made from the solution of $AlBr_3$ in ethyl bromide.[562] These salts are remarkable for dissolving in benzene and toluene. Potassium bromide will dissolve in a solution of aluminium tribromide in benzene up to $KBr:AlBr_3:$Benzene $= 0{\cdot}5:1:6{\cdot}5$; the solution has a conductivity of 4×10^{-3}, about 500 times as great as that of aluminium bromide[559] (see further, ref. [560]); at the same time the depression of the freezing-point by the aluminium bromide is reduced to about half by the addition of potassium bromide; this is not explained. From benzene the solid $CuAlBr_4$ was isolated; from toluene, $CuAlBr_4C_7H_8$; and from nitrobenzene LiBr, 2 $AlBr_3$, 2 $C_6H_5NO_2$.[561]

Only one complex *iodide* seems to be known, $K[AlI_4]$, which is stable on heating and to water (Weber, 1857).[563]

Friedel-Crafts Reaction

This is one of the most famous reactions in organic chemistry, and has been widely used ever since its discovery in 1877.[568–9] It consists essen-

[552] P. P. Fedoteev and K. Timoviev, *Z. anorg. Chem.* 1932, **206**, 263.

[553] N. Puschin and A. Baskow, ib. 1913, **81**, 357.

[554] E. Thilo, *Naturwiss.* 1938, **26**, 529.

[555] C. Brosset, *Z. anorg. Chem.* 1937, **235**, 139.

[556] S. v. Náray-Szabó and K. Sasvari, *Z. Krist.* 1938, **99**, 27.

[557] J. Kendall, E. D. Crittenden, and H. K. Miller, *J.A.C.S.* 1923, **45**, 969.

[558] G. Malquori, *Atti R.* 1927, [6] **5**, 510; 1928, **7**, 745.

[559] V. A. Plotnikov and S. Jakubson, *Z. physikal. Chem.* 1928, **138**, 251.

[560] V. A. Plotnikov, I. A. Scheka, and V. A. Jankelevitsch, *J. Chem. Russ.* 1933, **3**, 481.

[561] Id., ib. 802.

[562] V. A. Plotnikov and E. J. Gorenbein, *J. Gen. Chem. Russ.* 1935, **5**, 1108.

[563] R. Weber, *Pogg. Ann.* 1857, **101**, 469.

[564] S. I. Jakubson, *Ber. Inst. Chem. Akad. Wiss. Ukraine*, 1940, **7**, 13, 17.

[565] U. I. Schvartzman, ib. 3.

[566] H. Ulich, A. Keutmann, and A. Geierhaas, *Z. Elektrochem.* 1943, **49**, 292.

[567] G. S. Forbes and H. H. Anderson, *J.A.C.S.* 1944, **66**, 931.

[568] C. Friedel and J. M. Crafts, *C.R.* 1877, **84**, 1392, 1450; **85**, 74.

[569] James Mason Crafts, Friedel Memorial Lecture, *J.C.S.* 1900, **77**, 1006.

tially in a reaction between an organic halide and a hydrocarbon (or a substituted hydrocarbon) in presence of aluminium chloride, whereby the two organic reactants lose a hydrogen and a chlorine atom, and the residues combine:

$$R\cdot H + R_1\cdot Cl = R\cdot R_1 + HCl.$$

It became of technical importance only after 1914,[575,576] when cheap aluminium chloride became available, and this is now used commercially for making many aromatic derivatives, ketones, aldehydes, phenols, acids, etc.; it serves in many reactions as a catalyst, and it causes degradations, substitutions, additions, and polymerizations.[575] A variety of other inorganic halides can be used in its place, some of them (like ferric[579] and gallic[574] chlorides) almost though scarcely quite as effective. Dermer *et al.*[577] found the reaction of acetyl chloride with toluene is hastened by the following chlorides, in order of diminishing efficiency:

$$AlCl_3 > SbCl_5 > FeCl_3 > TeCl_2 > SnCl_4 > TiCl_4 > TeCl_4 > BiCl_3 > ZnCl_2.$$

Normally the hydrogen in this reaction comes from an aromatic compound, and the halogen from an aliphatic; aromatic halides react only when the halogen is in the side chain; acyl halides are particularly effective. The reaction can, however, be extended to aliphatic hydrocarbons; acetyl chloride reacts with pentane or cyclohexane[582,585]; isopropyl cyclopentane is converted into dimethyl cyclohexane[583-4]; alkyl halides will exchange their halogen atoms with one another.[567,580-1]

The Friedel-Crafts reaction does not occur when the aromatic component contains a group which co-ordinates very strongly with aluminium chloride, such as a nitro-group or to a less extent two chlorine atoms. But nitrobenzene is a good solvent for the reaction.

The mechanism of this reaction is still obscure.[570-3] The original idea that a substitution product such as $Ar\cdot AlCl_2$ is formed has been disproved. It is certain that the aluminium chloride co-ordinates with the halide, and quite possible, as we have seen (p. 426), that it does so with the aromatic

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[570] H. Wieland *et al.*, *Ber.* 1922, **55**, 2246.

[571] Id., ib. 1919, **52**, 898.

[572] Id., ib. 1920, **53**, 201.

[573] Id., ib. 1921, **54**, 1770.

[574] H. Ulich and G. Heyne, *Z. Elektrochem.* 1935, **41**, 509.

[575] E. C. Britton, *Ind. Eng. Chem., News Edn.* 1941, 251.

[576] A. A. Ashdown, *Ind. Eng. Chem.* 1927, **19**, 1063.

[577] O. C. Dermer, D. M. Wilson, F. M. Johnson, and V. H. Dermer, *J.A.C.S.* 1941, **63**, 2881.

[578] F. Fairbrother, *J.C.S.* 1937, 503.

[579] L. F. Martin, P. Pizzolato, and L. S. McWaters, *J.A.C.S.* 1935, **57**, 2584.

[580] G. Dougherty, ib. 1929, **51**, 576.

[581] J. W. Walker, *J.C.S.* 1904, **85**, 1082.

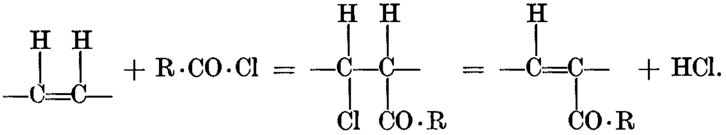
[582] H. Hopff, *Ber.* 1931, **64**, 2739.

[583] M. B. Turova-Poljak and T. A. Slovochotova, *J. Gen. Chem. Russ.* 1940, **10**, 1435.

[584] C. D. Nenitzescu and I. P. Cantuniari, *Ber.* 1933, **66**, 1097.

[585] C. D. Nenitzescu and J. Chicos, ib. 969.

hydrocarbon also. Fairbrother,[578] using aluminium chloride containing radioactive chlorine, has shown that complete exchange occurs between this and acetyl or tertiary butyl chloride; he therefore supposes that $[AlCl_4]^-$ and $[\text{carbonium}]^+$ ions are the first products. Wieland[570–3] has shown that unsaturated open-chain hydrocarbons react with acyl chlorides in presence of aluminium chloride to give addition products which then lose hydrogen chloride to form unsaturated ketones:



$$\overset{\mathrm{H}}{\underset{|}{}}\!\!\!-\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}- + \mathrm{R\cdot CO\cdot Cl} = -\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{CO\cdot R}}{\overset{\mathrm{H}}{\mathrm{C}}}- = -\overset{\mathrm{H}}{\mathrm{C}}=\underset{\mathrm{CO\cdot R}}{\mathrm{C}}- + \mathrm{HCl}.$$

This is no doubt similar to the mechanism of the Friedel-Crafts reaction. See also ref. [566].

GROUP III A

THIS subgroup consists of scandium, yttrium; lanthanum and the fourteen succeeding elements up to lutecium 71; and actinium, of whose chemistry we know very little. They are all rare, and some very rare; and the similarity of their properties makes the pure compounds even less accessible than we should expect from their rarity.

The phrase 'rare earth metals' is sometimes used for the whole eighteen elements of the subgroup, and even stretched to include thorium, which does not belong to the group at all; sometimes it is confined to the fifteen elements from lanthanum 57 to lutecium 71. It is perhaps better to adopt Goldschmidt's name 'lanthanides' for lanthanum and its fourteen successors, which obviously form a class by themselves.

The atomic structures may be briefly discussed. After 18 Argon 2.8.8, further electrons are added in the new fourth quantum group in 19 Potassium 2.8.8.1 and 20 calcium 2.8.8.2. But the third quantum group can expand, ultimately to 18, and will begin to do so as soon as the nuclear charge is large enough. The spectra show that this change begins with 21 Scandium, which is not 2.8.8.3 but 2.8.(8+1) 2. This process continues with the succeeding elements Ti, V, Cr, etc., and it is not until we have passed 30 Zn = 2.8.18.2 (and reached 31 Ga) that the fourth quantum group has more than 2 electrons. Along the series of the III A elements this structure (8+1) 2 is repeated, one quantum number higher each time, in yttrium and lanthanum. After lanthanum, the fourth group begins to grow towards its limit of 32, which it reaches in lutecium, 14 places later. Meanwhile the (8+1) 2 of the fifth and sixth quantum groups remain unchanged through the whole series, and that is why they are all included in the third periodic group.

		1	*2*	*3*	*4*	*5*	*6*
	21 Sc	2	8	8+1	2		
	39 Y	2	8	18	8+1	2	
Lanthanides	57 La	2	8	18	18	8+1	2
	58 Ce	2	8	18	18+1	8+1	2
	59 Pr	2	8	18	18+2	8+1	2
	60 Nd	2	8	18	18+3	8+1	2
	. . .						
	70 Yb	2	8	18	18+13	8+1	2
	71 Lu	2	8	18	18+14 32	8+1	2

In lutecium 71 the fourth quantum group is full. In the next element 72 the last electron has to go to the fifth group, giving

72 Hf : 2 8 18 32 8+2 2

which thus belongs to the fourth periodic group, where it follows zirconium.

The lanthanides, 57-71, provide a unique example of the gradual development of an internal electronic group in the atom, while the outer groups remain unchanged. Although our knowledge of the chemistry of many of the elements in question is very imperfect, we know enough to be able to trace the more important effects of this development.

Chemical Properties of Group III A

In their general behaviour the elements of this subgroup come between the very weakly basic aluminium and the strongly basic alkaline earth metals. As their basicity increases on the whole with the atomic number, scandium has more resemblance to aluminium, and lanthanum to calcium. Some of the elements, such as cerium and europium, show abnormal valencies of 4 or 2 (see p. 449), but the normal valency is always 3.

The metals are readily oxidized with large evolution of heat, and form solid black hydrides, probably metallic. The oxides when heated with carbon in the electric furnace give a series of carbides MC_2, which are readily hydrolysed by water with the evolution mainly of acetylene with some methane. This suggests that they are salts of the acetylide ion $M[C{\equiv}C]$, though that would involve a valency of 2 for the metal, even for cerium and praseodymium.

The hydroxides $M(OH)_3$ are insoluble in water and in alkali; they have no acidic character. Lanthanum oxide, La_2O_3, hisses in water like quicklime. The chlorides are easily soluble in water and in alcohols; the fluorides, carbonates, oxalates, and phosphates are insoluble. The sulphates are much more soluble than those of the alkaline earths, and show the characteristic fall of solubility with rise of temperature.

These elements have a moderate tendency to complex formation, the co-ordination number being usually 6, but occasionally 8 (the limit for all except scandium).

SCANDIUM

SCANDIUM was discovered in 1879 by Nilson, who recognized it as the Ekaboron of Mendeleeff; it was found in euxenite, and later in gadolinite. Though widely distributed, it is often regarded as one of the rarest of the elements. It has, however, been shown (V. M. Goldschmidt[586]) that it occurs in the earth's crust to at least 5 parts per million, so that it is as common as arsenic, and nearly twice as common as boron. The colour of the blue form of beryl (aquamarine) is said[586a] to be due to traces of scandium. According to H. N. Russell[586] it is still more abundant in the sun, where it is the twenty-third commonest element (on earth it is not more than the fiftieth). Its separation is ordinarily based on the extreme insolubility of its double sulphate in saturated potassium sulphate solution, or on the extraction of the thiocyanate $Sc(CNS)_3$ with ether.[587]

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[586] V. M. Goldschmidt, *J.C.S.* 1937, 656.

[586a] S. Barovick, *C.R. Acad. Sci. U.R.S.S.* 1946, 53, 75.

[587] W. Fischer and R. Bock, *Z. anorg. Chem.* 1942, 249, 146.

The metal is dimorphic (α, cubic and β, hexagonal close-packed[588]). The preparation of an alkyl-etherate $ScEt_3,Et_2O$ from the trichloride and the Grignard reagent has been described[589] (along with that of the analogous yttrium compound), but not yet confirmed.

Scandium oxide, Sc_2O_3, is a white powder, incorrectly said to be dimorphic.[590] The hydroxide, precipitated by alkalies from solutions of the salts, is Sc_2O_3,H_2O or $ScO\cdot OH$; it has the same lattice as γ-$AlO\cdot OH$.[590]

Of the trihalides a slightly soluble ScF_3 is known (crystal structure[591]), and a soluble and considerably hydrolysed (1 per cent. in normal solution) trichloride. This last is said to be the only trichloride of Group III that is insoluble in alcohol.

Various oxy-acid salts, nitrates, sulphates, selenates,[592] etc., are known; there is a strong tendency to form basic salts of the type of $Sc(SO_4)OHaq$.

Numerous double salts have been described, many of which must be complex (sulphates, selenates, oxalates, carbonates[593]); according to Hevesy[594] complex formation is much more marked with the sulphates of scandium than with those of the rare earth metals (as we should expect).

A variety of complex halides of scandium are known, including complex fluorides of all three types $M[ScF_4]$, $M_2[ScF_5]$, and $M_3[ScF_6]$. There is also an acetylacetonate ScA_3,[596] subliming *in vacuo* at 200°, and melting at 187°; this is very high, as the acetylacetonates of lanthanum, cerium, praseodymium, neodymium, and samarium all melt between 144° and 151°.

YTTRIUM

THE occurrence of this element, and its position, and especially its basicity among the other elements of Group III A,[595] are discussed later (p. 446). There is little to say about the compounds in detail. The oxide is white when pure; it absorbs carbon dioxide from the air. The usual salts occur, and some complexes, including the fluoride $M[YF_4]$.

LANTHANIDES

THE elements from lanthanum 57 to lutecium (cassiopeium) 71, with the atomic structures 2.8.18.(18+n)(8+1) 2 where n increases from 0 to 14, form a class by themselves, with certain marked physical peculiarities.

The presence of an imperfect electronic group—of less than 8, or of more than 8 and less than 18, or of more than 18 and less than 32 electrons—leads to colour and paramagnetism. The colour is due to the fact that an

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[588] K. Meisel, *Naturwiss.* 1939, **27**, 230.

[589] V. M. Pletz, *C.R. U.R.S.S.* 1938, **20**, 27.

[590] W. B. Weiser and W. O. Milligan, *J. Phys. Chem.* 1938, **42**, 669.

[591] W. Nowacki, *Naturwiss.* 1938, **26**, 801.

[592] Z. Trousil, *Coll. Czech. Chem. Comm.* 1938, **10**, 290

[593] J. S. and J. P. Sterba-Böhm, ib. 8.

[594] G. v. Hevesy, *Die Seltenen Erden*, Springer, Berlin, 1927, p. 62.

[595] See further on this H. Bommer, *Z. anorg. Chem.* 1941, **248**, 397.

[596] Hevesy, *Selt. Erden*, p. 71.

electron in an imperfect group may be shifted to another vacant orbit in the same group by a quantum of energy small enough to correspond to visible light: whereas if the group is complete, the transference can only be to another group, and this involves a much larger energy quantum, which would cause absorption in the ultra-violet. The paramagnetism is due to the fact that every orbit has a paramagnetic moment. In complete groups —and in covalent links—these are coupled in pairs, so that their moments cancel out. But in incomplete groups of electrons this need not occur, and there can be a residual paramagnetic moment.

Paramagnetism

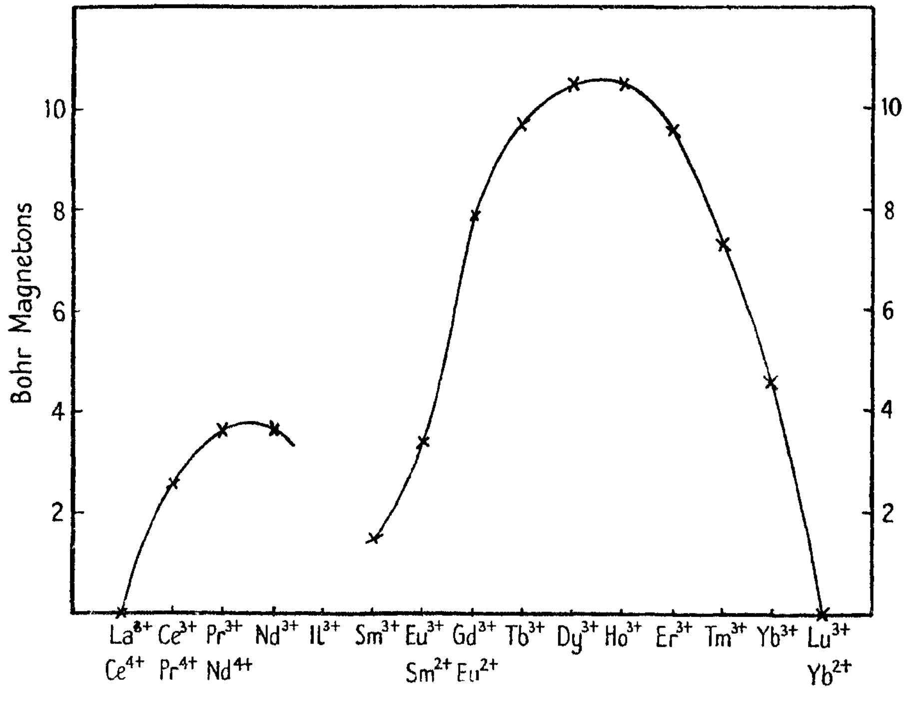
We are concerned here with the ions. The imperfections of the two outer groups (8+1), 2 disappear in the trivalent ions, these groups being reduced to one of 8: hence the effects will only be observed when the fourth quantum group is imperfect, having more than 18 but less than 32 electrons. Observation entirely confirms this. Thus Sc^{+++}2.8.8, Y^{+++}2.8.18.8; La^{+++}, 2.8.18.18.8; and the last of the series 71 Lu^{+++}, 2.8.18.32.8, are diamagnetic. So also is the ceric ion Ce^{++++}, which has the same structure as the trivalent La^{+++} ion. All the other lanthanide ions are paramagnetic. The observed moments in Bohr magnetons are as follows; for comparison the values calculated (1) by Hund and (2) by the more detailed method of van Vleck and Frank are quoted[597] (all at about 25° C).

	Calculated		
	Hund	*Van Vleck*	*Observed*
La (3+) Ce (4+)	0	0	0
Ce (3+) Pr (4+)	2·54	2·56	2·58
Pr (3+)	3·58	3·62	3·61
Nd (3+)	3·62	3·62	3·66
—	2·68	2·83	..
Sm (3+)	0·84	1·55—1·65	1·5
Eu (3+) Sm (2+)	0	3·40+3·51	3·4
Gd (3+) Eu (2+)	7·9	7·9	7·9
Tb (3+)	9·7	9·7	9·7
Dy (3+)	10·6	10·6	10·5
Ho (3+)	10·6	10·6	10·5
Er (3+)	9·6	9·6	9·6
Tm (3+)	7·6	7·6	7·3
Yb (3+)	4·5	4·5	4·6
Lu (3+) Yb (2+)	0	0	0

A plot of the moments of the trivalent ions against the atomic numbers is formed of two humps, a small one from La 59 to Sm 62 with a maximum at Pr 59 (3·61) and Nd 60 (3·66), and a large one from Sm to Lu 71, with a maximum at Dy 66 and Ho 67 (10·5). These last values are the largest

[597] Klemm, *Magnetochemie*, 1936, p. 110.

ionic moments known, and are about 1·8 times as great as those of Mn^{++} and Fe^{+++}, the strongest magnetic ions of the iron group (see refs. [598-9]).



Colour

Many of the rare earth salts are coloured. Pr 59 salts are green; Nd 60 reddish-violet; Sm 62, Dy 66, and Ho 67 are yellow; Er 68 pink, and Tm 69 green. La, Ce 58, Gd 64, and Lu 71 are colourless. There is an obvious relation between the colour and the paramagnetism: the elements near either of the two magnetic maxima are coloured, while those near the minima are colourless.

The absorption spectra of these coloured salts are of a very peculiar kind. Whereas coloured ions of other series give in solution broad absorption bands, 500-1,000 A.U. wide,* the rare earth salts give narrow bands, 5 to 10 A.U. wide, looking almost like a line spectrum. Now the light absorbed by any isolated atom must have a definite wave-length, and so give a sharp line. The broadening of the bands in solutions such as those of cupric salts is due to the Stark effect of the electric fields of neighbouring molecules, which break up the line into two, with a separation depending on the strength of the field; and as this varies for each ion in the solution,

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* i.e. between points where the absorption is half the maximum for the band.

[598] B. Cabrera, *J. Chim. Phys.* 1939, **36**, 237.

[599] J. Becquerel, W. J. de Haas, and J. H. van den Handel, *Physica*, 1936, **3**, 1133 (magnetism of Dy salts down to liquid helium temperatures).

the result is to spread the line into a band. The much greater sharpness of the absorption lines of the rare earth salts is evidence that the orbits concerned in the absorption are far less exposed to the fields of neighbouring molecules; this is a valuable confirmation of the theory, which ascribes the absorption to an electronic group that is relatively deep down in the atom, instead of being, as it is, for example, in the cupric ion 2.8.17, on the surface.

Recent work on the light-absorption of these ions is more of physical than of chemical interest. See refs. [600-7].

Natural Radioactivity

Two of the lanthanides, samarium and lutecium, have been found to be radioactive. In 1933 Hevesy[608] showed that samarium had a weak α-ray activity; Hosemann[609] showed that the α-particles had a range of 1·13 cm. in air at 15° and 1 atm. (a value also found by Taylor[610]), and that the number of particles was 89 per sec. per g. of Sm. The active isotope is ^{148}Sm. (see ref. [611]), as is shown by photographic emulsion tracks; from mass-spectrographic results the life of the active isotope must be about 10^{11} years.

Lutecium was shown by Heyden and Wefelmeier[612] to have a weak β-ray activity (less than Rb but more than K); they found no signs of activity with Tm, Yb, or Ho. Libby[613] finds that if the source is ^{176}Lu its half-life is 7×10^{10} years.

Artificial Radioactivity

Like nearly all elements the lanthanides under bombardment by neutrons are converted into radioactive isotopes.[614-15] This gives two values distinctive of each element, and not interfered with by others: the rate of decay of the isotope (varying from a few minutes to a few days), and the intensity, i.e. the amount of the isotope formed under a given bombardment, which varies in the ratio of 1,000 to 1. This should be important in following up the progress of a separation.

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[600] C. B. Ellis, *Phys. Rev.* 1936, ii. **49**, 875.

[601] F. H. Spedding, *J. Phys. Chem.* 1937, **5**, 160.

[602] F. H. Spedding, C. C. Moss, and R. C. Waller, ib. 1940, **8**, 908.

[603] J. H. van Vleck, *J. Phys. Chem.* 1937, **41**, 67.

[604] E. J. Miehan and G. C. Nutting, *J. Chem. Phys.* 1939, **7**, 1002.

[605] S. H. Freed, S. I. Weissman, and F. E. Fortess, ib. 824.

[606] S. H. Freed, S. I. Weissman, and G. J. Rotariu, ib. 1940, **8**, 291.

[607] S. H. Freed, S. I. Weissman, and F. E. Fortess, *J.A.C.S.* 1941, **63**, 1079.

[608] G. v. Hevesy, M. Pahl, and A. Hosemann, *Z. Phys.* 1933, **83**, 43.

[609] A. Hosemann, ib. 1936, **99**, 405.

[610] H. J. Taylor, *Nature*, 1935, **136**, 719.

[611] T. R. Wilkins and A. J. Dempster, *Phys. Rev.* 1938, ii. **54**, 315.

[612] M. Heyden and W. Wefelmeier, *Naturwiss.* 1938, **26**, 612.

[613] W. F. Libby, *Phys. Rev.* 1939, ii. **56**, 21.

[614] J. K. Marsh and S. Sugden, *Nature*, 1935, **136**, 102.

[615] G. v. Hevesy and H. Levi, ib. 103.

Relative Abundance of the Rare Earth Metals

Goldschmidt, by the analysis of all the known types of rare earth minerals, has obtained estimates of their relative abundance in the crust of the earth. The following table gives the results in parts per million or grammes per ton (1 g./ton = 1×10^{-4} per cent.).[616]

These figures show very markedly the greater stability of nuclei with an even number of positive charges.

Grammes per ton in the Crust of the Earth

21 Sc	5	64 Gd	6·3
39 Y	31	65 Tb	1·0
57 La	19	66 Dy	4·3
58 Ce	44	67 Ho	1·2
59 Pr	5·6	68 Er	2·4
60 Nd	24	69 Tm	0·3
61 Il	..	70 Yb	2·6
62 Sm	6·5	71 Lu	0·7
63 Eu	1·0		

Actinium: 2×10^{-7} mg. per ton.

Element No. 61, Illinium or Prometheum (Pm)[619b]

The discovery of this element was announced by Smith Hopkins, but he was not able to repeat the work, and it seems probable[617] that it has not yet been found in nature. It has, however, been made in both of the two possible ways, by the bombardment (D, *n*) of 60 Nd,[618] and by that (α, 2 *n*) of 59 Pr[619]; the product from Nd is a 61 of half-life a few hours, and that from Pr of about 200 days. (Pr is simple, 141, and so the long-lived 61 must have at. wt. 143; Nd has 7 isotopes, 142, 143, 144, 145, 146, 148, 150, and the shorter-lived 61 can have a mass number 1 greater than any of these.) Recently[619a] two active isotopes of this element, $^{147}61$ (3·7 years) and $^{149}61$ (47 hours), have been identified chemically among the fission products of uranium. A 1,000-kw. uranium pile should produce some 16 mg. of $^{147}61$ in a day.

The Lanthanide Contraction

In their chemical properties the lanthanides resemble one another very closely. There is, however, a definite gradation of properties, and this is related to the change of atomic number. In particular, the basicity of the hydroxides can be measured by several semi-quantitative methods (see p. 446), which agree in showing that the basicity diminishes regularly along the series: the most basic is lanthanum, and the least basic lutecium

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[616] V. M. Goldschmidt, *J.C.S.* 1937, 656.

[617] F. A. Paneth, *Nature*, 1942, **149**, 565.

[618] M. L. Pool and L. L. Quill, *Phys. Rev.* 1938, **53**, 437; H. B. Law, M. L. Pool, J. D. Kurbatov, and L. L. Quill, ib. 1941, **59**, 936.

[619] J. D. Kurbatov, D. C. MacDonald, M. L. Pool, and L. L. Quill, *Phys. Rev.* 1942, **61**, 106; C. S. Wu and E. Segrè, ib. 203.

[619a] J. A. Marinsky, L. E. Glendenin, and C. D. Coryell, *J.A.C.S.* 1947, **69**, 2781.

[619b] See J. A. Marinsky and L. E. Glendenin, *Chem. and Eng. News*, 1948, **26**, 2346.

71; and it is particularly noticeable that yttrium, which does not belong to the lanthanides at all, but to the earlier period, and according to the general rule is definitely less basic than lanthanum, comes in the middle of the lanthanides, somewhere near holmium 67.

Goldschmidt has pointed out that this is in accordance with the peculiar change of size of the ions which occurs when we go from La 57 to Lu 71. From the molecular volumes and crystal structures of the oxides M_2O_3 (which are of three crystal types), and those of the isomorphous sulphates $M_2(SO_4)_3, 8\,H_2O$ he arrives at the following values of the radii of the M^{+++} ions.

Radii of Trivalent Ions in A.U.

21 Sc	0·78	61 Il	..	67 Ho	1·05
39 Y	0·93	62 Sm	1·13	68 Er	1·04
57 La	1·22	63 Eu	1·13	69 Tm	1·04
58 Ce	1·18	64 Gd	1·11	70 Yb	1·00
59 Pr	1·16	65 Tb	1·09	71 Lu	0·99
60 Nd	1·15	66 Dy	1·07		

There is an invariable decrease in size as we go from one element to the next in order, which ultimately more than compensates for the increase between yttrium and lanthanum, so that the yttrium ion comes in the middle of the lanthanides, being about equal to holmium. On the Fajans principles, which apply especially to the A elements, the tendency of a hydroxide to dissociate is greater the larger its cation. Thus the contraction explains why the basicity of the lanthanides diminishes instead of increasing as we go from lanthanum to lutecium, and also why yttrium, though it belongs to another period in the table, comes in the middle of the series.

This contraction must mean that the effect of the added electrons in screening the positive charge on the nucleus does not quite balance the increase of the latter, so that the outer electrons are moving in a stronger positive field in lutecium than in lanthanum, and hence in smaller orbits. Thus the positive ion can get nearer to the hydroxyl oxygen in the hydroxide and deform it more, and so the dissociation and the basicity are diminished.[620]

Basicity of the Hydroxides

Qualitative determinations, for example of the order of precipitation of the hydroxides by alkalies, show that the basicity falls as the ion gets smaller, yttrium coming as we should expect near holmium. This is confirmed by various roughly quantitative methods, for example by treating the sulphate solution with potassium iodide and iodate and determining the iodine liberated,[621] or by measuring the rate of evolution of carbon dioxide from the sulphate and potassium carbonate[622]; these give the same

[620] v. Hevesy, *Selt. Erden*, p. 28.

[621] S. H. Katz and C. James, *J.A.C.S.* 1914, **36**, 779.

[622] P. H. M. P. Brinton and C. James, ib. 1921, **43**, 1446.

order of basicities, falling from lanthanum to lutecium, with yttrium about equal to holmium. The measurement by the glass electrode of the p_H in a solution containing precipitated hydroxide leads to the same results.[623] See further, ref. [624].

Metals

Practically all the rare earth elements have by now been got in the metallic state. At first[625] this was done by the electrolysis of the fused chloride, and later of an aqueous solution of the chloride, using a mercury cathode.[626-7] Another method is to reduce the chloride with an alkali metal.[628]

In a systematic investigation Klemm and Bommer[629-31] made the metal by reducing the halide MCl_3 in argon with liquid potassium (or in case of need rubidium or caesium), and distilled off the excess of alkali metal *in vacuo*. The resulting mixture $M + 3\,KCl$ could be used without separation to determine the magnetic properties of the metal, and by means of an X-ray powder diagram its crystal structure, from which the atomic volume in the metallic state could be calculated. The results[629-31] (which were confirmed by direct measurements of the densities) show in the main the usual lanthanide contraction; but the atomic volumes of europium and ytterbium are 35 and 27 per cent. above the curve, while samarium lies a little above and cerium a little below. This must be related to the abnormal valencies (see p. 449); the atomic volumes of metals usually fall with a rise of valency (compare Ba 36·7 with La 22·4, or Lu 18·0 with Hf 13·4). It thus appears that in the metallic state as in their compounds europium and ytterbium are largely and samarium to some extent divalent (or they behave as if they were so), and cerium is to some extent tetravalent. These conclusions are supported by the magnetic measurements of Klemm and Bommer.[629]

Compounds of the Lanthanide Metals

These can be discussed very briefly.

Hydrides. The pure metals absorb hydrogen readily *in vacuo*, giving isotherms like those for palladium, with a maximum concentration in the cold at 1 atmosphere corresponding to about $MH_{2\cdot7}$.[632-4] This may well be due to a compound MH_3 forming solid solutions with its metal.

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[623] J. A. C. Bowles and H. M. Partridge, *J. Ind. Eng. Chem.* (*Anal.*), 1937, **9**, 124.

[624] T. Moeller and H. E. Kremers, *J. Phys. Chem.* 1944, **48**, 395.

[625] W. Muthmann, H. Hofer, and L. Weiss, *Ann.* 1901, **320**, 231.

[626] E. E. Jukkola, L. F. Audrieth, and B. S. Hopkins, *J.A.C.S.* 1934, **56**, 303.

[627] D. H. West and B. S. Hopkins, ib. 1935, **57**, 2185.

[628] E. Zintl and S. Neumayer, *Z. Elektrochem.* 1933, **39**, 85.

[629] W. Klemm and H. Bommer, *Z. anorg. Chem.* 1937, **231**, 138.

[630] H. Bommer and E. Hohmann, ib. 1939, **241**, 268.

[631] W. Klemm and H. Bommer, ib. **264**.

[632] A. Sieverts and G. Müller-Goldegg, ib. 1923, **131**, 65.

[633] A. Sieverts and E. Roell, ib. 1925, **146**, 149.

[634] Id., ib. 1926, **150**, 261.

The curious *carbides* MC_2, apparently $M[C{\equiv}C]$, have already been mentioned (p. 440). See further, Wells.[635]

Nitrides. Many of these metals form nitrides MN of the 'interstitial' type[636]; these are discussed later (V. 663). Similar phosphides and bismuthides seem to occur.[637]

Calcides. The oxides, sulphides, and selenides of the rare earth metals are known in some detail, as well as some of the tellurides (oxides,[638-41] sulphides,[642-3] selenides[644]).

The oxides and selenides occur in three and the sulphides in two crystalline forms, the form adopted being strictly determined by the relative sizes of the two ions.

In addition to these M_2S_3 compounds some of these elements form disulphides MS_2 or M_2S_4. These might be either true disulphides of the tetravalent metal MS_2 or polysulphides of the trivalent, $M_2S_3{\cdot}S$. Since they are ionized the magnetic properties give a conclusive test. CeS_2 would be diamagnetic, like CeO_2, while $Ce_2S_3{\cdot}S$ should have about the same moment (2·6 Bohr magnetons) as Ce_2S_3; it is found to have 2·3. In the same way LaS_2 would have to be paramagnetic, like a cupric compound, while $La_2S_3{\cdot}S$ would be diamagnetic; the compound was found to be diamagnetic. In view of the great stability of tetravalent cerium, it is strange that no true CeS_2 should exist.

Trihalides

The trifluorides are little known; they are of the types MF_3 and $2\,MF_3$, H_2O, and are all very insoluble in water. Melting-points are CeF_3, 1,324° C.[645]; PrF_3 1,370°, NdF_3 1,410°.[646]

Of the other trihalides the melting-points,[647-54] if plotted against the atomic numbers of the metals, form for any one halogen two nearly linear

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[635] Wells, *S.I.C.* p. 457.

[636] Ib., p. 427.

[637] A. Iandelli and E. Botti, *Atti R.* 1936, [vi] **24**, 459; 1937, **26**, 233.

[638] V. M. Goldschmidt, F. Ulrich, and T. F. W. Barth, *Osloer Akad. Ber.* 1925, No. 5.

[639] V. M. Goldschmidt, T. F. W. Barth, and G. Lunde, ib. No. 6.

[640] V. M. Goldschmidt, ib. 1926, No. 2.

[641] H. v. Wartenberg and H. J. Reusch, *Z. anorg. Chem.* 1932, **207**, 1.

[642] W. Klemm, K. Meisel, and H. U. v. Vogel, ib. 1930, **190**, 123.

[643] M. Picon and Cogne, *C.R.* 1931, **193**, 595.

[644] W. Klemm and A. Koczy, *Z. anorg. Chem.* 1937, **233**, 84.

[645] Hevesy, *Selt. Erden*, p. 54.

[646] H. v. Wartenberg, *Naturwiss.* 1941, **29**, 771.

[647] F. Bourion, *Ann. Chim. Phys.* 1910, **20**, 547.

[648] W. Biltz and A. Voigt, *Z. anorg. Chem.* 1923, **126**, 39.

[649] G. Jantsch *et al.*, ib. 1929, **185**, 49.

[650] G. Jantsch and N. Skalla, ib. 1930, **193**, 391.

[651] G. Jantsch, N. Skalla, and H. Jawurek, ib. 1931, **201**, 207.

[652] G. Jantsch, H. Jawurek, N. Skalla, and H. Galowski, ib. 1932, **207**, 362.

[653] G. Jantsch, N. Skalla, and H. Grubitsch, ib. 1933, **212**, 65.

[654] G. Jantsch and K. Wein, *Mon.* 1936, **69**, 161.

curves, the first falling and the second rising; the break is for the chlorides at 65 Tb, for the bromides at about 61 Il, and for the iodides at 59 Pr. The heats of formation and solution and the solubilities of the trichlorides have been examined by Bommer and Hohmann.[655-8] The colours of the trihalides are very various,[649-653,659] and are of course darkest for the iodides and palest for the chlorides; the salts all darken on heating. For the crystal structure of the anhydrous trihalides, see Zachariasen.[660a]

The halides nearly all crystallize with 6 or 7 H_2O or both; the anhydrous halides are made by heating the hydrates in a stream of hydrogen halide to 350–600°. At still higher temperatures they lose halogen, forming the dihalides where these exist (Sm, Eu, Yb) or where they do not (as with thulium and lutecium[653]) the free metal.

Oxyhalides MO(hal) also occur; it has been shown[660] that LaOF has the same crystal lattice as fluorite CaF_2.

Salts of Oxy-acids

Some of these may be mentioned, with references to recent work, largely on crystal structure. Oxalates[661]: nitrates[662]; there is an important series of double nitrates, mainly of the type $M_2La(NO_3)_5, 4\ H_2O$[663-5]; there is a remarkably stable basic nitrite $LaO(NO_2)$,aq., stable to heat up to the boiling-point of sulphuric acid,[666] and a series of double nitrites

$$M'_3M'''(NO_2)_6{}^{667};$$

a series of dimethyl-phosphates $M[(CH_3)_2PO_4]_3$ have been made for use in separations[668]; the crystal structure of the sulphate $Sm_2(SO_4)_3, 8\ H_2O$,[670] and the ethyl sulphates $M[SO_4Et]_3, 9\ H_2O$[671] have been determined, as well as that of the bromate $Nd(BrO_3)_3,\ 9\ H_2O$.[669] For further details see Hevesy, *Selt. Erden*, pp. 64-73.

Abnormal Valencies

In addition to their group valency of 3, some of the lanthanides can assume a valency of 4, and others of 2 (other suggested valencies, with the

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[655] H. Bommer and E. Hohmann, *Naturwiss.* 1939, **27**, 583.

[656] Id., *Z. anorg. Chem.* 1941, **248**, 357.

[657] Id., ib. 373.

[658] Id., ib. 383.

[659] J. H. Kleinheksel and H. C. Kremers, *J.A.C.S.* 1928, **50**, 962.

[660] W. Klemm and H. A. Klein, *Z. anorg. Chem.* 1941, **248**, 167.

[660a] W. H. Zachariasen, *J. Chem. Phys.* 1948, **16**, 254.

[661] J. K. Marsh, *J.C.S.* 1943, 40.

[662] Id., ib. 1941, 561.

[663] G. Jantsch and S. Wigdorow, *Z. anorg. Chem.* 1911, **69**, 222.

[664] G. Jantsch, ib. 1912, **76**, 303.

[665] A. J. Grant and C. James, *J.A.C.S.* 1915, **37**, 2652.

[666] G. R. Sherwood, ib. 1944, **66**, 1228.

[667] H. C. Goswami and P. B. Sarkar, *J. Ind. Chem. Soc.* 1935, **12**, 608.

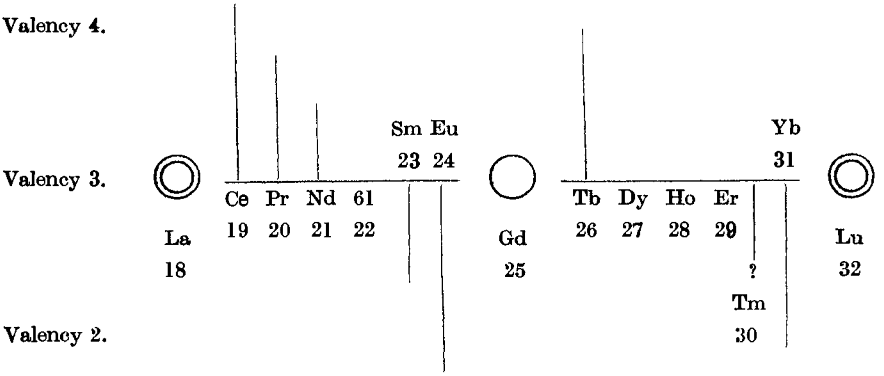
[668] J. K. Marsh, *J.C.S.* 1939, 554.

[669] L. Holmholz, *J.A.C.S.* 1939, **61**, 1544.

[670] W. H. Zachariasen, *J. Chem. Phys.* 1935, **3**, 197.

[671] J. A. A. Ketelaar, *Physica*, 1937, **4**, 619.

possible exception of 5 for Pr[672] cannot be justified). It is now clear that the elements that can be tetravalent are 58 Ce, 59 Pr, 65 Tb, and probably 60 Nd (Ce $\gg$ Pr $\gg$ Nd); while 62 Sm, 63 Eu, 70 Yb, and perhaps 69 Tm can be divalent (Eu $>$ Yb $>$ Sm). The reason for this distribution has been made clear.[673] The fourth quantum group is obviously exceptionally stable in La (18) and in Lu (32), and Klemm has pointed out[674-5] that the electronic arrangements deduced by Hund, and used by him to explain the paramagnetism of the ions,[676] show that the trivalent ion of 64 Gd, whose fourth quantum group is 25, half-way between the other two, must also be exceptionally stable. Jantsch and Klemm give the following simple diagram, in which the horizontal line represents the trivalency that is common to all these elements, and the vertical lines the direction of the abnormality, their lengths indicating its strength. The figures below the atomic symbols give the size of the fourth quantum group in the trivalent ion.



It will be seen that in every case the abnormality is such as to make the element approach in structure one of the three exceptionally stable forms, and the nearer it is to this form to start with, the greater is the stability of the abnormal valency.

Tetravalent Elements: Cerium

This is the most marked example; tetravalent cerium in its covalent (though not in its ionized) compounds is more stable than trivalent. If a cerous compound, such as the hydroxide, oxalate, or nitrate, is ignited in oxygen, the residue is not the sesquioxide Ce_2O_3 but the dioxide CeO_2. In the same way if a cerous solution is treated with alkali, the colourless cerous hydroxide which is precipitated is rapidly oxidized by the air, giving first deeply coloured cero-ceric compounds, and finally, yellow ceric hydroxide $Ce(OH)_4$. On the other hand, a solution of ceric hydroxide in

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[672] W. Prandtl and G. Rieder, *Z. anorg. Chem.* 1938, **238**, 225.

[673] G. Jantsch and W. Klemm, ib. 1933, **216**, 80.

[674] W. Klemm, *Z. anorg. Chem.* 1930, **187**, 29.

[675] Id., ib. 1932, **209**, 321.

[676] F. Hund, *Z. Phys.* 1925, **33**, 855.

hydrochloric acid evolves chlorine and goes over into cerous chloride $CeCl_3$. This phenomenon of the higher valency being less stable in the ionic, but more in the covalent state (as in the hydroxides), is not uncommon, as can be seen in the ferrous and ferric or the cobaltous and cobaltic compounds; the instability of the higher valency is due to the magnitude of the charge, and this is diminished or spread by covalency formation.

Tetravalent cerium behaves like an element of Group IV A, though owing to the lanthanide contraction its properties bring it between hafnium and thorium, and not between the almost identical zirconium and hafnium (see IV. 629). The true simple ceric salts scarcely exist at all, but they readily form complexes. A solution of ceric hydroxide in hydrochloric acid must contain the tetrachloride, but it soon evolves chlorine; in concentrated hydrochloric acid it forms a dark red liquid, presumably a solution of $H_2[CeCl_6]$, of which the pyridine, quinoline, and triethyl ammonium salts have been isolated.

Ceric oxide CeO_2, made by heating the cerous compound of any volatile acid in air, is white[677] or pale yellow; it melts above 2,600°, and has a fluorite lattice.[678]

Ceric hydroxide $Ce(OH)_4$, formed by the action of air or hydrogen peroxide[679] on cerous hydroxide in water in the cold, is colloidal and amorphous. It is less acidic and more basic than zirconium hydroxide, but acidic enough to form a series of 'cerates' such as Na_2CeO_3.[680] Like all $M(OH)_4$ compounds it is a very weak base. It gives no neutral nitrates, but only a basic salt $Ce(OH)(NO_3)_3, 3\ H_2O$.[682] The sulphate $Ce(SO_4)_2$ is much more stable, but probably not simple; it is a deep yellow solid giving a brownish solution, which slowly deposits a basic salt, but on addition of sulphuric acid turns red, presumably from the formation of $H_2[Ce(SO_4)_3]$. According to Jones and Soper[683] ceric sulphate gives no reactions for the ceric ion Ce^{4+} in solution, the whole of the cerium being in the anion. On the other hand, the perchlorate $Ce(ClO_4)_4$ seems to be a normal salt.[684]

A number of ceric double salts are known, some at least of which must be complex. There is a double carbonate of the composition

$$Na_6[Ce(CO_3)_5],\ 24 \text{ and } 0\ H_2O^{685}:$$

numerous double nitrates, all of the types

$$M'_2[Ce(NO_3)_6],\ 0\ H_2O \text{ and } M''[Ce(NO_3)_6],\ 8\ H_2O$$

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[677] J. F. Spencer, *J.C.S.* 1915, **107**, 1265.

[678] V. M. Goldschmidt, F. Ulrich, and T. F. W. Barth, *Osloer Akad. Ber.* 1925, No. 5.

[679] A. Lawson and E. W. Balson, *J.C.S.* 1935, 362.

[680] For the crystal structure see E. Zintl and W. Morawietz, *Z. anorg. Chem.* 1940, **245**, 26.

[681] J. K. Marsh, *J.C.S.* 1946, 15.

[682] Hevesy, *Selt. Erden*, p. 76.

[683] E. G. Jones and F. G. Soper, *J.C.S.* 1935, 802.

[684] R. L. Moore and R. C. Anderson, *J.A.C.S.* 1945, **67**, 167.

[685] L. Lortie, *C.R.* 1929, **188**, 915.

(M' = alkali metal; M'' = Mg, Mn″, Co″, Ni, Zn) which are bright red[686-7]; and double sulphates of which the simplest are the orange or yellow salts $M'_4[Ce(SO_4)_4]$, 2 H_2O.

Ceric acetylacetonate is remarkable. The trivalent compound CeA_3 has 3 H_2O.[688] The ceric compound $Ce(C_5H_7O_2)_4$ when made from aqueous solution is said to have[689] 11 H_2O, but as the corresponding zirconium[690] and hafnium[691] compounds both have 10 H_2O, the ceric compound probably has 10 also; but no explanation of the presence of this quite abnormal amount of water has been suggested.

Tetravalent Praseodymium

This is much less stable than Ce^{IV}, as is shown by the fact that PrO_2 will oxidize a cerous solution to a ceric. Only the oxide and one or two of its derivatives are known. When the praseodymous salt of a volatile acid is heated in oxygen or with potassium chlorate, the mixed oxide Pr_6O_{11} is first formed, and then PrO_2; both of these are black[692-4]; praseodymium dioxide, which has a fluorite lattice,[695] liberates chlorine from hydrochloric acid, oxidizes manganous salts to permanganates, and like cerium dioxide is reduced to the sesquioxide by hydrogen peroxide. It gives a sodium salt Na_2PrO_3, isomorphous with the 'cerate' above.[680]

Praseodymium is the one lanthanide which might be pentavalent, as it has 2 electrons more than the stable lanthanum. According to Prandtl and Rieder[672] there is some evidence that it can assume this valency; they find that if Pr_2O_3 mixed with a large excess of yttrium sesquioxide is heated to 350° under 10 atmospheres pressure of oxygen, it takes up 80 per cent. of the oxygen required to convert it into the pentoxide Pr_2O_5. Marsh, however,[681] got no evidence from the oxidation of its salts that praseodymium could be pentavalent.

Tetravalent Neodymium

Brauner and others found that neodymium sesquioxide on heating in oxygen takes up more of it to give a compound nearly of the composition Nd_4O_7 (or $Nd_1O_{1\cdot75}$); but there are no details of this, nor any later work on the subject.

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[686] R. J. Meyer and R. Jacoby, *Z. anorg. Chem.* 1901, **27**, 359.

[687] G. F. Smith, V. R. Sullivan, and G. Frank, *Ind. Eng. Chem.* [*Anal.*] 1936, **8**, 449.

[688] Hevesy, *Selt. Erden*, p. 71.

[689] A. Job, and P. Goissedet, *C.R.* 1913, **157**, 50.

[690] W. Biltz and J. A. Clinch, *Z. anorg. Chem.* 1904, **40**, 218.

[691] G. v. Hevesy and M. Lögstrup, *Ber.* 1926, **59**, 1890.

[692] W. Prandtl and K. Huttner, *Z. anorg. Chem.* 1925, **149**, 235.

[693] H. A. Pagel and P. H. M.-P. Brinton, *J.A.C.S.* 1929, **51**, 42.

[694] V. M. Goldschmidt, *Osloer Akad. Ber.* 1926, No. 2, p. 38.

[695] P. Scherrer, and J. Palacios, *Anal. Fis. Quim.* 1928, **26**, 309.

Tetravalent Terbium

Here again the tetravalency is confined to the oxide. TbO_2 can be made by heating the trivalent oxide or sulphate.[696] If the sesquioxide is heated in air it takes up more oxygen, but this is less firmly held than with praseodymium; if it is mixed with excess of yttrium sesquioxide and heated at 350° under 10 atmospheres pressure of oxygen, it goes to the dioxide TbO_2,[672] which has the same fluorite lattice as CeO_2.[697] It shows no tendency to form a pentavalent oxide.

[*Dysprosium*

As this is the next element to terbium it might be able to become tetravalent; but Jantsch and Wiesenberger have shown[698] that if it is heated in oxygen to any temperatures from 300° to 1,000°, or with potassium nitrate or chlorate, nothing more highly oxidized than the sesquioxide is obtained.]

Divalent Lanthanides

These are samarium, europium, ytterbium, and possibly thulium. The occurrence of divalent samarium, europium, and ytterbium is suggested by the large atomic volumes of the metals (p. 447). For the crystal structures of the dihalides, see ref. [699].

Samarium

The divalent compounds can be made by reduction with metals, usually as amalgams (see below, $SmSO_4$[702]) or by heating the trihalides, which begin to lose halogen *in vacuo* at the following temperatures[701]: $SmCl_3$ *ca.* 900°; $SmBr_3$ 700°; SmI_3 560°. In presence of hydrogen the decomposition begins with $SmCl_3$ at 450° and with SmI_3 at 350°.[700] Samarium di-iodide is a very dark green solid, melting at 840°; it is very sensitive to water; the dark green aqueous solution very soon loses its colour with evolution of hydrogen.[700] The sulphate, chromate, and phosphate of divalent samarium can be precipitated from the solution.

The oxide and sulphide SmO and SmS are unknown; they cannot be made by the reduction of the trivalent compounds. If, however, $SmCl_2$ is heated at 1,300° with tellurium in a stream of hydrogen, the product contains a small quantity of SmTe.[703]

If the trichloride is treated in anhydrous alcohol with calcium amalgam, the $SmCl_2$, which is insoluble in alcohol, is precipitated; this fact can be

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[696] G. Urbain and G. Jantsch, *C.R.* 1908, **146**, 127.

[697] V. M. Goldschmidt, F. Ulrich, and T. F. W. Barth, *Osloer Akad. Ber.* 1925, No. 3: No. 7, p. 38.

[698] G. Jantsch and E. Wiesenberger, *Mon.* 1936, **68**, 394.

[699] W. Döll and W. Klemm, *Z. anorg. Chem.* 1939, **241**, 239.

[700] G. Jantsch and N. Skalla, ib. 1930, **193**, 391.

[701] G. Jantsch, N. Skalla, and H. Jawurek, ib. 1931, **201**, 207.

[702] A. Brukl, *Angew. Chem.* 1939, **52**, 151.

[703] H. Senff and W. Klemm, *Z. anorg. Chem.* 1939, **242**, 92.

used for the separation of samarium.[702] Samarous iodide SmI_2 begins at very high temperatures to disproportionate to the tri-iodide and the metal.[700] In water the di-iodide has at first the conductivity of a tri-ionic salt, but this soon falls with the precipitation of the trivalent $Sm(OH)I_2$.[700]

Divalent Europium

The europous compounds[713] include the calcides, the halides, and the sulphate.

Europous fluoride, EuF_2. Made by Beck and Nowacki[709] by reducing EuF_3 in hydrogen at a red heat; it has a fluorite lattice. Klemm[711] makes it the same way in 3 hours at 1,100°. McCoy[714] says that EuF_2 oxidizes so quickly in air that if it is washed with methyl alcohol on a filter-paper this catches fire.

Europous chloride, $EuCl_2$. Made by the reduction of $EuCl_3$ in hydrogen[704] at 600°[711]; it is colourless. It forms a dihydrate $EuCl_2, 2\ H_2O$ which can be used to purify europium as it is very insoluble in concentrated hydrochloric acid;[708] in this it is very like $BaCl_2, 2\ H_2O$ with which it may probably be isomorphous.[707]

Europous bromide, $EuBr_2$, and *iodide*, EuI_2, are similar.

[EuO like SmO probably does not exist.[709]]

EuS: this can be got by reducing $Eu_2(SO_4)_3$ in H_2S,[709] or by heating $EuCl_2$ with excess of sulphur.[712] It is black when pure[712] and pyrophoric in air. It has a sodium chloride lattice.[710]

Europous selenide, EuSe (brownish-black), and the *telluride* EuTe (black) were made from $EuCl_2$ by heating with excess of Se or Te in hydrogen.[712] The sulphide selenide and telluride all have magnetic moments of 7·4 to 7·9 Bohr magnetons, which is the theoretical value for europous ions. They all have sodium chloride lattices.

Europous sulphate, $EuSO_4$.[706] Pauling[707] finds that it has the same lattice as $SrSO_4$ and $BaSO_4$.

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[704] G. Jantsch, H. Alber, and H. Grubitsch, *Mon.* 1929, **53**, 305.

[706] H. N. McCoy, *J.A.C.S.* 1936, **58**, 2279.

[707] Id. (with notes by others, including L. Pauling and G. P. Baxter), ib. 1937, **59**, 1131.

[708] G. P. Baxter and F. D. Tuemmler, *J.A.C.S.* 1938, **60**, 602.

[709] G. Beck and W. Nowacki, *Naturwiss.* 1938, **26**, 495 (*Nature*, 1938, **142**, 579).

[710] W. Nowacki, *Z. Krist.* 1938, **99**, 399.

[711] W. Klemm and W. Döll, *Z. anorg. Chem.* 1939, **241**, 233.

[712] W. Klemm and H. Senff, ib. 259.

[713] W. Noddack and A. Brukl, *Angew. Chem.* 1937, **50**, 362.

[714] H. N. McCoy, *J.A.C.S.* 1939, **61**, 2455.

[715] W. Klemm and W. Schüth, *Z. anorg. Chem.* 1929, **184**, 352.

[716] G. Jantsch, N. Skalla, and H. Jawurek, ib. 1931, **201**, 207.

[717] A. Brukl, *Angew. Chem.* 1937, **50**, 25.

[718] H. Senff and W. Klemm, *Z. anorg. Chem.* 1939, **242**, 92.

[719] G. Jantsch, N. Skalla, and H. Grubitsch, ib. 1933, **212**, 65.

[720] G. C. Walters and D. W. Pearce, *J.A.C.S.* 1940, **62**, 3330.

Divalent Ytterbium

The divalency of ytterbium was established by Klemm and Schüth, who made $YbCl_2$ in 1929[715]; the property has since been used for the separation of this element. Walters and Pearce[720] find the oxidation potential of the Yb^{+++}/Yb^{++} electrode to be 0·578 v.: for Eu it is known to be 0·43 v. The value for Sm should be greater, and that for Tm the greatest of the four. Thus Brukl[717] finds that on reducing the trivalent sulphates with a mercury cathode and a carbon anode, the $YbSO_4$ is precipitated.

$YbCl_2$ was made[715] by reducing $YbCl_3$ in hydrogen for some hours at 580-640°; it forms colourless crystals which give in water a yellow solution that on addition of acid evolves hydrogen. The anhydrous solid has only a minute paramagnetic susceptibility, indicating the presence of not more than 3 per cent. of lanthanide impurity (probably thulium and erbium, which were in fact shown to be present). It forms ammines with 8 and 2 NH_3. It is much more easily made than $SmCl_2$, and much more stable to NH_3 and especially to water; also while $SmCl_2$ is dark coloured, $YbCl_2$ is colourless.

Jantsch[716] found that in its halides ytterbium is more like samarium than europium. The effect of heating the trichlorides in hydrogen and hydrogen iodide is: $SmCl_3$ goes smoothly to SmI_3, and is not reduced below 650°; $EuCl_3$ is reduced at the ordinary temperature; $YbCl_3$ is converted into YbI_3 just below 500°, and just above it is reduced to YbI_2. The temperatures at which the halides begin to lose halogen *in vacuo* are:

$SmCl_3$	$SmBr_3$	SmI_3	$YbCl_3$	$YbBr_3$	YbI_3
ca. 900°	700°	560°	870°	700°	250°.

$YbCl_3$ is greenish-yellow; it decomposes to $Yb + YbCl_3$ below its melting-point. $YbBr_2$ is black; YbI_2 is canary-yellow: it begins to soften and decompose at 780°, but it has no definite melting-point.

The calcides (O—Te compounds) have been examined by Senff and Klemm.[718] The sesquitelluride was reduced with hydrogen at 950°: the product had only a trace of paramagnetism corresponding to 3 per cent. impurity. The selenide was obtained in equal purity after 8 hours at 1,250°. Both these compounds are black. Unlike the europium compounds they are oxidized in air in a few hours; both have NaCl lattices, and their dimensions are practically identical (*a* within 1/1000) with those of CaTe and CaSe respectively. (This gives $Yb^{++} = 1{\cdot}06$: Yb^{+++} is 1.00 A.U.)

(The calcides of the lanthanides are always harder to reduce to the divalent state than the halides: among them the oxides are hardest (they scarcely occur at all) and the tellurides the least difficult: just as the iodides are the easiest reduced of the halides.)

$YbSO_4$. According to Brukl[717] the solubility in water is increased by adding H_2SO_4: the g./litre at 17° are

H_2SO_4	0·2·*normal*	1·*normal*	8·*normal*
Grs./l.	4	8	80

This suggests complex formation.

Divalent Thulium?

Jantsch[719] thinks he has shown that thulium can also be divalent, which in view of its position is theoretically quite possible; but the evidence for it is extremely weak.

Separation of the Rare Earths

The history of the discovery and separation of the rare earth elements reflects the greatest credit on the chemists who took part in it. The work is extremely delicate and incredibly tedious. Up to 1920, when it was almost completed, there was no theoretical guidance as to the number or nature of the elements concerned. Now that the Bohr theory has given us a complete list, we can see that the chemists had already found nearly all those that exist, and had not accepted any that do not. R. J. Meyer's list in Abegg's *Handbuch* (1906) contains (in addition to scandium and yttrium) all the fifteen lanthanides except 61, whose existence is still very doubtful, and 71; and he rejects all the suggested elements which we now know not to exist.

The methods of separation[721] depend either (I) on differences of basicity, the heavier elements being the first to be precipitated on gradual addition of alkali or ammonia; or (II) on differences in solubility of the simple or double salts or organic compounds; or (III) where this is possible, on the conversion of particular elements to valencies other than 3. Processes I and II need to be repeated (especially owing to the formation of solid solutions) hundreds or even thousands of times; and as this can be done much more quickly by II than by I, method I is only valuable when the differences in basicity are large; III is the simplest method where it can be applied.

(I) Fractional precipitation of the hydroxides is useful in isolating the very weakly basic $Sc(OH)_3$ or the strongly basic $La(OH)_3$. In combination with method III it is used in the preparation of cerium salts, which are first oxidized to the much less basic tetravalent form.

(II) For this the ammonium or magnesium double nitrates are commonly used, but also the ferricyanides and oxalates[722]; recently the dimethylphosphates have been suggested.[723] Almost all conceivable salts have been tried, as well as organic derivatives such as the acetylacetonates or the benzoates[724]; the solvent is usually water, but alcohols and ethers have also been employed.[725-6]

(III) This is the most valuable method with those elements that can be reduced to the divalent state, which are, in the order of increasing ease of

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[721] For a general discussion of these see W. Prandtl, *Z. anorg. Chem.* 1938, **238**, 321.

[722] Id., ib. 65.

[723] J. K. Marsh, *J.C.S.* 1939, 554.

[724] R. C. Young, A. Arch, and W. V. Shyne, *J.A.C.S.* 1941, **63**, 957.

[725] W. Fischer, W. Dietz, and O. Jübermann, *Naturwiss.* 1937, **25**, 348.

[726] D. B. Appleton and P. W. Selwood, *J.A.C.S.* 1941, **63**, 2029.

reduction, samarium, ytterbium, and europium. With all three the most usual method of separation is through the divalent sulphates, which like the isomorphous barium sulphate are very insoluble, and are precipitated when a solution of the trivalent sulphate is reduced with sodium or calcium amalgam, or electrolytically. Thus with europium McCoy[727] passes the Eu‴ solution acidified with acetic acid over metallic zinc and into a magnesium sulphate solution in an atmosphere of carbon dioxide; $EuSO_4$ is then precipitated. Brukl[728] reduces electrolytically with a mercury cathode and precipitates as $EuSO_4$; if there is very little it can be co-precipitated with strontium sulphate. Kapfenberger[729] reduces in presence of sulphuric acid, oxidizes the precipitate, and re-reduces; starting with a mixture containing 3 per cent. Eu he gets up to 98 per cent. Eu after three reductions.

Another method is to reduce the trivalent salt in acetic acid solution with sodium amalgam, when the reduced lanthanide amalgamates with the mercury much more than the trivalent metals present.[730-1] It is even possible in this way with electrolytic reduction to separate the more reducible of two reducible elements (for example, europium from ytterbium).[732]

ACTINIUM 89

THIS was discovered in pitchblende by Debierne in 1899; it has not been isolated, but the atomic weight must be 223, since that of protoactinium has been shown (V. 852) to be 231. The amount present in a uranium mineral is about 1/300 of the radium, partly from its short half-life (20 years) and partly because it is derived through protoactinium from ^{235}U, of which there is only about 0·7 per cent. in uranium. An isotope of actinium is mesothorium II, half-life 6·2 hours. Hevesy looked for an inactive isotope of 89 in pitchblende residues, but in vain.[733]

Chemically[734] it on the whole resembles the lanthanides; as we should expect it is more basic than lanthanum but less than calcium. Its trivalency was established by Hevesy from the rate of diffusion of the ion.

For the properties of the so-called 'actinides' (elements 89-96) see VI. 1091.

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[727] H. N. McCoy, ib. 1935, **57**, 1756.

[728] A. Brukl, *Angew. Chem.* 1936, **49**, 159.

[729] W. Kapfenberger, *Z. anal. Chem.* 1936, **105**, 199.

[730] J. K. Marsh, *J.C.S.* 1942, 398, 523.

[731] Id., ib. 1943, 8.

[732] H. N. McCoy, *J.A.C.S.* 1941, **63**, 3432.

[733] See G. v. Hevesy and A. Guenther, *Z. anorg. Chem.* 1930, **194**, 162.

[734] G. v. Hevesy, *Selt. Erden*, p. 73.

GROUP III B

GALLIUM, INDIUM, THALLIUM

THESE three elements are all widely distributed in the earth's crust, but in very small concentrations, the amounts being in parts per million[735] Ga 15; In 0·1; Tl 0·3: compare B 3·0, Hg 0·5. With the exception of two very rare thallium minerals they do not form a high percentage of any mineral. They are found in amounts seldom exceeding 0·1 per cent. in the sulphides of heavy metals, especially of zinc and lead (indium and gallium) and of iron and copper (thallium). The peculiar double character of thallium, which resembles the heavy metals in some of its chemical properties, and the alkali metals in others, is shown by its occurrence in nature not only associated with heavy metals but also in many alkaline silicates (felspars and micas), in carnallite ($KCl,MgCl_2, 6\,H_2O$), and in natural alums. The metals and their compounds are more accessible than their rarity would lead us to expect, being usually prepared from the residues of commercial processes in which sulphides are used: gallium and indium from those of the zinc and lead smelters, and thallium from the flue-dust and chamber-mud of sulphuric acid works. All three elements were discovered by means of the spectroscope (thallium, Crookes, 1861; indium, Reich and Richter, 1864; gallium, Lecoq de Boisbaudran, 1875).

Chemically these elements are remarkable for their varying valencies. They all show the group valency of 3, but in addition gallium can be divalent, indium monovalent and apparently divalent, and thallium monovalent. The trivalency needs no further explanation. The monovalency implies the presence of the 'inert pair' of electrons, giving stability to the ion with 2 electrons in the outer group: (core) 3 going to $[(\text{core})2]^+$; this tendency is always greatest in the heavier elements of a B subgroup, but extends increasingly to the lighter elements in the later groups. Since in II B we found signs of it in mercury but not in cadmium, we should expect that in III B it would be more marked in thallium than in mercury, and would possibly appear to some extent in indium, but not in gallium. This agrees with observation. Monovalent gallium (with the possible exception of a doubtful sulphide Ga_2S) does not occur. Monovalent indium occurs, but only when it is stabilized by being covalent; the monovalent ion at once goes over to the trivalent ion and the metal:

$$3\,In^+ \rightarrow 2\,In + In^{+++}:$$

or is oxidized by water with evolution of hydrogen; whereas with thallium the monovalent is more stable than the trivalent state even when ionized; the thallic ion is reduced by almost every reducing agent, however weak, while a strong oxidizing agent is needed to convert a thallous compound into a thallic.

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[735] V. M. Goldschmidt, *J.C.S.* 1937, 656.

The divalent condition which occurs with gallium and perhaps with indium is not explained; it seems to involve a single inert electron:

$$\mathrm{Ga}^{++} \;=\; \text{-}(18),\, 1 \quad \text{or} \quad \text{–Ga-} \;=\; \text{-}(18),\, 1,\, \underline{4};$$

and this has no parallel elsewhere and no theoretical explanation. Divalent indium probably does not exist, the substances supposed to contain it being really compounds of monovalent and trivalent indium; but with gallium, where there is no serious evidence that the monovalent state occurs at all, the divalency seems beyond doubt. The divalent gallium compounds are unstable, and are oxidized by water to gallic compounds and hydrogen, but they certainly exist, and, apart from the coinage elements copper, silver, and gold, whose behaviour is fully accounted for, they are the only definite examples of a change of valency by a single unit that are known in the whole of the B elements.

Metals[736]

Melting- and boiling-points[737]

	M.pt.	*B.pt.*	*II B*	*B.pt.*	*Ratio of III/II b.pts. Abs.*
Al	639° C.	2,270° C.	. .	. .	. .
Ga	29·6°	*ca.* 2,030° C.	Zn	906° C.	2·0
In	156·2°	2,100°	Cd	764°	2·3
Tl	302·5°	1,460°	Hg	357°	2·8

In contrast to II B the melting-points rise with the atomic weight; the boiling-points fall, as in II B, and to nearly the same extent. The values of the Trouton constant[737] are In 23·4; Tl 22·9.

The three metals are white and very soft, gallium a little harder than the other two[736]; they can be cut with a knife even more easily than lead. Gallium, owing to its low melting-point and high boiling-point, has been used for filling quartz thermometers. The metals are not acted on (gallium, indium) or only superficially (thallium) by cold air, but they burn to the oxides when heated in it; the heats of oxidation are much smaller than those of the metals of III A, and so the oxides are easily reduced. They react readily with sulphur and the halogens.

Hydrides

It has been supposed that these elements form no hydrides; they certainly have little or no tendency to absorb hydrogen; thus Hagen and Sieverts[738] found that from 0° to 900° indium absorbs less than 1 mg. of hydrogen per kg. Quite lately, however, Wiberg and Johansen[739] have

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[736] E. Einecke, *Z. anorg. Chem.* 1938, **238**, 113–74, gives an elaborate examination of many of the properties of metallic gallium, especially as compared with those of indium and thallium.

[737] J. S. Anderson, *J.C.S.* 1943, 141.

[738] H. Hagen and A. Sieverts, *Z. anorg. Chem.* 1930, **185**, 228.

[739] E. Wiberg and T. Johansen, *Angew. Chem.* 1942, **55**, 38.

described a volatile gallium hydride Ga_2H_6. If the vapour of gallium trimethyl mixed with hydrogen is subjected to a glow discharge, the compound $Ga_2Me_4H_2$ can be isolated from the products. This has an extrapolated boiling-point of 172° C., but it decomposes when heated to 130° to give gallium trimethyl, hydrogen, and metallic gallium, and it is very sensitive to oxygen or moisture. (For the analogous Al compound see ref. [674].) This mixed gallium methyl hydride reacts with triethylamine thus:

$$3\ GaMe_4H_2 + 4\ NEt_3 = Ga_2H_6 + 4\ Me_3Ga \leftarrow NEt_3.$$

The hydride Ga_2H_6 so formed, whose molecular weight was determined, melts at −21·4° and has an extrapolated boiling-point of 139°; it decomposes into its elements at 130°.

Trivalent Gallium, Indium, and Thallium[740]

This is the normal group valency. The radii of the trivalent ions are:

		Sc	Y	*Rare earth metals*	(A)
		0·78	0·93	1·22—0·99	
B	Al				
(0·24)	0·83				
(calc.)		Ga	In	Tl	(B)
		0·62	0·92	1·05	

The ions of gallium, indium, and thallium, not having an inert gas structure, should have a stronger deforming power than the A ions of the same size. This is found to be so. Aluminium is more like gallium than scandium in behaviour; gallic hydroxide $Ga(OH)_3$ is definitely amphoteric in character, but it is a weaker base than aluminium hydroxide, and a stronger acid (see below, p. 466). It forms gallates such as $K[GaO_2]$ corresponding to the aluminates $M[AlO_2]$; indium behaves in the same way, giving indates $M[InO_2]$, but thallium does not; thallic hydroxide has no amphoteric behaviour; it is a weak base, but not an acid. Accordingly the hydroxides precipitated on adding alkali to a solution of a gallic or indic salt are soluble in excess of alkali, but with a thallic salt they are not. The ions are colourless; the salts are highly hydrolysed in solution; the oxides, hydroxides, carbonates, oxalates, phosphates, and sulphates are insoluble in water, but all the other ordinary salts are soluble.

The tendency to complex formation increases rapidly from gallium, where it is very weak, to thallium.

Alkys and Aryls

The dialkyl thallic salts $[TlAlk_2]X$ have long been known (see below, p. 463), but it is only of recent years that the trialkyl compounds of these three elements have been prepared ($GaAlk_3$ 1932; $InAlk_3$ 1934; $TlAlk_3$ 1930).

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[740] For a review of the salts of gallium see E. Einecke, *Angew. Chem.* 1942, 55, 40; and of those of indium, R. Juza, ib. 45.

Gallium Trialkyls

Triethyl gallium $GaEt_3$ was prepared[741-2] by heating metallic gallium with mercury diethyl for some hours. It has been further examined by Laubengayer and Gilliam.[746] It is a liquid melting at —83·2° and boiling at 142·8°; gallium trimethyl[743-5] melts at −15·8° (as usual higher than the ethyl compound) and boils at 55·7°. Gallium triethyl is monomeric in the vapour between 85° and 100°, but dimeric in benzene solution at the freezing-point. The gallium trialkyls seem to be less sensitive to oxygen than those of aluminium, but they are spontaneously inflammable in air even at −76° C.[743] and are immediately hydrolysed by water to the base $Alk_2A.OH$, but unlike the thallium alkyls (which stop at this point) they are further decomposed by hot water to give the monalkyl hydroxide $Alk \cdot Ga(OH)_2$.

These gallium trialkyls form very stable co-ordination compounds with amines and ethers, which are described later (p. 472).

The curious methyl-hydride of gallium $Ga_2Me_4H_2$ has already been mentioned under the hydride (p. 459).

Gallium triaryls. Gallium triphenyl $Ga(C_6H_5)_3$ was prepared by Gilman and Jones[747] by the action of gallium on mercury diphenyl at 130°. It melts at 166° and is fairly reactive in the usual ways; for example, on treatment with benzoyl chloride it has all its phenyl groups replaced by chlorine, whereas thallium triphenyl only has one.

Indium Trialkyls and Triaryls

Indium trimethyl was made[748] by heating metallic indium with mercury dimethyl at 100° for 8 days; it is a solid which can be sublimed *in vacuo.* It melts at 88·4°[746] and boils under 1 atmosphere at 135·8°; the Trouton constant is 24·5, which suggests association. It is monomeric in the vapour at 80–135°,[746] but tetrameric in benzene solution by the freezing-point.[748] By electron diffraction Pauling and Laubengayer[749] found the In—C distance to be 2·16±0·4 A.U. (theory 2·21); the valency angles could not be determined, but with a valency sextet we should expect the molecule to be planar, with angles of 120°.

Indium trimethyl is very readily oxidized, and loses methane in presence of moisture. The three methyl groups can be removed successively[748]; in 10 days at −78° oxygen acts on it to give the oxide $(InMe_2)_2O$; moisture at the ordinary temperature removes two methyl groups as methane, and dilute acids remove all three, with the formation of a salt InX_3.

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[741] L. M. Dennis and W. Patnode, *J.A.C.S.* 1932, **54**, 182.

[742] G. Renwanz, *Ber.* 1932, **65**, 1308.

[743] C. A. Kraus and F. E. Toonder, *Proc. Nat. Acad. Wash.* 1933, **19**, 292.

[744] E. Wiberg, T. Johannsen, and O. Stecher, *Z. anorg. Chem.* 1943, **251**, 114.

[745] O. Stecher and E. Wiberg, *Ber.* 1942, **75**, 2003.

[746] A. W. Laubengayer and W. F. Gilliam, *J.A.C.S.* 1941, **63**, 477.

[747] H. Gilman and R. G. Jones, ib. 1940, **62**, 980.

[748] L. M. Dennis, R. W. Work, and E. G. Rochow, ib. 1934, **56**, 1047.

[749] L. Pauling and A. W. Laubengayer, ib. 1941, **63**, 480.

Indium trimethyl differs sharply from the gallium trialkyls in forming no ammines or etherates at −35° or any temperature above this.

Indium Triaryls

Indium triphenyl is made from metallic indium and mercury diphenyl.[750-1] It melts at 208°; it is easily soluble in chloroform or benzene, and in solution is readily oxidized by air. It reacts at once and quantitatively with bromine or iodine; by regulating the amounts we can get the monobromide Φ_2InBr, melting above 300°, easily soluble in benzene, and converted by water into indic hydroxide $In(OH)_3$; with bromine it gives the dibromide $\Phi \cdot InBr_2$, and finally indium tribromide $InBr_3$. The iodides are similar, and so is the monochloride Φ_2InCl.[752]

Indium triphenyl is not acted on in boiling benzene by mercury[751] (unlike thallium triphenyl, which gives mercury diphenyl and thallium amalgam): on oxidation it gives phenol and hydroxy-diphenyl

$$C_6H_5 \cdot C_6H_4 \cdot OH.$$

But in boiling xylene carbon dioxide converts it into benzoic acid (18 per cent.) and diphenyl; thallium triphenyl behaves similarly; this suggests that at the higher temperature there is some dissociation into indium monophenyl (not otherwise known) and diphenyl.

In general the indium alkyls and aryls are more reactive than those of gallium, and much more than those of thallium.

Thallium Trialkyls

Thallium triethyl was first made by Groll[753] by the action of lithium ethyl in ligroin on diethyl thallium chloride $[Et_2Tl]Cl$; the yield is almost quantitative. It can also be made from ethyl chloride and sodium-thallium alloy. It was further investigated by Rochow and Dennis.[754] It is a bright yellow mobile liquid, freezing at −63° to a nearly colourless solid, and boiling at 55°/1·5 mm., or (extrapolated) at 192° under 1 atmosphere. It decomposes on heating to 130° into thallium and hydrocarbons, and the same change occurs slowly on standing, especially in the light; this is like the behaviour of the cadmium and mercury alkyls, and shows that the Tl—C bond is very weak. It fumes in the air, though it is not spontaneously inflammable, and it is decomposed by water or dilute acids to diethyl thallium hydroxide $[Et_2Tl]OH$ or its salts but no farther. It is soluble in ether, but forms no etherates and no ammines. For other thallic trialkyls see refs. [753,755].

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[750] W. C. Schumb and H. I. Crane, *J.A.C.S.* 1938, **60**, 306.

[751] H. Gilman and R. G. Jones, ib. 1940, **62**, 2353.

[752] A. E. Goddard, Friend's *Textbook of Inorganic Chemistry*, vol. xi, pt. 1 (1928), p. 235.

[753] H. P. A. Groll, *J.A.C.S.* 1930, **52**, 2998.

[754] E. G. Rochow and L. M. Dennis, ib. 1935, **57**, 486.

[755] S. F. Birch, *J.C.S.* 1934, 1132.

Thallium trimethyl is produced almost quantitatively by the action of thallous halide and methyl iodide on lithium methyl[758]:

$$2\,MeLi + MeI + TlX = Me_3Tl + LiX + LiI.$$

The reaction occurs in ether; the etherate $Me_3Tl \leftarrow OEt_2$ (like the indium compound, but unlike those of aluminium and gallium) is not very stable, and the trimethyl can be separated by distillation under 30–80 mm.

Thallium trimethyl melts at 38·5°, and at that temperature is colourless as solid and as liquid, though it becomes pale yellow on warming; it is liable to explode violently if it is heated above 90° (like the methyls of cadmium, lead, platinum, and copper); the extrapolated boiling-point is 147°. Unlike indium trimethyl it is monomeric by the freezing-point in benzene. In view of this the boiling-point is remarkably high (bismuth trimethyl boils under 1 atmosphere 37° lower, at 110°), as is also that of thallium triethyl (192°). Thallium trimethyl is spontaneously inflammable in air, and is hydrolysed by water to Me_2TlOH.[758] It is miscible with ether and with benzene.

Thallium Triaryls

Thallium triphenyl $Tl\Phi_3$ was first made by Birch[755] from lithium phenyl and diphenyl thallium chloride, and was further examined by Gilman and Jones.[756-7] It melts at 169°, is oxidized by air, and reacts with water and acids; in this it resembles the gallium and indium compounds, but is quite unlike those of mercury; the products are salts of the diphenyl thallium cation $[Tl\Phi_2]^+$. If it is treated in boiling xylene (not in boiling benzene) with carbon dioxide it gives (like the indium compound) diphenyl and benzoic acid. For more of these triaryls see ref. [759].

In their reactions with benzoyl chloride all three phenyl groups of aluminium triphenyl are replaced, two of those of boron triphenyl, and only one of those of thallium triphenyl.

Dialkyl and Diaryl Thallium Compounds

As we have seen, all these three elements form compounds with two hydrocarbon groups and one acid radical, but while the indium and gallium compounds readily lose the remaining hydrocarbon radicals, the thallic compounds show a peculiar stability, much greater than that of the trialkyls; hence they were discovered long before them (Hansen, 1870); they are practically always salts, except the complexes.

These salts are of the type $[Alk_2Tl]X$. They are readily formed by the action of a Grignard reagent on a thallic halide; they are very stable, and are not acted on by air or water, the alkyl groups being as firmly attached as in a substituted ammonium. This stability is, however, less[760] when

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[756] H. Gilman and R. G. Jones, *J.A.C.S.* 1939, **61**, 1513.

[757] Id., ib. 1940, **62**, 2357.

[758] Id., ib. 1946, **68**, 517.

[759] R. K. Abbott, *Iowa State Coll. J. Sci.* 1943, **18**, 3.

[760] E. Krause and A. v. Grosse, *Ber.* 1925, **58**, 1933.

the carbon attached to the thallium is secondary; the isopropyl and isobutyl compounds are broken down on boiling in water. The stability of this group of compounds is obviously due to the fact that in the ion the thallium has the same structure as a mercury atom in its dialkyl compounds:

$$\left.\begin{array}{l}\text{Hg in HgEt}_2\\ \text{Tl in [TlEt}_2]^+\end{array}\right\}\ (60)\ (18)\ \underline{4}$$

and that the shared quartet is as stable with thallium as with its neighbour. It is owing to the stability of this ion that the thallium trialkyls only lose one alkyl group when treated with water.

It has been shown[761-2] that in dimethyl thallium chloride bromide and iodide the two valencies of the thallium (—C—Tl—C—) lie in a straight line, like those of the mercury in mercury dimethyl, as we should expect with a valency quartet. In the chelate diketone derivatives, on the other hand, such as dimethyl thallium acetylacetonate,[763] the 4 thallium valencies are tetrahedral, the valency group here being an octet.

In general the dialkyl thallic ion closely resembles the thallous ion. The hydroxide is a strong base, though not quite so strong as thallous hydroxide, as its salts are rather more hydrolysed at high dilutions[764]; but conductivity measurements show[765] that it is much stronger than Alk·Hg·OH or Alk_3PbOH; even the diaryl thallic hydroxides are stronger than these mercury and lead bases; in decinormal solution Φ_2TlOH is about 60 per cent. dissociated and CH_3·Hg·OH about 0·3 per cent. (dissociation constants roughly 0·9 and 10^{-4} respectively).

Numerous salts, especially of diethyl thallium, are known. They are all colourless; the colourless diethyl thallium iodide is in striking contrast to the red thallous iodide. The salts of oxy-acids are mostly rather less soluble than the thallous salts, especially the nitrate and the chlorate, but the sulphate perchlorate and acetate are easily soluble. The halides show a close resemblance in relative solubility to those of monovalent thallium and silver, the values (in g. to 100 g. of water at about 20°) being:

X =	F	Cl	Br	I
$[Et_2Tl]X$ . .	*ca.* 100	2·76	. .	0·1
TlX . . .	802	3·58	12·74	1·25
AgX . . .	1,815	0·025	0·0018	$2{\cdot}9\times10^{-5}$

The fluorides of dialkyl thallium, though they are so soluble in water, are insoluble in benzene, in which the other halides dissolve readily, suggesting that the fluorides are always ionized, while the other halides can

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[761] H. M. Powell and D. M. Crowfoot, *Nature*, 1932, **130**, 131.

[762] Id., *Z. Krist.* 1934, **87**, 370.

[763] E. G. Cox, A. J. Shorter, and W. Wardlaw, *J.C.S.* 1938, 1886.

[764] A. J. Berry and T. M. Lowry, *J.C.S.* 1928, 1748.

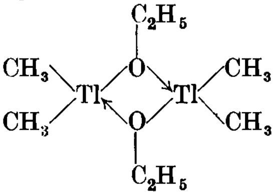
[765] F. Hein and H. Meininger, *Z. anorg. Chem.* 1925, **145**, 95.

[766] E. Krause and P. Dittmar, *Ber.* 1930, **63**, 1953.

go over into the covalent state. This is supported by the behaviour of the higher fluorides, such as those of diamyl and dihexyl thallium; these, while still soluble in water, are sufficiently soluble in benzene for their molecular weights in that solvent to be determined, and it is found[766] that in benzene they are highly polymerized, like the tetra-alkyl ammonium salts in non-dissociating solvents; they presumably form aggregates of ion-pairs.

The diaryl thallium salts[767] are in general very similar to the dialkyl, but they are more stable and less soluble.

The covalent dialkyl thallium compounds are confined to the oxy-derivatives, the alkylates and the derivatives of β-diketones and β-keto-esters, and in all of them the thallium has its covalency increased to 4 by co-ordination. The *alkylates* $Alk_2Tl \cdot O \cdot Alk$ were prepared by Menzies[768-70] from the dialkyl bromides and thallous alkylate. They afford a remarkable example of the relatively high melting-points of certain methyl compounds. The methoxide $Me_2Tl \cdot O \cdot Me$[769] forms crystals melting at 179°, while the ethoxide $Me_2Tl \cdot O \cdot Et$ is a mobile liquid boiling at 110-20° under 15 mm., miscible with hexane and benzene. Cryoscopic measurements of the molecular weight of the ethoxide in benzene[770] show it to be dimeric, the structure presumably being



in which the thallium atoms have fully shared octets.

Mono-alkyl and Mono-aryl Thallium Compounds

These compounds, of the type $R \cdot TlX_2$, have been made in the aryl series by Challenger, who showed[771] that if phenyl boric acid $\Phi \cdot B(OH)_2$ is boiled in water with excess of thallic chloride it gives the monophenyl dichloride $\Phi \cdot TlCl_2$, m.pt. 234°, which is much more soluble in water than the diphenyl salt $\Phi_2Tl \cdot Cl$; the bromide $\Phi \cdot TlBr_2$ is made in the same way, and the *p*-tolyl and *p*-bromophenyl compounds are similar.[772] The relative instability of the mono- as compared with the diphenyl compounds is shown by the fact that the monophenyl dichloride $\Phi \cdot TlCl_2$ is converted by long boiling with water into the diphenyl salt Φ_2TlCl and thallic chloride; the bromide undergoes a similar change on long standing.

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[767] E. Krause and A. v. Grosse, ib. 1925, 58, 272.

[768] R. C. Menzies, *J.C.S.* 1930, 1573.

[769] R. C. Menzies and A. R. P. Walker, ib. 1934, 1131.

[770] R. C. Menzies, *J. Soc. Chem. Ind. Review*, 1930, 539.

[771] F. Challenger and B. Parker, *J.C.S.* 1931, 1462.

[772] F. Challenger and O. V. Richards, ib. 1934, 405.

The methyl and ethyl compounds of this series have been made by Melnikov and Gratscheva,[773] but few of their properties seem to be known.

Nitrides

The only known nitrides (apart from the azides) are those of gallium and indium.[774-5] If the metal is heated in ammonia at 1,200° a grey powder of GaN is formed; it has a wurtzite lattice, suggesting that it is a covalent giant molecule. Indium nitride InN, which is made[775] by heating $(NH_4)_3InF_6$ to 600°, is similar, and has the same lattice.

Oxides and Hydroxides

Gallium sesquioxide, Ga_2O_3, cannot be made by heating the metal in air, which only oxidizes it up to the composition GaO, probably to a mixture of the metal and the sesquioxide; but it is formed when the nitrate, sulphate, or alum is ignited, or when the hydrated oxide precipitated from a gallic salt is heated. It is dimorphic,[776] having a low-temperature α-form, which goes over at 380° to the β-.[780] It melts at 1,740°.[777] Like ferric oxide and alumina it is very inactive to acids after ignition; it will not dissolve in alkali.

At least two hydrated oxides occur, $GaO\cdot OH$ and $Ga(OH)_3$; the former is probably[778-9] the precipitate produced in a gallic solution by alkali; it has the lattice of diaspore α-$AlO\cdot OH$. The radii of the gallic aluminium and ferric ions are Al^{+++}0·83 A., Ga^{+++}0·62, Fe^{+++}0·67, and the three oxides behave in the same way. This oxide $GaO\cdot OH$ is stable in contact with water up to 300°, but above that the β-form of Ga_2O_3 becomes stable. The trihydroxide $Ga(OH)_3$ can be got in the presence of water at about 170°, and is apparently a metastable phase.[780]

Gallium hydroxide is much more acidic than aluminium hydroxide, and even the second hydrogen atom is considerably replaced in solution by sodium.[781] The solubility curve of gallium hydroxide in sodium hydroxide solution has a maximum at 10·3-normal NaOH, where the soluble trisodium gallate is present; the mono- and di-sodium salts are insoluble.[781a] On the other hand, the alkaline properties of gallium hydroxide are much weaker than those of aluminium hydroxide. Both these differences indicate that the deforming power of the gallium (which has not an inert gas number) is greater than that of aluminium (which has) in spite of its larger size.

[773] N. N. Melnikov and G. P. Gratscheva, *J. Gen. Chem. Russ.* 1935, **5**, 1786.

[774] J. V. Lirmann and H. S. Schdanov, *Acta Phys. Chem. U.R.S.S.* 1937, **5**, 306.

[775] R. Juza and H. Hahn, *Z. anorg. Chem.* 1938, **239**, 285.

[776] W. H. Zachariasen, *Brit. Chem. Abstr.* 1929, 1131.

[777] H. v. Wartenberg and H. J. Reusch, *Z. anorg. Chem.* 1932, **207**, 1.

[778] W. O. Milligan and H. B. Weiser, *J.A.C.S.* 1937, **59**, 1670.

[779] J. Böhm and G. Kahan, *Z. anorg. Chem.* 1938, **238**, 350.

[780] A. W. Laubengayer and H. R. Engle, *J.A.C.S.* 1939, **61**, 1210.

[781] R. Fricke and W. Blencke, *Z. anorg. Chem.* 1925, **143**, 183. This paper contains a bibliography of gallium from 1909 to 1925.

[781a] B. N. Iranov-Emin and Y. I. Rabovik, *J. Gen. Chem. U.S.S.R.* 1947, **17**, 1061.

Gallium hydroxide is very soluble in ammonia solution, and can thus be separated from aluminium, ferric iron, and other metals.

Indium Oxide and Hydroxide

Indium sesquioxide (unlike gallium sesquioxide) can be made by heating the metal in air; it is also got by heating the hydroxide, carbonate, nitrate, or sulphate. Its crystal structure is that of the A series of rare earth sesquioxides (see above, p. 446). It is to some extent volatile at temperatures above 1,000°. It is soluble in acids but not in alkalies, though the indate $Mg[InO_2]_2$ has been got by the action of magnesium oxide on a boiling indium trichloride solution.

Indic hydroxide, $In(OH)_3$, separates when alkali is added to a solution of an indic salt; though gelatinous it has a definite lattice structure,[778] and dehydrates sharply at 170° C. to the sesquioxide. According to Moeller[782] its solubility in water at 20° is $0{\cdot}37 \times 10^{-3}$ mg. per litre.

Thallic Oxide and Hydroxide

Thallic oxide Tl_2O_3 can be made like the indium compound by the action of air on the heated metal, by heating the thallic salt of a volatile acid, or by precipitating a thallic solution with alkali. It is a black powder; on heating it begins to lose oxygen and form the thallous oxide Tl_2O at 100°, and at 700° has a dissociation tension of 115 mm.[783] Under a pressure of 25 cm. of oxygen thallic oxide melts at 717°.[783]

Unlike the gallium and indium analogues, thallic oxide forms no hydrates. The precipitate from a salt solution is shown by its X-ray pattern to be the anhydrous oxide,[784-5] and the trihydroxide $Tl(OH)_3$ has been shown not to exist. The solubility of the oxide in water is $0{\cdot}251 \times 10^{-5}$ mg./litre at 25°.

Sulphides, Selenides, Tellurides

Gallium. The sesquisulphide Ga_2S_3 can be made by passing sulphur vapour over gallium at 1,300°[786] or hydrogen sulphide at 800°[787]; it is a yellow solid melting at 1,250°.

The selenide Ga_2Se_3 (m.pt. over 1,020°) and the telluride (m.pt. 790°) have also been made.[788]

Indium. Indium sesquisulphide is described[789] as occurring in two forms, yellow and red. From feebly acid solutions of indic salts hydrogen sulphide precipitates a yellow solid looking like cadmium sulphide, which may be

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[782] T. Moeller, *J.A.C.S.* 1941, **63**, 2625.

[783] A. B. F. Duncan, *J.A.C.S.* 1929, **51**, 2697.

[784] G. F. Hüttig and R. Mytyzek, *Z. anorg. Chem.* 1930, **192**, 187.

[785] M. S. Sherrill and A. J. Haas, *J.A.C.S.* 1936, **58**, 952.

[786] A. Brukl and G. Ortner, *Naturwiss.* 1930, **18**, 393.

[787] W. C. Johnson and B. Warren, ib. 666.

[788] W. Klemm and H. v. Vogel, *Z. anorg. Chem.* 1934, **219**, 45.

a hydrated form; it darkens on drying, but does not go to the red form.[789] The red form is obtained from the elements[790]; it is non-volatile, is not attacked by water, and burns on heating in air to the oxide. It melts at 1,050°.[791] Thiel[790] obtained indium sesquisulphide by the thermal analysis of mixtures of the elements. Indium selenide In_2Se_3 (m.pt. 890°) and the telluride In_2Te_3 (667°) were also obtained.[788]

Thallium. If a solution of a thallic salt is treated with hydrogen sulphide a mixture of thallous sulphide Tl_2S and sulphur is precipitated. But Carstanjen[792] showed that thallic sulphide Tl_2S_3 can be made by fusing thallium with excess of sulphur, and distilling off the excess. It is a black mass melting at 260°.[793]

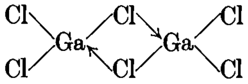
Trihalides of Gallium, Indium, and Thallium

All four trihalides of gallium and of indium are known, but of thallium only the trifluoride and the trichloride are stable, owing to the readiness with which thallium goes over to the thallous state. The following table[794-5] gives the melting- and boiling-points, and (where this is known) the equivalent conductivity of the liquid at its melting-point.

	GaF_3	$GaCl_3$	$GaBr_3$	GaI_3	InF_3	$InCl_3$	$InBr_3$	InI_3	TlF_3	$TlCl_3$
M. pt.	950° subl.	77·9°	121·5°	212°	1,170°	586°	436°	210°	550°	? 25°
B.pt.	..	201·3°	279°	346°	1,200°	..	..	..	..	..
Equiv. condy.	..	10^{-7}	5×10^{-6}	0·02	..	14·7	6·4	2·3	..	..

Gallium. The hydrated trifluoride GaF_3, 3 H_2O is obtained[796] from gallic hydroxide and hydrofluoric acid; on heating this gives a basic salt. Anhydrous gallic fluoride GaF_3 can be made[794] by heating the complex salt $(NH_4)_3$ $[GaF_6]$ in a stream of fluorine at 250–400°. It begins to sublime at 800°, and does so readily at 1,000°. It is very slightly soluble in water (24 mg./litre at the ordinary temperature), whereas the trihydrate is readily soluble, and so must be complex; indium trifluoride behaves in the same way.

Gallic chloride, bromide, and iodide. The boiling-points (above) indicate that while the trifluoride is ionized, the other trihalides are mainly covalent, though the conductivity of the iodide shows that it must contain a small proportion of ions in the fused state. In the vapour the chloride is largely dimeric, the dimers no doubt having the structure



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[789] Cl. Winkler, *J. prakt. Chem.* 1867, **102**, 273; *Ann. Chim. Phys.* 1868, [iv] **13**, 490.

[790] A. Thiel, *Z. anorg. Chem.* 1904, **40**, 280.

[791] A. Thiel and H. Luckmann, ib. 1928, **172**, 365.

[792] E. Carstanjen, *J. prakt. Chem.* 1867, **102**, 65.

[793] I. I. Iskoldski, *Chem. Centr.* 1931, ii. 1396.

[794] O. Hannebohn and W. Klemm, *Z. anorg. Chem.* 1936, **229**, 337.

(like aluminium and gold chlorides); the bromide is less associated, and the iodide only slightly; Fischer and Jübermann[795] find the percentage of monomeric form at the boiling-point under 1 atmosphere pressure to be $GaCl_2$ (201°) 2 per cent.; $GaBr_2$ (279°) 30 per cent.; GaI (346°) 87 per cent.; Laubengayer and Schirmer[797] find the percentage of monomeric trichloride at 1 atmosphere to be 1·5 at 200° and almost 80 at 500°. These results are confirmed by electron diffraction measurements[798-9]; which show that gallium trichloride and tribromide are dimeric and planar (the Ga has fully shared octet); the interatomic distances (the theoretical distances follow in brackets) are Ga—Cl 2·22 (2·25); Ga—Br 2·38 (2·40); Ga—I 2·49 (2·59). (In the first two the gallium is 4-covalent, and in the third 3-covalent.) The dipole moment of gallium trichloride has been found by Ulich and Heyne[800] to be practically zero in benzene, carbon disulphide, and carbon tetrachloride.

In the Friedel-Crafts synthesis of benzophenone from benzene and benzoyl chloride gallium chloride[801] causes a quicker reaction than aluminium chloride, though this is stopped before completion by some unknown by-reaction. The reaction of benzene with alkyl halides is also quicker with gallium than with aluminium chloride.[802]

Indium halides. The anhydrous trifluoride is made[794] by passing fluorine over indium sesquioxide at 500°, or over ammonium indiofluoride $(NH_4)_3InF_6$. Like gallium trifluoride the anhydrous compound is very slightly soluble in water (40 mg./100 g. at the ordinary temperature) and so is not affected by it, while the hydrate InF_3, 3 H_2O has a solubility of 8·49/22°[803]; hence the hydrate must be a complex.

Other halides. Electron diffraction[798-9] shows that indium trichloride, tribromide, and tri-iodide are all dimeric in the vapour, with the distances (theoretical values are added in brackets) In—Cl 2·46 (2·43), In—Br 2·57 (2·58), In—I 2·76 (2·77). Their colour gets darker as the atomic weight of the halogen increases, and is always darker in the liquid; thus in the solid state indium trichloride and tribromide are colourless, and the triodide is yellow; in the liquid the trichloride is yellow and the other two are pale brown.

$InCl_3$, 4 H_2O and $InBr_3$, 5 H_2O have been made[803]; the solubilities of the hydrated trihalides are at 22°:

InF_3	$InCl_3$	$InBr_3$	InI_3
8·49	183·3	557	1,091

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[795] W. Fischer and O. Jübermann, ib. 1936, **227**, 227.
[796] W. C. Johnson and J. B. Parsons, *J. Phys. Chem.* 1932, **36**, 2588.
[797] A. W. Laubengayer and F. B. Schirmer, *J.A.C.S.* 1940, **62**, 1578.
[798] D. P. Stevenson and V. Schomaker, ib. 1942, **64**, 2514.
[799] H. Brode, *Ann. d. Phys.* 1940, **37**, 344.
[800] H. Ulich and G. Heyne, *Z. physikal. Chem.* 1941, B **49**, 284.
[801] Id., *Z. Elektrochem.* 1935, **41**, 509.
[802] See further, H. Ulich, *Angew. Chem.* 1942, **55**, 37.
[803] F. Ensslin and H. Dreyer, *Z. anorg. Chem.* 1942, **249**, 119.

Thallium Trihalides

Owing to the strong tendency of the thallic compounds to go to the thallous state, the trihalides are relatively unstable and little known. Thallium trifluoride was prepared[794] by passing a stream of fluorine over thallic oxide; the reaction begins at the ordinary temperature, but it is best carried out at 300°; the dark brown sesquioxide is thus converted into the pure white fluoride. This is at once decomposed by moist air, turning brown and evolving fumes of hydrofluoric acid; it can be kept in an atmosphere of fluorine. If it is heated alone it blackens and decomposes at 500°, but in fluorine it melts without decomposition at $500 \pm 10°$.

Thallic chloride, $TlCl_3$, can be made by passing chlorine into water containing thallous chloride or the granulated metal; on evaporation a tetrahydrate $TlCl_3, 4\,H_2O$ separates out,[804] which forms long needles melting at 36-7°; solubility 75·7/17°.[805] *In vacuo* it loses water slowly and is converted into the anhydrous salt which melts at 25°.[805] It begins to lose chlorine at 40° and does so rapidly at 100°.

Thallic bromide, $TlBr_3$, can be made in the same way; it forms a monohydrate.[806] It is much less stable than the chloride, and loses bromine with great ease to give the complex salt Tl_2Br_4 (i.e. $Tl'[Tl''' Br_4]$). Mixed chlorobromides $TlCl_2Br$ and $TlClBr_2$ are also known[805,807]; they form tetrahydrates, and lose halogen with the greatest ease.

Thallic iodide, TlI_3, offers a curious problem. The compound TlI_3 can be made by adding potassium iodide to a thallic solution; it forms black crystals which lose iodide very readily. But this is perhaps not a true thallic iodide but thallous periodide $Tl'[I_3]$ (or possibly $[I—Tl—I]^+I^-$). This is supported by the fact that it is isomorphous with the alkaline tri-iodide.[808] Maitland and Abegg[809] consider that in solution there is equilibrium between the two forms, but incline to think that the solid is the thallous salt; it would thus be one of the few examples of inorganic tautomerism. More recently Berry and Lowry[810] have shown that in solution in alcohol thallium tri-iodide does not give the absorption of an I_3 ion, but this still leaves the question of the structure of the solid open. The properties of the ethylene diamine compound (below, p. 473) support the view that the tri-iodide (but not the tribromide or trichloride) has or readily assumes the perhalide structure.

Salts of Oxy-acids: Gallic

These are few and little known. The nitrate $Ga(NO_3)_3$,aq. can be made by evaporating a solution in concentrated nitric acid, and loses its water

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[804] A. S. Cushman, *Amer. Chem. J.* 1901, **26**, 505.
[805] V. Thomas, *C.R.* 1902, **135**, 1051.
[806] R. J. Meyer, *Z. anorg. Chem.* 1900, **24**, 321.
[807] V. Thomas, *C.R.* 1902, **134**, 545.
[808] H. L. Wells and S. L. Penfield, *Z. anorg. Chem.* 1894, **6**, 312.
[809] W. Maitland and R. Abegg, ib. 1906, **49**, 341.
[810] A. J. Berry and T. M. Lowry, *J.C.S.* 1928, 1748.

of crystallization at 40°; it begins to decompose at 110°, and by 200° is entirely converted into the sesquioxide Ga_2O_3 (Lecoq de Boisbaudran, 1878).

Gallic sulphate (Lecoq de Boisbaudran, 1875-6) can be made directly; it has 18 molecules of water,[811] like aluminium sulphate. It is very soluble in water and in 60 per cent. alcohol, but not in ether. It gives an ammonium alum $NH_4Ga(SO_4)_2\ 12\ H_2O$, which forms solid solutions with ordinary alum.[812] A selenate is also known.[813]

The perchlorate $Ga(ClO_4)_3$, 9·5[814] or 9[815] H_2O goes to the hexahydrate at 120°, and at 175° decomposes to form basic salts; it is very soluble in water and alcohol.

An oxalate has also been prepared, with 4, 2, and 0 H_2O; the anhydrous salt is formed at 170° to 180°, and at 195° goes over to the sesquioxide.[816]

Indic Salts of Oxy-acids

Indium carbonate $In_2(CO_3)_3$ (Winkler, 1868) is insoluble in water but dissolves in ammonium carbonate solution forming a complex. A very soluble formate, an acetate, and a very slightly soluble oxalate are known (Winkler, 1868).

Indium nitrate $In(NO_3)_3, 4{\cdot}5\ H_2O$ crystallizes from a strongly acid solution; at 100° it changes slowly to $In(NO_3)_3, 1{\cdot}5\ H_2O$ (Winkler, 1865, 1868).

Indium sulphate crystallizes with some difficulty from its solution in concentrated sulphuric acid in the anhydrous state[817]; if it is recrystallized from water and dried at 100° the hexahydrate $In_2(SO_4)_3, 6\ H_2O$ is formed. There are several acid sulphates, which are perhaps complex. The indium alums of ammonium, rubidium, and caesium are known, but not those of lithium sodium or potassium.[818–21]

Indium forms a rather insoluble anhydrous iodate $In(IO_3)_3$: solubility 0·067/20°[822]; and a deliquescent perchlorate $In(ClO_4)_3, 8\ H_2O$.[822]

Thallic Salts of Oxy-acids

Of the simple thallic salts of oxy-acids relatively little is known, though numerous complex or presumably complex salts of these oxy-acids have been made. An account of these salts is given by Abegg.[823] Some of them may be briefly mentioned.

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[811] R. Fricke and W. Blencke, *Z. anorg. Chem.* 1925, **143**, 183.

[812] W. N. Hartley and H. Ramage, *J.C.S.* 1897, **71**, 533.

[813] L. M. Dennis and J. A. Bridgman, *J.A.C.S.* 1918, **40**, 1531.

[814] L. S. Foster, *J.A.C.S.* 1939, **61**, 3122.

[815] D. J. Lloyd and W. Pugh, *J.C.S.* 1943, 76.

[816] G. Centola, *Congr. Int. Quim.* 1934, **9**, iii. 230.

[817] R. E. Meyer, *Ann.* 1869, **150**, 137.

[818] C. Chabrié and E. Rengade, *C.R.* 1901, **131**, 1300.

[819] Id., ib. **132**, 472.

[820] Id., *Bull. Soc. Chim.* 1901, [3] **25**, 566.

[821] J. Locke, *Am. Chem. J.* 1901, **26**, 166.

[822] F. C. Mathers and C. G. Schluederberg, *J.A.C.S.* 1908, **30**, 212.

[823] Abegg, pp. 445–8 (1906).

Thallic formate[825] and acetate[826] can be made from concentrated acid solution. The oxalates are probably[824,826] all complex; the simple oxalate $Tl_2(C_2O_4)_3$ does not seem to exist.

Thallic nitrate $Tl(NO_3)_3$ is formed in concentrated nitric acid, and has 3 H_2O; water turns it brown at once.[806,827]

The thallic sulphates[824,828] are probably all complex.

Complexes of Trivalent Gallium, Indium, and Thallium

As we should expect of the trivalent atoms of a B subgroup, all three elements form numerous complexes. In the earlier B subgroups the tendency to do this usually rises with the atomic weight, but here the instability of the trivalent state in thallium rather interferes.

The complexes in which the trialkyls act as acceptors form a special case. In the later periodic groups (especially in Group IV), where the atoms have a full octet, the presence of alkyl groups diminishes the co-ordinating power; thus that of stannic chloride falls rapidly as successive chlorine atoms are replaced by alkyls. Here, however, the central atom in the monomeric form of the trialkyls has only a valency sextet, which cannot be completed by back co-ordination, and so is the more ready to act as acceptor. Gallium trialkyls form very stable ammines and etherates; but for some reason this power does not extend to indium and thallium.

Gallium trialkyl ammines are formed by dissolving the trialkyl in liquid ammonia.[829] $(CH_3)_3Ga{\leftarrow}NH_3$ is a white crystalline substance melting at 31°; with hydrogen chloride in ether it forms the chloride

$$(CH_3)_2ClGa{\leftarrow}NH_3,$$

but the chlorine atom readily reacts with the NH_3 to give the amide $Me_2Ga{-}NH_2$.[829-30]

Gallium trialkyl etherates[741-3] (refs. on p. 461 above). These compounds of the type $R_3Ga{\leftarrow}OEt_2$ can be made by treating gallic chloride with the Grignard reagent in ether. They are liquids quickly decomposed by oxygen or water. $Me_3Ga{\leftarrow}OEt_2$ freezes at −76° and boils at 98°; the vapour is shown by its density to be 70 per cent. dissociated at 25°.[743]

In other than the alkyl or aryl derivatives all three elements form ammines, those of gallium and indium being very like the ammines of aluminium. Solid ammines with large numbers of NH_3 molecules have been obtained from the trichlorides tribromides and tri-iodides of gallium and indium[831-3] and with smaller numbers from the trifluorides,[834] where

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[824] R. J. Meyer and E. Goldschmidt, *Ber.* 1903, **36**, 238.

[825] W. O. Rabe and H. Steinmetz, *Z. anorg. Chem.* 1903, **37**, 88.

[826] R. Abegg and J. F. Spencer, ib. 1905, **46**, 406.

[827] R. J. Meyer, *Z. anorg. Chem.* 1902, **32**, 72.

[828] H. Marshall, *Proc. R. S. Edin.* 1899, **22**, 596.

[829] C. A. Kraus and F. E. Toonder, *Proc. Nat. Acad. Wash.* 1933, **19**, 292.

[830] Id., *J.A.C.S.* 1933, **55**, 3547.

[831] Gallium: W. Klemm, W. Tilk, and H. Jacobi, *Z. anorg. Chem.* 1932, **207**, 187.

[832] Indium: W. Klemm, ib. 1926, **163**, 241.

[833] W. Klemm and E. Tanke, ib. 1931, **200**, 344, Anm. 3.

the highest are GaF_3, 3 NH_3 and InF_3, 3 NH_3. These fluoride ammines cannot be made from anhydrous gallium or indium trifluoride, presumably because the lattice energy is too great; when this has been diminished by conversion into the trihydrate, and the latter if treated with liquid ammonia, the 3 H_2O molecules are replaced by NH_3.* GaF_3, 3 NH_3 has a dissociation tension of 1 atmosphere at 163°; that of InF_3, 3 NH_3 is rather greater.[834] Indium trichloride also forms an ammine with 3 molecules of pyridine.[835-6]

The *thallic trihalides* absorb ammonia and no doubt form ammines, but these are decomposed by water with precipitation of the hydroxide $Tl(OH)_3$. The thallic amines formed with ethylenediamine are, however (in consequence of the chelation), much more stable. Hieber and Sonnekalb[837] showed that these *en* ammines could be made in water, by treating an aqueous solution of a thallic trihalide with *en*. They obtained from thallic chloride and bromide the compounds

$$TlCl_3,en,\ 1\,H_2O : TlCl_3en_2,\ 1\,H_3O : TlCl_3en_3,\ 3\,H_2O : TlBr_3en_2 : TlBr_3en_3,\ 2\,H_2O.$$

These gave clear solutions in water at first, but from them thallic hydroxide separated slowly. The ethylene diamine compound made from thallic iodide is remarkable. It is precipitated from a solution of $TlCl_3en_3$ by potassium iodide, and has the composition TlI_3en. While all the rest of these ammines are colourless, this is brick-red; it is much less soluble in water than the others, but is soluble in ethylene dibromide and in nitrobenzene; cryoscopic measurements in the last solvent show that here it is less than 10 per cent. dissociated. These peculiarities certainly seem to show that it is $[enTl]I_3$, and to support the view (p. 470) that thallium tri-iodide has or can readily assume the structure of thallous periodide $[Tl]I_3$; it might, however, be $[TlenI_2]I$.

Oxygen Complexes

Only a few open-chain complexes of this kind are known, such as $TlCl_3,EtOH$ and $TlCl_3,OEt_2$. Klemm and Kilian[834] say that in general elements of the B subgroups have a greater tendency to co-ordinate with ammonia rather than oxygen compounds, than those of the A subgroups; but this statement, though it is supported by the fact (p. 467) that gallium hydroxide can be separated from alumina through its solubility in ammonia, needs some modification in view of the behaviour of chromium, cobalt, and platinum. With our present subgroup it would seem that neither the nitrogen nor the oxygen complexes are very stable unless they are chelate.

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* Cobaltous fluoride behaves in the same way: see VIII. 1378.

[834] W. Klemm and H. Kilian, ib. 1939, **241**, 94.

[835] C. Renz, *Z. anorg. Chem.* 1901, **36**, 101.

[836] Id., *Ber.* 1904, **37**, 2110.

[837] W. Hieber and F. Sonnekalb, *Ber.* 1928, **61**, 555.

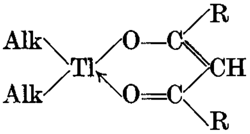
Double nitrates are said[838] to be formed by indium, but their composition and structure are uncertain; a crystalline salt of the composition $K_2[Tl(NO_3)_5],H_2O$ was obtained from a concentrated acid solution.[839]

Double sulphates of indium of the type $[Et_2NH_2]\cdot[In(SO_4)_2]$ with various amounts of water are known[840] and may be complex. Similar double sulphates of thallium, of the two types $M[Tl(SO_4)_2]$ and $M_3[Tl(SO_4)^3]$, are also known.[841]

Chelate derivatives of β-diketones and the like are known with gallium and indium and in addition there is a series of such derivatives formed by the dialkyl thallium radicals.

Diketone compounds of the simple MA_3 type are formed[842-3] by nearly all the elements of Group III (including several rare earth metals), but curiously not by thallium, which only gives the thallic type R_2TlA, and the thallous TlA. The acetylacetonates of gallium and indium, GaA_3 and InA_3, melting at 194° and 186°, both subliming at 140° under 10 mm., are very similar to one another, and to the aluminium compound AlA_3 (m. pt. 193°) which also sublimes at 140° under 10 mm. pressure. These Group III acetylacetonates are of three crystalline forms, α, β, γ, the distribution being AlA_3, α; GaA_3 α and β; InA_3, β and γ; ScA_3 and FeA_3γ.[843]

The β-diketone derivatives of dialkyl thallium have been examined by Menzies[844-6]; they are obviously chelate compounds of the type given here.



They are readily made from the dialkyl thallium ethoxides and the diketones in petroleum ether. Their melting-points fall steadily as the size of the alkyl increases:

	Acetyl-acetone	*Propionyl-acetone*	*Dipropionyl-methane*
Tl′	161°	86° decp.	68·5°
Me_2Tl	214°	162°	121°
Et_2Tl	200°	147°	116°
n-Pr_2Tl	181°	108°	89°
n-Bu_2Tl	138°	72°	41°

The differences between the melting-points of the dimethyl and the diethyl thallium compounds is much less than between dimethyl thallium

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[838] L. M. Dennis and W. C. Geer, *Ber.* 1904, **37**, 961.
[839] R. J. Meyer, *Z. anorg. Chem.* 1900, **24**, 321.
[840] J. B. Ekeley and H. A. Potratz, *J.A.C.S.* 1936, **58**, 907.
[841] R. J. Meyer and E. Goldschmidt, *Ber.* 1903, **36**, 238.
[842] C. Chabrié and E. Rengade, *C.R.* 1900, **131**, 1300; 1901, **132**, 472.
[843] G. T. Morgan and H. D. K. Drew, *J.C.S.* 1921, **119**, 1058.
[844] R. C. Menzies and E. R. Wiltshire, ib. 1932, 2604.

methoxide, m.pt. 179° (p. 465) and dimethyl thallium ethoxide, melting below 0°; indeed the differences in the above table between the dimethyl and diethyl compounds is less than that between the succeeding pairs of homologues (mean differences Me_2Tl—Et_2Tl 11°; Et_2Tl—Pr_2Tl 28°; Pr_2Tl—Bu_2Tl 42°). They are to some extent (up to 40 per cent.) associated in benzene by the freezing-point.[845]

These compounds are hydrolysed by water and can be titrated with acid, but they seem[846] to be somewhat volatile in steam.

The corresponding derivatives of β-ketoesters such as acetoacetic are very similar, but rather less stable, and more highly associated in solution.[844, 846]

Oxalato-compounds occur with all three elements. Neogi and Dutt[847] have made the salts $M_3[Ga(C_2O_4)_3]$, 3 H_2O, where M = Na, K, and NH_4; they resolved this anion through the strychnine salt, and obtained optically active potassium and ammonium salts.

With indium Moeller[848] has shown that the oxalate $In_2(C_2O_4)_3$ forms double salts, all of the type $M[In(C_2O_4)_2]$, aq. (Na, 3 H_2O; K, 4 H_2O; NH_4, 2 H_2O); they are slightly soluble in cold water, and more in hot. No trioxalato-compounds $M_3[In(C_2O_4)_3]$ could be prepared.

With thallium, salts of both types (di- and trichelate) are known[841, 849-50]; the free acid $H[Tl(C_2O_4)_2]$, 3 H_2O is a crystalline powder stable to cold water, of which the potassium (3 H_2O) and ammonium (1 H_2O) salts are known. The ammonium and pyridinium salts (both anhydrous) of the trichelate type $M_3[Tl(C_2O_4)_3]$ have also been prepared.

Complex sulphides. These remarkable complexes are formed by indium and thallium, but probably not by gallium. A solution of an indic salt gives with alkaline sulphides a white precipitate of the composition $M[InS_2]$aq. (Na, 1 H_2O: K, anhydrous: NH_4 doubtful). They are all only slightly soluble in water, and in the air are slowly oxidized to sulphate.[851-2] The corresponding thallic salt $K[TlS_2]$ can be made[853-4] by fusing thallous sulphate with potassium carbonate and sulphur, and is a dark red powder.

Complex sulphides of a similar type are formed by mercury, such as $K_2[HgS_2]$ (see under mercury, II. 331); the mercury in these has the same valency group as the indium and the thallium in their sulphide complexes, with 4 shared electrons if we write the anions with co-ordinate links, as

$$[S\leftarrow Hg\rightarrow S]^{--},\ [S\leftarrow In\rightarrow S]^{-},\ [S\leftarrow Tl\rightarrow S]^{-},$$

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[845] E. R. Wiltshire and R. C. Menzies, ib. 2734.

[846] R. C. Menzies and A. R. P. Walker, ib. 1936, 1678.

[847] P. Neogi and N. K. Dutt, *J. Ind. Chem. Soc.* 1938, **15**, 83.

[848] T. Moeller, *J.A.C.S.* 1940, **62**, 2444.

[849] W. O. Rabe and H. Steinmetz, *Ber.* 1902, **35**, 4447; *Z. anorg. Chem.* 1903, **37**, 88.

[850] R. Abegg and J. F. Spencer, ib. 1905, **44**, 379; H. Schäfer and R. Abegg, ib. **45**, 297.

[851] R. E. Meyer, *Ann.* 1869, **150**, 137.

[852] R. Schneider, *J. prakt. Chem.* 1874, [ii] **9**, 209.

[853] R. Schneider and Preiss, *Pogg. Ann.* 1870, **138**, 604.

[854] R. Schneider, ib. 1875, **151**, 437; **153**, 588.

resonance with the doubly linked form being of course possible. That the shared quartet is stable with thallium as it is with mercury we have already seen in the stable dialkyl thallium ion.

Complex Halides

These are the most numerous class of complexes with all the three elements. The distribution, however, is curious. Gallium forms only complex fluorides: indium so far as is known only chlorides and bromide and thallium complex chlorides, bromides, and iodides.

Complex gallic fluorides. The first of these were made by Hannebohn and Klemm,[855] and they were further examined by Pugh.[856–7] They are made by mixing the components in solution in dilute hydrofluoric acid. They are all of the type M_3GaF_6, but their hydration is very peculiar (Li, 0 aq.; Na, 0 aq.: both recrystallised from water; K, 1 aq.: Rb, 2 aq.; Cs, 2 aq.; NH_4, 0 aq.); the hydrated forms lose their water on heating to 230°.

Later[857] Pugh prepared a series of salts of divalent metals, especially of the type $M''[GaF_5]$, 7 H_2O or $M''[GaF_5(OH_2)]$, 6 H_2O, all readily soluble in water, where $M'' = Mn''$, Co'', Ni, Cu'', Zn, and Cd.

Gallium forms no complex halides with other halogens than fluorine.

Complex indium halides. These are all chlorides or bromides. Meyer[851] prepared the soluble salts $K_3[InCl_6]$, 1·5 H_2O and $(NH_4)_2[InCl_5(OH)_2]$. Ekeley and Potratz[840] made a series of complex indium chlorides and bromides of alkyl-ammoniums, of all types from $MInX_4$ to M_4InX_7, the (apparent) covalency of the anion being on the whole greater the fewer alkyls were attached to the nitrogen.

Complex thallic halides. These are formed with all the halogens except fluorine. They are of the types $MTlX_4$, M_2TlX_5, and M_3TlX_6, as well as a binuclear type $M_3Tl_2Cl_9$, whose structure has been determined (see below). The chlorides are of all three types: for example, $H[TlCl_4]$, 3 H_2O[858]; type $M_2[TlCl_5]$, K, 1 and 2 aq.; Rb, 1; Cs, 1 and 0 aq.; type $M_3[TlCl_6]$ Li, 8 aq. (very soluble); Na, 12 aq. (very soluble); K, 2 and 0; Rb, 2, 1, and 0.[859] The bromides are mainly of the type $M[TlBr_4]$; no M_2TlBr_5 is known and only one $M_3[TlBr_6]$, the anhydrous rubidium salt.

The lattice of the binuclear salt $Cs_3Tl_2Cl_9$ has been shown[860–1] to contain anions Tl_2Cl_9, each formed of two $TlCl_6$ octahedra with the 3 Cl atoms of one face in common. Hoard and Goldstein[862] find similar TlX_6 octahedra in K_3TlCl_6, 2 H_2O and in Rb_3TlBr_6, 8/7 H_2O.

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[855] O. Hannebohn and W. Klemm, *Z. anorg. Chem.* 1936, **229**, 341.

[856] W. Pugh, *J.C.S.* 1937, 1046.

[857] Id., ib. 1959.

[858] R. J. Meyer, *Z. anorg. Chem.* 1900, **24**, 321.

[859] J. H. Pratt, ib. 1895, **9**, 19.

[860] H. M. Powell and A. F. Wells, *J.C.S.* 1935, 1008.

[861] J. L. Hoard and L. Goldstein, *J. Chem. Phys.* 1935, **3**, 199.

[862] Id., ib. 645.

Divalent Gallium and Indium

There is some doubt whether the apparently divalent indium compounds really are so, or are made up with trivalent and monovalent atoms. With gallium there is no such doubt, because there is no real evidence for monovalent gallium, and on the grounds of analogy it is unlikely to exist (see below, p. 480).

Divalent Gallium

There is little evidence for the separate existence of any gallous compounds other than the halides and perhaps a sulphide, though a reducing solution can be made which may contain gallous ions Ga^{++}, or perhaps a gallous complex. Abegg suggests[863] that all gallous compounds are covalent, and that when they ionize they are converted (like cuprous ions) into the metal and gallic ions.

The existence of gallous oxide GaO has not been confirmed; the substance so called has been shown[864] to be a mixture of the metal and the sesquioxide (p. 480). On the other hand, Brukl and Ortner claim[865] to have obtained the *sulphide* GaS by passing hydrogen over the sesquisulphide Ga_2S_3 at 400°; it sublimes *in vacuo* at 800° and melts at 960°; its X-ray pattern was, however, not examined.

Gallous chloride, $GaCl_2$, was prepared by Lecoq de Boisbaudran[866] in 1881, and its vapour density was found by Nilson and Pettersson[867] to be within 1 per cent. of that of $GaCl_2$ at 1,000°, and three-quarters of this at 13-1,400°. Fifty years later Laubengayer and Schirmer[868] re-examined it. They made it as before by heating gallium trichloride with the metal to 175°, and purified it by distillation *in vacuo*. It forms colourless crystals melting at 170·5°. According to Lecoq de Boisbaudran it boils at 535°, but Laubengayer and Schirmer found that on heating in a vacuum it begins at 200° to decompose into the trichloride and the metal, and does so rapidly at higher temperatures. They got values of the vapour density at 400-470° indicating a considerable amount of $GaCl_2$ molecules with some polymers. Klemm and Tilk[869] have shown that solid gallous chloride is diamagnetic, from which they infer that the polymers have Ga—Ga links. Fused gallous chloride is a conductor of electricity.[870] It dissolves in benzene without change, but is decomposed by water with evolution of hydrogen.[868]

Gallium dibromide and di-iodide have also been made, and appear to be similar to the chloride; but neither has been examined recently.

The only other gallous compound described is the sulphate $GaSO_4$,

[863] *Gallium*, 1906, p. 370.

[864] A. Brukl and G. Ortner, *Z. anorg. Chem.* 1931, **203**, 23.

[865] Id., *Naturwiss.* 1930, **18**, 393.

[866] P. E. Lecoq de Boisbaudran, *C.R.* 1881, **93**, 294, 329, 815.

[867] L. F. Nilson and O. Pettersson, ib. 1888, **107**, 527.

[868] A. W. Laubengayer and F. B. Schirmer, *J.A.C.S.* 1940, **62**, 1578.

[869] W. Klemm and W. Tilk, *Z. anorg. Chem.* 1932, **207**, 161.

[870] W. Hampe, *Jahresber.* 1888, **1**, 388.

which is supposed to be present in the strongly reducing solution obtained when gallous oxide or the mixture that goes by that name is dissolved in sulphuric acid.[871]

Divalent Indium

Monovalent indium undoubtedly occurs, and substances which have the composition of divalent indium compounds may be complexes of some kind with equal numbers of monovalent and trivalent indium atoms in the molecule. These compounds of apparently divalent indium seem again to be practically confined to the halides, but an oxide has been described, though its existence is very doubtful.

Indous oxide, InO. Winkler[872] and Thiel[873] obtained an easily oxidized powder of approximately this composition by reducing indium sesquioxide with indium or hydrogen, but they could not isolate the compound. Klemm and v. Vogel[874] tried in vain to make it by heating the sesquioxide In_2O_3 with the oxide In_2O for days to 350-650°; the product gave X-ray lines for In_2O_3 and In_2O only.

The dihalides, especially the dichloride and the dibromide, are much more certain.

Indium difluoride, InF_2. Hannebohn and Klemm[875] got signs that in the reduction of indium trifluoride to indium by hydrogen at lower temperatures there is an arrest at about InF_2, and the product gives a new X-ray pattern, free from that of the trifluoride; they think this may be indous fluoride InF_2 (it might of course be $In'[In'''F_4]$).

Indium dichloride, $InCl_2$. A solid of this composition is formed when indium is heated in a stream of hydrogen chloride gas to about 200°[876-7]; it forms white crystals which melt at 235°.[878] There are signs that at the melting-point it is partly decomposed into the mono- and trichlorides. The vapour density was measured by Nilson and Pettersson[876] who found (for $InCl_2 = 1$) 1·21 at 958°, 1·03 at 1,167°, and 1·01 at 1,350°; this indicates a strong tendency to polymerization at the lower temperatures (it must be remembered that the equimolecular mixture of $InCl + InCl_3$ will have the same vapour density as $InCl_2$).

Indium dichloride, like gallium dichloride, is at once hydrolysed by water, but unless an acid is present metallic indium is deposited and no hydrogen liberated; moreover, there is evidence[879] that the monochloride is an intermediate product, and that the reaction goes in two stages:

$$\begin{aligned}(1)\ 2\,InCl_2 &= InCl + InCl_3\\(2)\ 3\,InCl &= 2\,In + InCl_3\end{aligned}$$

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[871] A. Dupré, *C.R.* 1878, **86**, 720.

[872] Cl. Winkler, *J. prakt. Chem.* 1867, **102**, 273.

[873] A. Thiel, *Z. anorg. Chem.* 1904, **40**, 280.

[874] W. Klemm and H. U. v. Vogel, ib. 1934, **219**, 45.

[875] O. Hannebohn and W. Klemm, *Z. anorg. Chem.* 1936, **229**, 337.

[876] L. F. Nilson and O. Pettersson, *Z. physikal. Chem.* 1888, **2**, 657.

[877] A. Thiel, *Z. anorg. Chem.* 1904, **40**, 280.

[878] W. Klemm, ib. 1926, **152**, 252.

[879] C. Renz, *Ber.* 1903, **36**, 1847, 2751, 4394.

Aiken, Haley, and Terrey[880] find indium dichloride, made by the action of hydrogen containing 15 per cent. of hydrogen chloride on indium trichloride not above 600°, to be a white crystalline substance melting at 235° and boiling at 570°; it resembles stannous chloride $SnCl_2$ very closely in physical properties, even in the lattice, as shown by X-ray powder diagrams; they conclude that the solids have the structures $Sn''[Sn''''Cl_4]$ and $In''[In'''Cl_4]$ respectively, though the X-ray diagrams do not seem to show this in detail.

Indium dibromide, $InBr_2$, was made by Thiel[877] in the same way as the chloride. It can be freed from the more volatile tribromide by sublimation. Its vapour density at 1,300° was found to be 0·79 of the value for $InBr_2$, indicating a 65 per cent. dissociation into the monobromide and bromine. In its reaction with water the dibromide shows even more clearly than the dichloride that the change goes in two stages; the first products are the mono- and tribromides, and it is only gradually on warming that the former is converted into the metal and the tribromide.

Indium di-iodide, InI_2, may exist,[827] but has never been isolated.

It is thus very doubtful whether indium can really be divalent. We should expect (on the analogy of neighbouring B subgroups) that indium (but not gallium) could be monovalent, though with less stability in that state than thallium; and this is found to be so. But as the undoubted divalency of gallium is unparalleled and unexplained, we cannot say whether we should expect this valency to be shown by indium as well. The facts are compatible with either view: these dihalides of indium may be true divalent compounds InX_2 or they may be dimeric molecules with one monovalent and one trivalent indium atom. Thus all the properties of the dichloride are compatible with its having in the solid the structure $In'[In'''Cl_4]$, and breaking up on volatization and otherwise to $InCl+InCl_3$, like thallium 'dichloride' $TlCl_2$ which clearly is thallous thallichloride $Tl'[Tl'''Cl_4]$ (see below, p. 480). The conductivities of the three indium chlorides just above their melting-points[878] show that they all behave as salts:

	$InCl$	$InCl_2$	$InCl_3$
Melting-points . . .	225°	235°	586°
Spec. conductivity . .	0·83	0·23	0·42
Equivalent conductivity .	33·4	6·9	14·7

The molecular volumes[881] of the dihalides may be compared with the mean of the values for the mono- and trihalides, although these should only be equal if the dihalide was a mixture and not a compound of the other two, which the melting-points make very improbable.

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[880] J. K. Aiken, J. B. Haley, and H. Terrey, *Trans. Far. Soc.* 1936, **32**, 1617.

[881] W. Klemm and F. Dierks, *Z. anorg. Chem.* 1934, **219**, 42.

Molecular volumes at 25°

	InX	InX_2	$\frac{InX+InX_3}{2}$	InX_3
X = Cl	36·0	51·0	50·0	63·9
Br	39·3	65·1	57·0	74·7
I	45·4	78·3	75·7	105·9

Klemm and Tilk[882] find that indium mono- and dichloride, as well as the trichloride and tribromide, are diamagnetic in the solid state, and hence conclude that the solid dichloride in the dimeric form must either be $In[InCl_4]$ or have an In—In link. The same difficulty occurs with gallium, as we have seen. See further, reference [883].

The apparently divalent thallium compound $(TlCl_2)_x$ is clearly $Tl'[Tl'''Cl_4]$: (p. 479).

Monovalent Gallium?

There is no satisfactory evidence for this. Brukl and Ortner[864] obtained a brown solid of the composition Ga_2O by heating the sesquioxide Ga_2O_3 with gallium, but found no evidence of its individuality. Klemm and Schnick[884] showed that the oxide so made, which had a composition between GaO and Ga_2O, gave no new X-ray lines. Their thermal measurements showed that the heat of oxidation of gallium by oxygen gas per g. atom of oxygen taken up is 86 k.cals. when the product is Ga_2O_3, and 82 when it has the composition Ga_2O, suggesting that the latter is a mixture of the sesquioxide and the metal.

There is rather more evidence for a sulphide and a selenide. Brukl and Ortner[885] after reducing gallium sesquisulphide with hydrogen at 400° got a sublimate of the composition Ga_2S; and Klemm and v. Vogel[874] got Ga_2Se as a black solid in the thermal analysis of the system Ga, Se. But with neither substance was any definite evidence of individuality obtained.

The production of galium monochloride GaCl was claimed by Nilson and Pettersson,[886] but this has never been confirmed. Laubengayer and Schirmer[868] found no traces of it when the trichloride was heated at 175° with a large excess of the metal.

We may thus conclude that monovalent gallium does not exist, which is to be expected from the distribution of the inert pair of electrons in the neighbouring B subgroups.

Monovalent Indium

This seems to occur, though it is far less stable than monovalent thallium. We have evidence for the oxide, sulphide, selenide, and tellu-

[882] W. Klemm and W. Tilk, ib. 1932, **207**, 175.

[883] C. Robert and M. Wehrli, *Helv. Phys. Acta*, 1935, **8**, 322.

[884] W. Klemm and I. Schnick, *Z. anorg. Chem.* 1936, **226**, 353.

[885] A. Brukl and G. Ortner, *Naturwiss*, 1930, **18**, 393.

[886] *C.R.* 1888, **107**, 527.

ride, for the chloride InCl, the bromide InBr, and perhaps the iodide InI. In water the ion In^+ at once goes to In^{+++} and metallic indium.

Oxide In_2O. Thiel and Luckmann[887] separated this oxide from the sesquioxide by sublimation *in vacuo* at 700°. This was confirmed by Klemm and v. Vogel[874]; they found that In_2O is very difficult to make, and they could not get it in the pure state. Indium sesquioxide was reduced by hydrogen at temperatures not above 400°, and from the product the monovalent indium oxide In_2O was sublimed off *in vacuo* at 750°; about a decigram was obtained in 8 hours. This oxide has its own X-ray pattern; it is not hygroscopic and does not turn red litmus blue; it is not acted on by cold water, but aqueous hydrochloric acid dissolves it with evolution of hydrogen.

A monosulphide In_2S was found by Thiel,[888] and was confirmed by Klemm and v. Vogel,[874] who also got the selenide In_2Se and the telluride In_2Te.

Indium monohalides. Indium monochloride InCl was first made by Nilson and Pettersson[889] by treating the dichloride (made from indium and hydrogen chloride) with indium; this was confirmed by Klemm.[878] He made it by adding excess of indium to warm dichloride; the reaction is very quick, and the monochloride can then be distilled over in a vacuum. There are two enantiotropic forms, one yellow and the other red; the red is stable above 120°; the melting-point is 225°; the liquid is blood-red. According to Nilson and Pettersson the vapour density at 1,100-1,400° is 1·05 times that of InCl. In presence of water the monochloride is at once converted into indium trichloride and metallic indium.

Indium monobromide, InBr, was made in the same way by Thiel.[888] This also is a red liquid giving a red solid, but apparently at higher temperatures a yellow sublimate. The vapour density at 1,300° is 1·06 times that of InBr; hot water quickly converts it into the tribromide and the metal.

A red monoiodide possibly exists, but it could not be isolated.[888]

Monovalent Thallium

This is the stable valency of thallium, especially in the ionized state[890]; thallic compounds are reduced to thallous by practically all reducing agents, even hydrogen peroxide (with evolution of oxygen).[891] The relations are exactly parallel to those which hold for lead, which in its salts is practically always divalent, the ion having two electrons in its outer group which are not reactive; this is what is meant by the 'inert pair'. The two ions have the same E.A.N.:

$$\begin{array}{ll} 81\ \mathrm{Tl}: (60)\cdot(18)\ 2,\ 1 & \mathrm{Tl}^+: (60)\cdot(18)\ 2 \\ 82\ \mathrm{Pb}: (60)\cdot(18)\ 2,\ 2 & \mathrm{Pb}^{++}: (60)\cdot(18)\ 2 \end{array}$$

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[887] A. Thiel and H. Luckmann, *Z. anorg. Chem.* 1928, **172**, 353.

[888] A. Thiel, ib. 1904, **40**, 280.

[889] *C.R.* 1888, **107**, 500; *Z. physikal. Chem.* 1888, **2**, 657.

[890] See M. Sherrill and A. J. Haas, *J.A.C.S.* 1936, **58**, 952.

[891] P. V. Gogorischvili and V. N. Kalgina, *J. Gen. Chem. Russ.* 1938, **8**, 302, 305.

The suggestion that the thallous ion like the mercurous is diatomic, and is $[Tl{=}Tl]^{++}$, corresponding to $[Hg{-}Hg]^{++}$ was disproved by Woodward,[892] who showed that a concentrated solution of thallous nitrate (unlike one of mercurous nitrate) gave no Raman lines that could not be accounted for by the anion. The thallous compounds are nearly all salts, and are to be compared with the salts of other monovalent cations, especially the alkali metals and silver. The ionic radii and the mobilities[893] of some of these cations are:

	Tl^+	K^+	Rb^+	Cs^+	Ag^+
Ionic radius . .	1·49	1·33	1·49	1·65	1·13
Mobility/18° . .	65·6	64·7	67·5	68·0	54·3

Monovalent thallium shows analogies both to the alkali metals and to silver. The ion is colourless; the hydroxide TlOH is very soluble in water (nearly 40 per cent. at 25°), and is highly ionized, though the hydrolysis of the salts shows that it is not so strong a base as potassium hydroxide. The salts are nearly all anhydrous, like those of ammonium, potassium, rubidium, caesium, and also silver. The halides are more volatile than the monohalides of Group I, and usually have lower melting-points. For example:

	TlF[a]	KF	CuF	AgF	TlCl	KCl	CuCl	AgCl
B.pt.	655°	1,490°	. .	. .	806°	1,411°	1,367°	1,554°
M.pt.	327°	846°	908°	435°	430°	768°	430°	449°

a = [894]

The thallous oxy-acid salts have solubilities similar to those of the alkalies, but rather smaller, as is shown by the following list (solubilities in g./100 g. water at 20° or 25°):

Carbonates				*Sulphates*			*Nitrates*			
Tl′	Li	Na	Ag	Tl′	K	Ag	Tl′	K	Cs	Ag
6	1·33	29·4	0·104	6·19	11·1	0·84	9·6	31·6	23·0	254·0

A further resemblance is that the thallous ion can form a polysulphide Tl_2S_5, and also perhaps (as we saw when discussing thallic iodide) a polyiodide $Tl'[I_3]$.

On the other hand, some thallous salts, especially the halides, have resemblances to those of silver as opposed to the alkalies. The chloride bromide and iodide are only slightly soluble in water, more so indeed than those of silver, and about as much as those of divalent lead. In the

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[892] L. A. Woodward, *Phil. Mag.* 1934, [vii] **18**, 823.

[893] For mobility of the thallous ion see S. J. Bates, *J.A.C.S.* 1913, **35**, 534.

[894] E. Hayek, *Z. anorg. Chem.* 1935, **225**, 47.

following table the solubilities are given in moles of salt to 100 litres of water at 25°:

	F	Cl	Br	I
Tl	359	1·6	0·20	0·0254
Ag	1,430	0·00136	0·000073	0·0000108
Pb	0·27	3·40	2·64	0·164
K	1,657	476	589	681

The values for the fluorides are quoted to show that the sharp contrast between these and the other halides occurs with thallium and silver but not with the alkali metals.

Other points of resemblance to silver and not to the alkalies are that thallium forms an insoluble chromate and an insoluble sulphide Tl_2S, which is precipitated even in the presence of acetic acid.

On the other hand, monovalent thallium, like the alkalies, is devoid of the power which silver has of forming ammines in aqueous solution. But it has some, though not much, power of complex formation, whereas the alkalies have practically none; thus the solubility of thallous oxalate is increased by the addition of potassium oxalate.

Most thallous salts (for example, the sulphate chromate and nitrate) are isomorphous with those of the heavier alkali metals, and the thallous ion can replace them in practically all their double salts, including the alums. This is clearly because the thallous and rubidium ions are of exactly the same size (radius 1·49 A).

But the structure of the thallous ion (60) (18) 2, which is not that of an inert gas or an alkaline ion, may be expected to give it a larger external field and a greater deforming power. That this is so is shown in the crystal structures, especially of the halides. Thallous chloride bromide and iodide all have caesium chloride (8:1) lattices, while the corresponding rubidium salts have sodium chloride (6:1) lattices; this shows that the view formerly proposed by Goldschmidt, that the form of an ionic lattice is determined solely by considerations of close packing, is not strictly true. Again, since the ionic radii of thallium and rubidium are the same, their corresponding salts should have the same molecular volumes. This is true for the sulphates and selenates, as Tutton has shown, but not for the halides; the molecular volume of rubidium chloride is 43·2, while that of thallous chloride is 34·3, and the bromides and iodides show similar differences. The difference of lattice will not account for this, but on the contrary should make the volume of the thallous salt rather larger. It has recently been found that the photochemical dissociation of the vapour of thallous chloride is that of a covalent and not an ionized molecule; it is like that of cuprous or silver chloride, not potassium chloride. Hence, probably the thallous ion, unlike that of rubidium, has sufficient deforming power to produce, at least to some extent, a covalent link with chlorine bromine or iodine, though not with the less deformable fluorine; and the resemblance of the oxy-salts of monovalent thallium to those of the alkalies suggests that in these compounds it is fully ionized, as the small deformability of fluorine and of oxygen would lead us to expect.

Individual Thallous Salts

All attempts to prepare thallous alkyls or aryls Tl·R have failed.

Thallous cyanide, TlCN, is very like an alkaline cyanide, but rather less soluble (sol^y 16·8/28°; of potassium cyanide 71·5/25°), and the solution seems rather more hydrolysed, indicating that thallous hydroxide is a weaker base than potassium hydroxide.

Thallous nitride: the only one known is the azide TlN_3,[895] which is easily soluble in water, and (like an alkaline azide) not explosive.

Thallous oxide, Tl_2O, made by drying the hydroxide at 100°, or by passing air and steam over granulated thallium,[896] is a black hygroscopic solid, attacking glass when heated, and melting at about 300°.

Thallous hydroxide, Tl·OH, is formed at once by the action of water on the oxide, but the heat evolved is much smaller than with an alkaline oxide, being 3·12 k.cals.[897] for thallous oxide as compared with 42·1 for potassium oxide. Hence the hydroxide loses all its water at 100°. It is a yellow solid, very soluble in water (solubility about 39/25°).[898] It is a fairly strong base, absorbing carbon dioxide from the air and attacking the skin and glass. It can be used for the alkylation of hydroxyl groups, the thallous derivative being treated with alkyl iodide.[899]

Thallous Alkyloxides

These are peculiar compounds. Thallium reacts with oxygen in the presence of alcohols to give compounds of the composition Tl·O·Alk.[900-1] Their chemical behaviour is what we should expect from their formulae, being very like that of their alkaline analogues; they are at once hydrolysed reversibly by water to the hydroxide and the alcohol, and they can be made by treating the hydroxide with the alcohol in excess. Their physical behaviour, however, is quite different from that of the alkaline alkoxides, which are solids with all the characteristics of salts. Of the known thallous alkylates only the methylate and the cyclohexylate are solids; the ethyl, propyl, butyl, and amyl derivatives are all liquids, thallous ethylate melting at −30°. The solids are soluble in benzene (solubility of the methylate 3·16/25°) and the liquids are miscible with it, showing that they are covalent compounds. On the other hand, they have no perceptible vapour pressure up to 100°, where they begin to decompose, and the liquid ethylate is only imperfectly miscible (about 9 per cent. at 25°) with ethyl alcohol. These properties suggest that they are covalent compounds

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[895] L. M. Dennis, M. Doan, and A. C. Gill, *J.A.C.S.* 1896, **18**, 970.

[896] R. Phillips and W. W. Hartmann, ib. 1933, **55**, 3065.

[897] R. de Forcrand, *C.R.* 1923, **176**, 873.

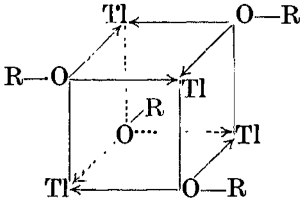
[898] F. Bahr, *Z. anorg. Chem.* 1911, **71**, 85.

[899] C. M. Fear and R. C. Menzies, *J.C.S.* 1926, 937.

[900] Lamy, *Ann. Chim.* 1864, [4] **3**, 373.

[901] G. W. A. Kahlbaum, K. Roth, and P. Seidler, *Z. anorg. Chem.* 1902, **29**, 223.

highly polymerized. This is so.[902] The molecular weights measured by the freezing-point in benzene, and by the boiling-point in methyl and ethyl alcohol, are always high and increase rapidly with concentration, a value of 4 TlOR being reached in 0·2 molar solution if not before; this molecular weight does not sensibly increase at higher concentrations. The high polymerization accounts for the physical peculiarities, but we need a formula which will explain why the polymerization goes up to 4, and especially why it stops there. This is fulfilled by the cubic structure



In this every oxygen is of the form $\overset{\uparrow}{\underset{\downarrow}{—\mathrm{O}—}}$ like the central oxygen in beryllium basic acetate (II. 213); every thallium atom is of the form $\overset{\downarrow}{\underset{\uparrow}{\mathrm{Tl}}}—$; it has increased its original valency group of 3 by 1 for the normal covalency and by 2 × 2 for the two co-ordinate links, so that it has acquired a complete octet 2, $\underline{6}$, which explains the relative stability. The thallium atom, though it is strictly monovalent, resembles a thallic rather than a thallous atom in that the first electron pair is not inert, but forms part of the octet.

This structure is supported by the observation (p. 465) that dimethyl thallium ethoxide $Me_2Tl \cdot O \cdot Et$ is dimeric and not tetrameric; a cubic structure for this compound would involve a decet of electrons for the thallium, while the dimeric formula gives it a fully shared octet.

Thallous sulphide, Tl_2S, is a black insoluble substance; its crystals have been shown[903] to have a layered lattice like that of lead iodide; the distances are normal and the m.pt. 433°. A selenide (grey, m.pt. 340°) and a telluride have been made.

There is also a polysulphide Tl_2S_5 made by adding thallous chloride to a solution of ammonium polysulphide[904]; it forms black shining crystals, m.pt. 310°.[905] The formation of polysulphides of this kind is characteristic of the alkalies.

Thallous Halides

Thallous fluoride, TlF: m.pt. 327°, b.pt. 655 ± 10°,[906] forms no hydrate, and its solubility in water is very large (80/15°). It has an unusual crystal structure,[907] with a kind of deformed sodium chloride lattice.

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[902] N. V. Sidgwick and L. E. Sutton, *J.C.S* 1930, 1461.
[903] J. A. A. Ketelaar and E. W. Gorter, *Z. Krist.* 1939, **101**, 367.
[904] K. A. Hofmann and F. Hochtlen, *Ber.* 1903, **36**, 3090.
[905] I. I. Iskoldski, *Chem. Centr.* 1931, ii. 1396 (not in *B.C.A.*).

Thallous chloride, TlCl: m.pt. 430°, b.pt. 806°[908]; sol^y 0·39/25°. It is colourless, but it darkens on exposure to light like silver chloride. Chlorine converts it first into the double chloride Tl_2Cl_3 or $Tl_3[TlCl_6]$ (see below) and then into thallic chloride.

Thallous bromide, TlBr: m.pt. 456°, b.pt. 815°[908]; sol^y 0·048/20°.[909] It has a caesium chloride lattice.

Thallous iodide TlI: m. pt. 440°, b. pt. 824°[908]; sol^y 0·0079/25°, is a black liquid solidifying to a red solid, which again changes at about 170°[910] to a yellow. The red form has a caesium chloride lattice, the yellow a kind of layer lattice.[911]

Two types of halide intermediate between the thallic and the thallous are known; they have the atomic proportions TlX_2 and Tl_2X_3, and can be made by the action of the halogen X_2 on the thallous halide TlX in presence or absence of water. Chlorides, bromides, and chlorobromides have been made.[912-13] They should obviously be written

$$(TlX_2)_2 = Tl[Tl'''X_4] \quad \text{and} \quad (Tl_2X_3)_2 = Tl'_3[Tl'''X_6].$$

They form yellow or red crystals, and split up easily on heating into thallous + thallic halides.

Thallous Salts of Oxy-acids

Thallous carbonate, Tl_2CO_3, melts at 272°; its sol^y is 5·2/18°; the solution has an alkaline reaction. A remarkable vermilion thiocarbonate Tl_2CS_3 has been described,[914] made by the action of carbon disulphide on a suspension of thallous sulphide Tl_2S in alkali; it is stable in the cold, but loses all its carbon disulphide in a vacuum at 100°. Its formation is a delicate test for thallium.

A very soluble *formate* and *acetate* are known, and an *oxalate* with a sol^y 1·87/25°.

Thallous nitrate, $TlNO_3$, is trimorphic, and isodimorphic with potassium nitrate; it melts at 206°, and decomposes at 300° to thallic oxide and oxides of nitrogen. Sol^y 9·55/20°.[915]

Thallous sulphate, Tl_2SO_4, is isomorphous with the sulphates of potassium, rubidium, and caesium; it melts at 632° and volatilizes at a bright red heat; at its melting-point it is reduced by hydrogen to thallous sulphide and thallium. Its sol^y is 4·87/20°.[915]

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[906] E. Hayek, *Z. anorg. Chem.* 1935, **225**, 47.

[907] J. A. A. Ketelaar, *Z. Krist.* 1935, **92**, 30.

[908] H. v. Wartenberg and O. Bosse; *Z. Elektrochem.* 1922, **28**, 384.

[909] W. Böttger, *Z. physikal. Chem.* 1903, **46**, 602.

[910] See A. F. Benton and R. D. Cool, *J. Phys. Chem.* 1931, **35**, 1762.

[911] L. Helmholz, *Z. Krist.* 1936, **95**, 129.

[912] A. S. Cushman, *Amer. Chem. J.* 1900, **24**, 222.

[913] V. Thomas, *Ann. Chim. Phys.* 1907, [8] **11**, 204.

[914] M. Picon, *C.R.* 1932, **195**, 1274.

[915] Lord Berkeley, *Phil. Trans.* 1904, **203**, 211.

Several oxy-halide salts are known. The *chlorate* $TlClO_3$ is isomorphous with potassium chlorate, but forms only an imperfect series of solid solutions with it. Sol^y 3·92/20°.

Bromate $TlBrO_3$: sol^y 0·347/20°.

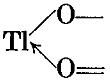
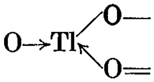
Iodate $TlIO_3$: sol^y 0·058/20°.

Perchlorate $TlClO_4$: m.pt. 500° (Carnelley 1884); sol^y 16.8/25°. It is isomorphous with ammonium and potassium perchlorates.

Thallous Complexes

These are rare, and almost confined to those formed through oxygen or sulphur, the former being mainly chelate.

Numerous derivatives of β-diketones and β-keto-esters have been made. They are all of the monochelate type TlA, but are remarkable for their tendency to associate.

Thallous acetylacetonate[916-18] is made from acetyl acetone and thallous hydroxide in alcohol; it forms white crystals melting with decomposition at 153°; it is soluble in benzene but hydrolysed by water, in which the thallium content can be determined by titration with acid. Many similar compounds have been made,[918-19] from benzoyl acetone, methyl acetyl and methyl benzoyl acetone, acetoacetic ester, salicylaldehyde, etc. With the acetylacetonate Kurowski found a normal molecular weight by the boiling-point in alcohol, but later work[902] suggests that chemical interaction may have affected the result; in benzene the molecular weight of the acetoacetic ester compound was found by the boiling-point[902] to rise to the dimeric value in 10 per cent. solution. In the monomeric form the thallium atom in the group  $\mathrm{Tl}\begin{smallmatrix}\diagup\mathrm{O}-\\ \nwarrow\mathrm{O}=\end{smallmatrix}$ has the valency sextet 2, $\underline{4}$, so that association either through a Tl=Tl linkage or through  $\mathrm{O}\rightarrow\mathrm{Tl}\begin{smallmatrix}\diagup\mathrm{O}-\\ \nwarrow\mathrm{O}=\end{smallmatrix}$ is to be expected.

Kurowski found[916] that the addition of a trace of carbon disulphide to a solution of one of these thallous diketone compounds gave an orange precipitate (see further, ref. [919]).

Thallous chloride and nitrate form complexes with urea, in which presumably the thallous ion is co-ordinate through the sulphur, in the form $[\mathrm{Tl}(\leftarrow \mathrm{S{=}C(NH_2)_2})_4]\mathrm{X}$. Cox, Shorter, and Wardlaw[920] have examined the structures with X-rays. They find the complex cation to have a planar configuration; this is very remarkable, as the thallium here has a decet of valency electrons, and so the configuration should be derivable from the trigonal bipyramid by the removal of the atom attached to one point.

[916] E. Kurowski, *Ber.* 1910, **43**, 1078.

[917] G. T. Morgan and H. W. Moss, *J.C.S.* 1914, **105**, 195.

[918] G. H. Christie and R. C. Menzies, ib. 1925, **127**, 2372.

[919] F. Feigl and E. Bäcker, *Mon.* 1928, **49**, 401.

[920] E. G. Cox, A. J. Shorter, and W. Wardlaw, *J.C.S.* 1938, 1886.

GROUP IV

ELEMENTS AND ATOMIC RADII

		Ge	Sn	Pb		
		1·22	1·40	1·46		
		ion^{4+}	0·74	0·84		
C	Si					
0·77	1·17					
		Ti	Zr	(Ce)	Hf	Th
		1·36	1·48	1·65	1·48	1·65
		ion^{4+}	0·87	1·02	0·87	1·10

THIS group marks a new departure in atomic behaviour, because here for the first time we meet atoms which can all form valency octets directly, without the help of co-ordination. This property distinguishes Groups IV, V, VI, and VII from the preceding groups, and involves a marked difference in chemical character.

The valency octet is always a very stable form of combination, especially when it is in the fully shared 4-covalent form, and it is precisely this form which the Group IV elements can produce, so that we first meet the octet in its most stable condition. Further, the stability of the octet is undoubtedly increased when it forms part of an inert gas configuration, as in CH_4, (2) $\underline{8}$ (Neon (2) 8), though the importance of this is not so great as was once supposed. Now in the fourth group the inert gas number is possessed by the atoms in their 4-covalent state of the typical and B elements, but not by those of the A elements; and the same is true of the three following groups. Hence from Group IV onwards the first two elements of every group belong definitely more to the B than to the A subgroups, whereas in Groups I, II, and III they are more closely allied to the A elements. Two obvious points of difference are that the typical and B elements can form volatile hydrides and volatile alkyl derivatives, which the A elements can not.

The resemblance of the A to the B subgroup is not large in Group IV, but it gets still less in the succeeding groups: in these the B elements are dominated by the octet formation, but they give mixed octets (electrons partly shared) while the resemblance between the A and B is confined to the 4-covalent compounds with the group valency, and these become diminishingly important as we reach the later groups (e.g. in SO_4 and CrO_4 and in ClO_4 and MnO_4).

The distinction between the IV A and IV B subgroups is obviously not of the same simple kind as in the earlier groups: we can no longer say that the A elements are distinguished by being more metallic. This question of metallic character largely depends on the stability of the lower valency states, since with cations these must always be the most metallic.

In discussing the general characters of the Group we may confine ourselves in the first instance to the compounds in which these elements have the normal group valency of 4. In the lower valencies the differences between A and B become very marked. The typical and B elements have essentially only one lower valency, that of 2, while the A, as transitional elements, can be trivalent as well.

The deforming power of the charge on a quadrivalent cation is so large that ionization in this valency only occurs with the heaviest elements. Carbon, silicon, germanium, and titanium do not form monatomic ions; tin, zirconium, hafnium, and also lead (in the plumbic state, perhaps because in ionizing solvents it nearly always goes either to Pb^{++} or to PbO_2) only do so to a most minute extent. Thorium, the largest and heaviest member of the series, stands alone in forming a stable cation, and having no more tendency to go over to the covalent state than, say, magnesium.

Carbon occupies such a peculiar position, in respect both to its properties and to our knowledge of them, that it must be treated separately. The tetravalent compounds of silicon and the B elements will follow, and then the divalent compounds of the same series. The A elements will be discussed later.

CARBON

Carbon is unique among the elements in the number and variety of the compounds which it can form. Over a quarter of a million have already been isolated and described, but this gives a very imperfect idea of its powers, since it is the basis of all forms of living matter. Moreover, it is the only element which could occupy such a position. We know enough now to be sure that the idea of a world in which silicon should take the place of carbon as the basis of life is impossible; the silicon compounds have not the stability of those of carbon, and in particular it is not possible to form stable compounds with long chains of silicon atoms. If our theory of the relation of atomic structure to properties is sound, it must give reasons for the unique position which carbon occupies.

These reasons are essentially two. In the first place, the typical 4-covalent state of the carbon atom is one in which all the formal elements of stability are combined. It has an octet, a fully shared octet, an inert gas number, and in addition, unlike all the other elements of the group, an octet which cannot increase beyond 8, since 4 is the maximum covalency possible for carbon. Hence the saturated carbon atom cannot co-ordinate either as donor or as acceptor, and since by far the commonest method of reaction is through co-ordination, carbon is necessarily very slow to react, and even in a thermodynamically unstable molecule may actually persist for a long time unchanged. More than 50 years ago Victor Meyer drew attention to the characteristic 'inertness' (*Trägheit*) of carbon in its compounds, and there can be no doubt that this is its main cause.

There is, however, another reason for the multiplicity of carbon compounds, and this is that the affinity of carbon for the most diverse elements, and especially for itself, for hydrogen, nitrogen, oxygen, and the halogens, does not differ very greatly: so that even the most diverse derivatives need not vary much in energy content, that is, in thermodynamic stability.

	X—X	X—H	X—O	X—Cl
X = C	81·6	98·8	81·5	78·0 k.cals.
X = Si	42·5	75·1	89·3	85·8 ,,
Diff. (C)—(Si)	+39·1	+23·7	−7·8	−7·8 ,,

This may be seen from a comparison of the values for a few of the more important links of carbon and silicon. The much larger values for carbon in the links to itself and to hydrogen, as compared with that to oxygen

$$(\mathrm{C—C})-(\mathrm{C—O} = +0{\cdot}1 : (\mathrm{Si—Si})-(\mathrm{Si—O}) = -46{\cdot}8$$
$$(\mathrm{C—H})-(\mathrm{C—O}) = +17{\cdot}3 : (\mathrm{Si—H})-(\mathrm{Si—O}) = -14{\cdot}2$$

will obviously favour large carbon molecules, in which there are many C—C and C—H links.

Elementary Carbon

Carbon occurs in the earth's crust to 0·08 per cent. (800 parts per million: compare phosphorus 786; chlorine 480; manganese 930).

There are two natural isotopes of carbon,[1] with the masses 12·0036[2] and 13·0089,[3] the amount of the latter being about 1·1 per cent.[4] The concentration of the ^{13}C has been increased by a chemical method[5] (passing carbon dioxide over potassium hydrogen carbonate solution containing carbonic anhydrase, an enzyme which accelerates the hydration of carbon dioxide), and by Hertz's diffusion method[6,7,8] with methane. Recently ^{13}C has become a commercial product in America, being used as a 'tracer' element.

Artificial radioactive isotopes ^{10}C (half-life 8·8 seconds),[9] ^{11}C (20·4 min.),[10] and ^{14}C (4,700 years)[11] have been described.

Carbon occurs in two crystalline forms, diamond, almost the hardest of known solids, and graphite, almost the softest.

Diamond

The elucidation of the structure of diamond was one of the earliest triumphs of X-ray crystal analysis.[12] It has the typical 'giant' molecule, coextensive with the whole crystal. Every carbon atom has four others covalently attached to it at the points of a tetrahedron, at a distance of 1·54 A. Thus the crystal can be broken only by severing the strong C—C links, which explains its hardness. Some details of the structure are still in dispute,[13] and it has been shown[14] that about 1 per cent. of diamonds are abnormal in having no absorption band at 8 μ, being transparent up to 2,250 A; these also give a photo-electric current. The abnormality (which is not due to impurities) is not fully explained; these diamonds have the same dielectric constant (5·35 at 20°) as ordinary diamonds.[15,16]

Artificial Diamonds. Various efforts have been made[17] to convert other forms of carbon into diamond. Diamond is the unstable allotrope (see below, p. 493) under the ordinary pressure from low temperatures up to at

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[1] A. S. King and R. T. Birge, *Phys. Rev.* 1927, **30**, 825.

[2] J. Mattauch, ib. 1940, ii. **57**, 1155.

[3] F. A. Jenkins and D. E. Wooldridge, ib. 1936, ii. **49**, 882.

[4] A. O. Nier and E. A. Guldbransen, *J.A.C.S.* 1939, **61**, 697.

[5] H. C. Urey, A. H. W. Aten, and A. S. Keston, *J. Chem. Phys.* 1936, **4**, 622.

[6] P. Capron, J. M. Delfosse, M. de Hemptinne, and H. S. Taylor, ib. 1938, **6**, 656.

[7] P. Capron and M. de Hemptinne, *Bull. Acad. Roy. Belge*, 1938, [v] **24**, 641.

[8] A. O. Nier, *Phys. Rev.* 1940, ii. **57**, 30.

[9] L. A. Delsasso, M. G. White, W. Barkas, and E. C. Creutz, ib. 1940, ii. **58**, 586.

[10] A. K. Solomon, ib. 1941, ii. **60**, 279.

[11] A. F. Reid, J. R. Dunning, S. Weinhouse, and A. v. Grosse, ib. 1946, ii. **70**, 431.

[12] W. H. and W. L. Bragg, *Proc. Roy. Soc.* 1913, **89**, 277.

[13] See C. V. Raman, *Proc. Ind. Acad. Sci.* 1944, **19 A**, 189. See also *Nature*, 1945, **155**, 69, 144, 171, 234, 572.

[14] R. Robertson, J. J. Fox, and A. E. Martin, *Phil. Trans.* 1934, **232**, 463.

[15] L. G. Groves and A. E. Martin, *Trans. Far. Soc.* 1940, **36**, 575.

[16] S. Whitehead and W. Hackett, *Proc. Phys. Soc.* 1939, **51**, 173.

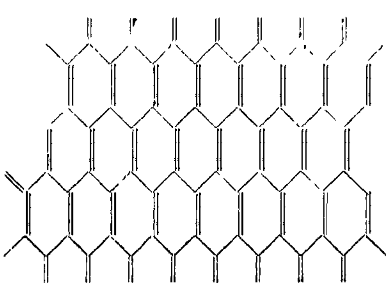
[17] See a review by C. H. Desch, *Nature*, 1943, **152**, 148.

least 2,300°,[18] but it is 1·6 times as dense as graphite; hence the conditions that favour its formation are a high pressure (to make it stable) and a high temperature (to overcome the inertness). Attempts to effect the change under these conditions were made by Moissan in 1894 and later (*Comptes Rendus*), and by Parsons[19] in 1907-20, both of whom claimed success. They both obtained minute hard crystals which were supposed to be diamonds, but these were never satisfactorily identified, and are now lost. Earlier attempts were made by J. B. Hannay in 1880,[20] by heating oils to high temperatures in thick welded steel tubes. Some of the small crystals supposed to have been formed in this way have been preserved, and were lately shown by careful examination[21] to include some real diamonds, all of the peculiar type II (mentioned above) of Robertson, Fox, and Martin,[14] which is only found in about 1 per cent. of natural diamonds. It appears, however,[22] that Hannay's statements cannot be trusted. So it seems that the artificial production of diamonds has never yet been shown to have been a success. The calculation of Simon (see below, p. 493) makes it very improbable that it should have succeeded.

Graphite

Graphite is a two-dimensional giant molecule; it consists of sheets of regular hexagons (like rabbit netting), the interatomic distances within the sheet being 1·42 A; these sheets are piled on one another at distances of 3·41 A, a normal distance of nearest approach of two atoms that are not linked.[23-7] This explains why graphite is so extremely soft (it is the only solid that can be used as a lubricant) while diamond is so hard. A diamond can only be broken by breaking the covalent C—C links. In graphite the same is true within the sheet, but the sheets are held together only by the weak van der Waals forces between unlinked atoms, and so can be separated very easily. The distance between the sheets causes graphite to have a much lower density (2·22) than diamond (3·51).

In graphite therefore all the four valencies of each carbon atom are employed within the sheet. The four are not enough to give true aromatic rings, but rather a quinone-like structure with two double links per hexagon instead of three, as shown below:



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[18] P. L. Günther, P. Geselle, and W. Rebentisch, *Z. anorg. Chem.* 1943, **250**, 357.

[19] C. A. Parsons, *Proc. Roy. Soc.* 1907, **79**, 532; *J. Inst. Metals*, 1918, **20**, 5; *Phil. Trans.* 1920, **220**, 67.

The positions of the double links are evened out by resonance so that the crystal is symmetrical, the mean multiplicity of the links being 1·33 instead of 1·5 as in benzene (and the links therefore longer, 1·42 instead of 1·39 A).

Diamond and Graphite. The heats of combustion at 25° and 1 atm. have been found to be[29-30]: diamond 94·49 k.cals; graphite 94·04: difference +0·45 k.cals. Hence the stable form at 25° under ordinary pressure is graphite. It has been shown experimentally to be so up to at least 2,300°.[18] More recently Bridgman[28] has exposed graphite, either alone or seeded with diamonds, to pressures of from 15,000 to 30,000 kg./cm.^{2} at 2,000°. When the graphite was alone, no diamonds were formed; when it was seeded, the diamonds went over completely to graphite at this temperature under 15,000 kg./cm.^{2}, but less readily as the pressure rose, until at 30,000 there was no change. Hence above this pressure we should expect the graphite to go over to diamond, but this could not be tested experimentally. Simon[31] has calculated by the Nernst equation, using the older value of 0·160 k.cals. for the heat of transformation, that the two allotropes are in equilibrium under 8,400 atm. at 300° K., and under 34,000 atm. at 1,500° K.; Rossini's value of 0·46 k.cal. would make these pressures about 15,000 and 40,000 atm. respectively. This makes it very unlikely that any of the efforts so far made to produce diamonds have succeeded.

Heat of Atomization

A knowledge of the heat of conversion of graphite (or diamond) into a monatomic gas is necessary to the calculation of the strength of all the links that carbon forms. Unfortunately this value is not yet certain. Direct determinations of the heat of evaporation are useless, because the vapour contains an uncertain amount of C_2 molecules. The best evidence is from the heat of dissociation of carbon monoxide, but this gives, according to the mode of interpretation of the results, either 124·3 or 170·4 k.cals./g.atom.[32,33] The weight of recent evidence is more in favour of 170·4, which is adopted in this book; see references [34-40a].

[20] J. B. Hannay, *Proc. Roy. Soc.* 1880, **30**, 188, 450.

[21] F. A. Bannister and K. Lonsdale, *Nature*, 1943, **151**, 334.

[22] Lord Rayleigh, *Nature*, 1943, **152**, 597. Later letters (M. W. Travers, ib. 726; J. W. French, ib. 1944, **153**, 112) do not seriously weaken Lord Rayleigh's charge.

[23] P. Debye and P. Scherrer, *Phys. Z.* 1917, **18**, 291.

[24] J. D. Bernal, *Proc. Roy. Soc.* 1924, **106**, 749.

[25] O. Hassel and H. Mark, *Z. phys.* 1924, **25**, 317.

[26] H. Ott, *Ann. Phys.* 1928, **85**, 81.

[27] H. Lipson and A. R. Stokes, *Proc. Roy. Soc.* 1942, **181**, 101.

[28] P. W. Bridgman, *J. Chem. Phys.* 1947, **15**, 92.

[29] E. J. Prosen and F. D. Rossini, *J. Res. Nat. Bur. Stand.* 1944, **33**, 439.

[30] E. J. Prosen, R. S. Jessup, and F. D. Rossini, ib. 447.

[31] F. Simon, *Handbuch der Physik*, 1926, **101**, 375.

[32] P. Goldfinger and W. Jeunehomme, *Trans. Far. Soc.* 1936, **32**, 1591.

[33] *Chem. Bond*, p. 54.

[34] E. H. Lloyd and W. G. Penney, *Trans. Far. Soc.* 1939, **35**, 835.

[35] G. J. Kynch and W. G. Penney, *Proc. Roy. Soc.* 1941, **179**, 214.

Graphite melts about 3,600° C.[41-2] As might be expected from its layer structure, many of its physical properties have very different values along and across the sheets. Thus it has a magnetic susceptibility along the plane of $-0{\cdot}5 \times 10^{-6}$, and perpendicular to it of -22×10^{-6},[43] and single crystals have been shown[44] to have a resistance of 10^{-4} ohms./cm.³ in the basal plane and from 2 to 3 ohms (over 20,000 times as much) across it.

'*Amorphous*' *Carbon.* Native graphite is crystalline, though it rarely forms visible crystals. Artificial graphite, commonly made by decomposing carbon compounds by heat, forms particles which are larger the higher the temperature at which they are produced; thus with carbon from carbon monoxide at 700° they have a diameter of about 196 A, and at 400° of about 39 A[45]; other forms are often 14–25 A across (5 to 8 carbon hexagons); but they still have the graphite structure. This is true even of 'amorphous' forms, such as that deposited by methane on silica at 1,000°, which consists[46] of a random distribution of groups of 3 or 4 parallel graphite sheets,[47-50] or of soot, which absorbs potassium just like ordinary graphite[52] (see also ref. [53]).

A result of the layer structure of graphite, and the very small forces between the layers, is the formation of a variety of 'interstitial' compounds by the insertion of partial or complete layers of other atoms or molecules between those of carbon. The vapours of potassium, rubidium, and caesium, if they are brought in contact with graphite *in vacuo*, are absorbed, giving compounds of definite formulae, such as KC_8 and KC_{16}[50-1]; the products, which are brown and catch fire at once in air, are shown by X-ray diagrams to be made up of alternate layers of carbon hexagons and metallic atoms.[52]

A better-known group are the compounds with oxygen, including Brodie's 'graphitic acid'. Hofmann points out[54] that the work of many chemists from Brodie in 1860 onwards has shown that graphite can be

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[36] A. G. Gaydon, and W. G. Penney, ib. 1945, **183**, 374.

[37] E. C. Baughan, *Nature*, 1941, **147**, 542.

[38] H. A. Skinner, *Trans. Far. Soc.* 1945, **41**, 645.

[39] N. V. Sidgwick and H. D. Springall, *Nature*, 1945, **156**, 599.

[40] L. H. Long and R. G. W. Norrish, *Proc. Roy. Soc.* 1946, **187**, 337.

[40a] H. D. Hagstrum, *Phys. Rev.* 1947, **72**, 947.

[41] E. Ryschkevitsch and F. Merck, *Z. Elektrochem.* 1927, **32**, 45 (m.pt. 3,570° C.).

[42] J. Basset, *J. Phys. Radium*, 1939, [vii] **10**, 217 (triple pt., 3,730°/101 atm.).

[43] N. Ganguli and K. S. Krishnan, *Proc. Roy. Soc.* 1941, **177**, 168.

[44] K. S. Krishnan and N. Ganguli, *Nature*, 1939, **144**, 667.

[45] U. Hofman and D. Wilm, *Z. physikal. Chem.* 1932, B **18**, 401.

[46] A. H. White and L. H. Germer, *J. Chem. Phys.* 1941, **9**, 492.

[47] J. Biscoe and B. E. Warren, *J. Appl. Phys.* 1942, **13**, 364.

[48] U. Hofmann, A. Ragoss, and F. Sinkel, *Kolloid. Z.* 1941, **96**, 231.

[49] M. v. Ardenne and U. Hofmann, *Z. physikal. Chem.* 1941, B **50**, 1.

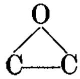
[50] K. Fredenhagen and G. Cadenbach, *Z. anorg. Chem.* 1926, **158**, 249.

[51] K. Fredenhagen and K. Suck, ib. 1929, **178**, 353.

[52] A. Schleede and M. Wellmann, *Z. physikal. Chem.* 1932, B **18**, 1.

[53] J. Gibson, M. Holohan, and H. L. Riley, *J.C.S.* 1946, 456.

[54] U. Hofmann and E. König, *Z. anorg. Chem.* 1937, **234**, 311.

oxidized, especially by potassium chlorate in a mixture of nitric and sulphuric acids, to a substance in which the carbon sheets are themselves unchanged, but oxygen is inserted, presumably in the form of  groups,[57] between them, their distances apart being increased from 3·41 to more than 6 A; the C:O ratio varies from 3·5:1 to 2·2:1.[65] The heat of combustion per g. of carbon is the same for graphitic oxide as for graphite, so that the heat of formation of the oxide from graphite and oxygen gas must be equal to zero.[63] On heating, much carbon monoxide and dioxide comes off. This 'graphitic oxide' has an acid reaction (hence Brodie's name of graphitic acid), but only because the peripheral carbon atoms are oxidized to carboxyl groups.

The sheets having been loosened in this way, other molecules can be introduced between them, some, such as water and alcohol, without further expansion.[55] Strong acids react with the graphite if it is oxidized in their presence, and give a kind of salt. Sulphuric acid forms a compound of the approximate composition $[C_{24}]^+(HSO_4)^-, 2\,H_2SO_4$.[56] This is decomposed by water and cannot be purified, but it still retains the hexagonal sheets of the graphite. Salts of similar composition can be obtained in the same way[56] with nitric, phosphoric, arsenic, selenic, and perchloric acids; the separation of the carbon sheets is 8·25 A for selenic acid, and 7·8 to 7·9 for all the rest, i.e. there are two acid groups between every two sheets. If there is less acid, or less oxidation, the expansion occurs only after every second, third, fourth, etc., sheet.

Similar reactions must be the cause of the peculiar phenomenon of 'puffing up' (*Aufblähen*) shown by certain natural graphites[58]; if they are moistened with nitric and sulphuric acids and then heated, they expand enormously along one axis and assume a concertina-like structure; thus one specimen from Ticonderoga after treatment with nitric acid while it remained 4 mm. across expanded in thickness from 0·5 to 90 mm., the sheets being thus 1,200 A or 0·0012 mm. apart, about 150 times the swelling of ordinary graphite. This is presumably due to some peculiar orientation of the hexagons in adjacent sheets (see further, ref. [59]).

For further details on the oxidation of graphite see Ruff[62] (a general lecture on the reactions of solid carbon), and references [59–61,63–6].

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[55] U. Hofmann and W. Rüdorff, *Trans. Far. Soc.* 1938, **34**, 1017.

[56] W. Rüdorff and U. Hofmann, *Z. anorg. Chem.* 1938, **238**, 1.

[57] U. Hofmann and R. Holst, *Ber.* 1939, **72**, 754.

[58] H. Thiele, *Z. anorg. Chem.* 1932, **207**, 340.

[59] H. Boersch and L. Meyer, *Z. physikal. Chem.* 1935, B **29**, 59.

[60] E. N. Greer and B. Topley, *Nature*, 1932, **129**, 904.

[61] W. Rüdorff, *Z. physikal. Chem.* 1939, B **45**, 42.

[62] O. Ruff, *Trans. Far. Soc.* 1938, **34**, 1022.

[63] U. Hofmann, A. Frenzel, and E. Csalán, *Ann.* 1934, **510**, 1.

[64] J. D. Lambert, *Trans. Far. Soc.* 1936, **32**, 452.

[65] L. Meyer, ib. 1938, **34**, 1056.

[66] V. Sihvonen, ib. 1062.

Fluorine and Bromine react with graphite in much the same way as oxygen. Ruff has shown[67] that norite (a form of 'amorphous' carbon) absorbs fluorine on heating, with explosions if the temperature is below 700°; volatile fluorides from CF_4 to C_5F_{12} are given off, and a grey solid of the composition CF remains; on further heating this again evolves volatile fluorides, leaving a residue of graphite. X-ray analysis shows that in this 'carbon monofluoride' the graphite sheets retain their hexagonal network, but their distance apart is increased from 3·41 to 8·17 A. The substance is insoluble in all solvents and in cold alkali, but is decomposed by fusion with sodium peroxide or sodium, and on reduction with zinc and acetic acid is reconverted into graphite; its electrical resistance is 36 times that of graphite. It is difficult to give it any precise structure.

Bromine vapour is absorbed by graphite in the same way up to 84 per cent. ($CBr_{0\cdot77}$), the sheets being then 7·05 A apart; the bromine can be removed by a stream of air.[68]

Even ferric chloride can be inserted in alternate layers between the carbon sheets, up to 60 per cent. $FeCl_3$ ($C_9\cdot FeCl_3$)[69]; the magnetic moment of the iron is not altered, showing that there are no Fe—C links.

Compounds of Carbon

In its compounds carbon has valencies of 4, 3, and 2, the first being by far the most numerous. Of the tetravalent compounds many are dealt with elsewhere, under their other components; here we discuss, in addition to some wider questions, the general relations of the hydrocarbons, the metallic alkyls and aryls, the binary carbides of the metals and semimetals, and the oxygen compounds.

Carbon and Hydrogen

The main types of hydrocarbons are two, the aliphatic and the aromatic. The saturated aliphatic hydrocarbons (paraffins) are all derivable from methane by the successive replacement of hydrogen atoms by methyl groups; they are thus all built on a skeleton in which the valency angles are near to the tetrahedral angle of 109·5°, and the distances between two linked carbon atoms 1·54 A. The continuation of this replacement to infinity would give a giant molecule with these angles and distances, made entirely of carbon except for the hydrogen atoms on the surface (which for a crystal of 1 $mm.^3$ would amount to 2×10^{-8} per cent.)—in other words to a diamond.

The parent aromatic hydrocarbons are formed either of one 6-carbon ring or of several joined by having 2 ortho-carbon atoms in common. X-ray examination has shown that in all of them the ring is strictly planar; not only the 6 carbon atoms of the ring itself, but also the 6 atoms attached to it (e.g. the 6 methyl carbons of hexamethyl benzene) lie in one plane. Hence two or more fused rings must also be coplanar, and this has been

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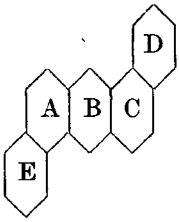
[67] O. Ruff and O. Bretschneider, *Z. anorg. Chem.* 1934, **217**, 1.

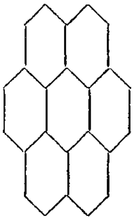
[68] W. Rüdorff and H. Schulz, ib. 1940, **245**, 121.

[69] W. Rüdorff, ib. 383.

established experimentally for every number of such rings up to 5 (Fig. I) and even for coronene (Fig. II)[70-2] (benzene ring A; naphthalene A, B; anthracene A, B, C; chrysene A, B, C, D; dibenzanthracene A, B, C, D, E).



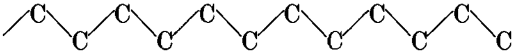
(I)



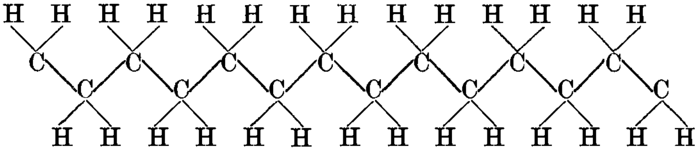
(II)

Moreover, in all these compounds the C—C distance is 1·39 A in the outer and nearly the same in the inner rings, and the valency angles are always those of a regular hexagon, 120°. The extension of this model to infinity would give a giant sheet molecule all made of carbon hexagons with no hydrogen except on the periphery, with the angles 120° and the distances near 1·4 A, which is exactly what we have in graphite.

The saturated aliphatic compounds with open chains can be of the length of several hundred or even a thousand atoms.[73] In the crystalline state (and as condensed surface films on water) they always have a planar zigzag structure



with a C—C distance of 1·54 A and a valency angle of about 110°; this was first established for $C_{29}H_{60}$[74] and $C_{60}H_{122}$,[75] but it is found with all long chains of CH_2 groups, whatever the terminal groups may be (see further, refs. [76-7]). This is evidently due to the mutual repulsion of the C—H bonds or the hydrogen atoms, this arrangement giving the greatest distance between them (see below, p. 500):



Saturated ring compounds (polymethylenes) have been made of all sizes from 3 to 34 atoms. The famous Baeyer theory of strain[78] ascribed to the

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[70] J. M. Robertson and J. G. White, *Nature*, 1944, **154**, 605.

[71] Id. *J.C.S.* 1945, 607.

[72] C. A. Coulson, *Nature*, 1944, **154**, 797.

[73] Brit. Pat. 471,590.

[74] A. Müller, *Proc. Roy. Soc.* 1928, **120**, 437.

[75] J. Henstenberg, *Z. Krist.* 1928, **67**, 583.

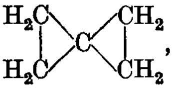
[76] M. L. Huggins, *J. Phys. Chem.* 1939, **43**, 1083.

[77] C. W. Bunn, *Trans. Far. Soc.* 1939, **35**, 482.

[78] A. v. Baeyer, *Ber.* 1885, **18**, 2277.

rings an instability proportional to the deflexion of the valency angles from the normal 109·5° (for C=C 109·5°: for C_3 49·5°: C_4 19·5°: C_5 1·5°). This assumes that the ring is planar, which no doubt is true for rings up to C_5, since that involves the least strain; but with all larger rings the angle for a plane ring is too large, and this excess (and hence the strain) can be made to disappear if the atoms are not required to lie in a plane, and X-ray diffraction[81] and other evidence show that these rings are no longer planar. For the thermodynamic properties and their bearing on the structure see the references: cyclopentane,[78a] alkyl cyclohexanes.[78b] The strain in the smaller rings is shown in their energy-content. The heat of formation of cyclopropane (m.pt. −127·62°, b.pt. −32·86°, Trouton constant 19·9[84]), is about 10 k.cals. and for cyclobutane about 1 k.cal. less than would be calculated from the number of CH_2 groups using the values obtained from rings of 5 and more atoms.[79,83]*

A remarkable 3-ring compound is spiropentane



made[85] by the action of zinc dust on penterythritol bromide $C(CH_2Br)_4$; electron diffraction has shown[86] that the product has this structure, with the two rings in perpendicular planes; the C—C distances from the central carbon are markedly short (1·48 A), and those between the peripheral carbons rather short (1·51); the C—C distances in cyclopropane are also rather short (1·52).[87] On reduction with hydrogen under pressure, in presence of platinic oxide, it gives neopentane $C(CH_3)_4$ and 1,1-dimethyl cyclopropane, with some isopentane.[87a]

The larger rings are commonly made by Ruzicka's method[82] of heating the salts of the dicarboxylic acids $(CH_2)_n(COOH)_2$ to form cyclic ketones,

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* According to W. Hückel[79] the heats of combustion of the polymethylenes $(CH_2)_n$ per CH_2 are:

$n = 2$	3	4	5	6	7	8	15	17	30
170	168·5	165·5	159	158	158	158	157	157·2	156·7

More recent results given by Spitzer and Huffman[80] are:

$n = 5$	6	7	8
158·7	157·4	158·3	158·6

[78a] J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J.A.C.S.* 1947, **69**, 2483.

[78b] C. W. Beckett, K. S. Pitzer, and R. Spitzer, ib. 2488.

[79] W. Hückel, *Ber.* 1920, **53**, 1277.

[80] R. Spitzer and H. M. Huffman, *J.A.C.S.* 1947, **69**, 211.

[81] A. Müller, *Helv. Chem. Acta*, 1933, **16**, 155.

[82] L. Ruzicka *et al.*, ib. 1926, and subsequent years.

[83] L. Ruzicka and P. Schläpfer, ib. 1933, **16**, 162.

[84] R. A. Ruehrwein and T. M. Powell, *J.A.C.S.* 1946, **68**, 1063.

[85] M. J. Murray and E. H. Stevenson, ib. 1944, **66**, 812.

[86] J. Donohue, G. L. Humphrey, and V. Schomaker, ib. 1945, **67**, 332.

[87] L. Pauling and L. O. Brockway, ib. 1937, **59**, 1223.

[87a] V. A. Slabey, ib. 1947, **69**, 475.

which can then be reduced to polymethylenes. The yield diminishes as the ring grows larger, but this difficulty can be partially overcome by using cations of higher valency such as thorium:

$$[(CH_2)_n(COO)_2]_2Th = Th(CO_3)_2 + 2(CH_2)_nCO \rightarrow (CH_2)_{n+1}.$$

The resulting compounds (as the heats of combustion given above show) are equally stable, as we should expect if they are strainless. The difficulty of formation is due to the fact that the chance of the ends of the anion chain coming together is less the longer the chain; this chance would seem to increase with the charge of the cation; see further references [92-5].

Similar relations are observed in heterocyclic rings containing oxygen[96-7] or nitrogen[98-9]; among the latter the rate of the reaction

$$hal\cdot(CH_2)_nNH_2 \longrightarrow (CH_2)_nNH$$

has been shown[98] to be (ring size $= n+1$)

Ring size . . .	3	4	5	6	7
1,000 K. . . .	36	0·5	30,000	500	1

Free and Restricted Rotation

It has long been assumed that a singly linked atom can rotate freely (with its attached atoms) round the line of the link. More recent work has, however, shown that this freedom can be restricted in four different ways:

I. By direct steric hindrance, as in certain diphenyl compounds (the 'block' theory of asymmetry).

II. Through interatomic or inter-link repulsions, as in ethane.

III. Through dipole attractions and repulsions as in ethylene dichloride and largely in esters.

IV. Through the possibilities of resonance in certain positions, as occurs to some extent with the esters, and in many other types of compound as well.

The discussion of the last two of these would take us too far into organic chemistry (see, for example, refs.[84-91]); but something may be said of I and II.

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[88] L. E. Sutton, *Trans. Far. Soc.* 1934, **30**, 789.

[89] R. J. B. Marsden and L. E. Sutton, *J.C.S.* 1936, 1383.

[90] R. H. Birtles and G. C. Hampson, ib. 1937, 10.

[91] C. E. Ingham and G. C. Hampson, ib. 1939, 981.

[92] L. Ruzicka *et al.*, *Helv. Chim. Acta*, 1930, **13**, 1152.

[93] L. Ruzicka, *Bull. Soc. Chim. Belge*, 1932, **41**, 565.

[94] Id., *Helv. Chim. Acta*, 1934, **17**, 78.

[95] Id., *Chem. and Ind.* 1934, p. 2.

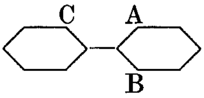
[96] L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1928, **11**, 1159.

[97] W. H. Carothers and E. W. Spanagel, *J.A.C.S.* 1935, **57**, 929.

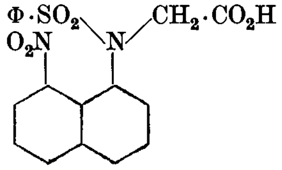
[98] H. Freundlich and G. Salomon, *Ber.* 1933, **66**, 355.

[99] L. Ruzicka, G. Salomon, and K. E. Meyer, *Helv. Chim. Acta*, 1937, **20**, 109.

I. '*Block*' *theory*. Certain diphenyl derivatives of the type



can be resolved into optically active forms. To explain this* it was suggested simultaneously by Bell and Kenyon,[100] and in more detail by Mills,[101] that when both *ortho* places on one ring and one on the other were occupied by large groups such as carboxyl or NO_2, the complete rotation of one ring about the median line of the molecule would be prevented, and two enantiomorphic forms would be produced. The truth of this theory was established by Mills and Elliott[102] by the resolution of the benzenesulphonyl derivative of 8-nitro-1-naphthyl glycine



where the NO_2 group in the peri-position interferes with the free rotation of the other nitrogen with its attached groups; later a similar example of a benzene derivative was found by Mills and Kelham.[103] Many other examples have since been found. In the diphenyl compounds the relation of the size of the groups to the stability and rate of racemization of the antimers has been studied in great detail by R. Adams and his colleagues.[104] The phenomenon has been used with great ingenuity by Meisenheimer *et al.*[105] to confirm his theory of the configuration of the isomeric oximes. For the theory of the optical activity of the diphenyl compounds see refs. [106,106a].

II. 'Ethane Barrier.' It is to be expected that in a molecule like that of ethane the rotation of one methyl group round the line joining the two carbon atoms, though it is commonly assumed to be free, involves certain changes in energy, with preferred positions separated by energy 'humps'. For these a value of about 0·3 k.cal. has been calculated,[107]† and this

* For the earlier history of this problem see C. K. Ingold, *Ann. Rep. Chem. Soc.* for 1926, **23**, 119.

† The mean energy of a gas collision at the ordinary temperature is about 0·6 k.cal. per mole, and no energy barrier that does not considerably exceed this will have any sensible effect in restricting the rotation.

[100] F. Bell and J. Kenyon, *Chem. and Ind.* 1926, **4**, 864.

[101] W. H. Mills, ib. 884.

[102] W. H. Mills and K. A. C. Elliott, *J.C.S.* 1928, 1292.

[103] W. H. Mills and R. M. Kelham, ib. 1937, 274.

[104] R. Adams *et al.*, *J.A.C.S.* 1928, **50**, and subsequent years.

[105] J. Meisenheimer, W. Theilacker, and O. Beisswenger, *Ann.* 1932, **495**, 249.

[106] W. Kuhn and R. Rometsch, *Helv. Chem. Acta*, 1944, **27**, 1080.

[106a] G. Baddeley, *Nature*, 1946, **157**, 694.

[107] H. Eyring, *J.A.C.S.* 1932, **54**, 3191.

seemed to be supported by the observed specific heats at low temperatures.[97] About 1935, however, it began to appear that the barrier is really much larger than this. Teller and Topley[109] found that the heat of hydrogenation of ethylene calculated from spectral data and by the methods of statistical mechanics agreed with observation only if a barrier of 3·0 k.cals. was assumed. Determinations of the entropy of ethane and of its specific heats down to 94° K. by Kemp and Pitzer,[110-11] Kistiakowsky[112-13] and others[114-19] agreed in showing the barrier to be about 3·0 k.cals. This was supported by measurements of the spectra, including the infra-red[105-8] and Raman[120-2] spectra. Similar values for the methyl group in other molecules have been found, as in propane[123-5] (3·4 k.cals.) and butane[126] (3·3 k.cals.). A list of the best values up to date is given by Aston *et al.*[127] for the observed potentials (in k.cals./mole) hindering the rotation of methyl groups (for references see original):

Ethane	3·15 2·75	Dimethyl sulphide	2·0
Propane	3·30 3·40	Methyl mercaptan	1·46
$C(CH_3)_4$	4·50	Methylamine	3·00 1·52
$Si(CH_3)_4$	1·30	Dimethyl ether	3·10 2·50
Propylene	2·12	Methyl alcohol	3·40
Acetone	1·00		

To these may be added styrene $C_6H_5—CH=CH_2$, where the specific heats show a barrier to rotation of 2·2 k.cals.[144]

These measurements do not decide whether in the preferred (stable) position the hydrogen atoms of one methyl group are directly above those of the other ('eclipse' position) or above the spaces between them ('staggered'). The eclipse view was put forward by Eucken[119] on spec-

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[108] A. Eucken and K. Weigert, *Z. physikal. Chem.* 1933, B **23**, 265.

[109] E. Teller and B. Topley, *J.C.S.* 1935, 876.

[110] J. D. Kemp and K. S. Pitzer, *J. Chem. Phys.* 1936, **4**, 749.

[111] Id., *J.A.C.S.*, 1937, **59**, 276.

[112] G. B. Kistiakowsky and F. Nazmi, *J. Chem. Phys.* 1938, **6**, 18.

[113] G. B. Kistiakowsky, J. R. Lacher, and F. Stitt, ib. 407.

[114] W. Hunsmann, *Z. physikal. Chem.* 1938, B **39**, 23.

[115] K. Schäfer, ib. B **40**, 357.

[116] J. B. Howard, *Phys. Rev.* 1937, ii. **51**, 53.

[117] Id., *J. Chem. Phys.* 1937, **5**, 442.

[118] Id., ib. 451.

[119] A. Eucken and K. Schäfer, *Naturwiss.* 1939, **27**, 122.

[120] J. Goubeau and J. Karweill, ib. 376.

[121] J. Karweill and K. Schäfer, ib. 382.

[122] B. L. Crawford, W. H. Avery, and J. W. Linnett, *J. Chem. Phys.* 1938, **6**, 682.

[123] B. P. Dailey and W. A. Felsing, *J.A.C.S.* 1943, **65**, 42.

[124] J. D. Kemp and C. J. Egan, ib. 1938, **60**, 1521.

[125] K. S. Pitzer, *J. Chem. Phys.* 1944, **12**, 310.

[126] B. P. Dailey and W. A. Felsing, *J.A.C.S.* 1943, **65**, 44.

[127] J. G. Aston, S. Isserow, G. J. Szasz, and R. M. Kennedy, *J. Chem. Phys.* 1944, **12**, 336.

trum evidence, and by Langseth[128-31] on the basis of the Raman spectra of the liquids; but it cannot be maintained.* A good summary of the arguments in favour of the staggered position is given by Pitzer and Gwinn.[133] Aston *et al.*[127] say that it is now generally agreed that the potential is due to repulsion, the evidence being the decrease of the barrier on going from tetramethyl methane to tetramethyl silicane and from dimethyl ether to dimethyl thioether, and the departure from planarity of the cyclohexane[132] and even apparently the cyclopentane ring.[134-5] To this may be added the lower values for propylene (2·0)[136] and dimethyl acetylene[137-8] (practically zero), and the zigzag arrangement of carbon chains (above, p. 497).

The cause of this repulsion is not yet clear. Eyring *et al.*[139] suggested that it was mainly due to resonance between the C—C links; but if so, it should be large in dimethylacetylene, where the shortening of the outer C—C links shows that such resonance occurs, whereas it is zero. Hence the cause must lie in the mutual repulsion of the hydrogen (or other) atoms, or possibly (Kistiakowsky)[140] of the electrons linking them to the carbons. So far there is no satisfactory way of deciding between these two theories.

These energy barriers are of the same order as the differences in the heats of hydrogenation of the olefines (see below, p. 507, and Kistiakowsky[141]).

For further papers on this subject see references [140,142-3,145,145a].

Paraffins

These are the saturated open-chain hydrocarbons C_nH_{2n+2}; they are typical covalent compounds, volatile[146,146b] and non-ionized. The following are some of the boiling- and melting-points:

	CH_4	C_2H_6	C_3H_8	*n.* C_4H_{10}	*iso*-C_4H_{10}	*Pentane*		$C(CH_3)_4$[a]	$C(C_2H_5)_4$[b]
						Norm.	*Iso.*		
M. pt. .	−184°	−172°	−187·7°	−138·3°	−145°	−129·7°	−159·8°	−19·5°	−31·1°
B. pt. .	−164°	−84°	−42·2°	−0·5°	−11·5°	+36·1°	+30°	+9·4°	146·4°

a = [148]; *b* = [148a]

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* For the answer to Eucken see Kistiakowsky and Nazmi.[112] Langseth's results imply that the cyclohexane molecule is planar, which is disproved by the results of X-ray diagrams and electron diffraction.[132]

[128] A. Langseth and B. Bak, *J. Chem. Phys.* 1940, **8**, 403.

[129] A. Langseth and H. J. Bernstein, ib. 410.

[130] A. Langseth, H. J. Bernstein, and B. Bak, ib. 415.

[131] Id., ib. 430.

[132] V. Schomaker and D. P. Stevenson, ib. 637.

[133] K. S. Pitzer and W. D. Gwinn, *J.A.C.S.* 1941, **63**, 3313.

[134] J. G. Aston, S. C. Schumann, H. L. Fink, and P. M. Doty, ib. 2029.

[135] J. G. Aston, H. L. Fink, and S. C. Schumann, ib. 1943, **65**, 341.

[136] D. Telfair and W. H. Pielmeier, *J. Chem. Phys.* 1941, **9**, 571.

[137] D. W. Osborne, C. S. Garner, and D. M. Yost, ib. 1940, **8**, 131.

[138] B. L. Crawford and W. W. Rice, *J. Chem. Phys.* 1939, **7**, 437.

[139] E. Gorin, J. Walter, and H. Eyring, *J.A.C.S.* 1939, **61**, 1876.

[140] G. B. Kistiakowsky, J. R. Lacher, and W. W. Ransom, *J. Chem. Phys.* 1938, **6**, 900.

It will be seen that among isomers the boiling-points are lower the more methyl groups are present,[150] while the melting-points are higher the greater the symmetry of the molecule (hexamethyl ethane melts at 100·7° C. (b.pt. 106·3° C.[149]) and *n*-octane at −56·9°). Examples of higher homologues are the normal compounds $C_{35}H_{72}$ (m.pt. +75°, b.pt. 344°/15 mm.) and $C_{70}H_{142}$ (m.pt. 105·3°).[151] The heats of fusion of hexamethyl benzene and of dicetyl $C_{32}H_{66}$ are 4·70 and 26·5 k.cals. per mole.[147] The Trouton constants of the lower members are about 20 (C_3H_8 19·4, *n*-C_5H_{12} 20·2). The liquids are almost perfect non-conductors; the specific conductivity of liquid propane from −90° to +15° is less than 5×10^{-7} gemmhos (1/100,000 of that of pure water); the dielectric constant at 0° is 1·61.[152]

Very careful measurements by Rossini[153–62, 164–6] of the heats of combustion of the lower paraffins, from which their heats of formation in the gaseous state can be calculated, have shown that when there are more than 5 carbon atoms in the molecule these latter are (with the normal paraffins) strictly additive for the links, being xA+yB, where there are x C—C and y C—H links, A and B being the heats of formation of such links. But when the number of carbon atoms is less than 6, the observed heat of formation becomes increasingly greater than the calculated, the differences being

No. of carbon atoms	*Differences (Obs.—Calcd.) at 25° C.*	*at 0° K.*
	k.cals.	
15	0±1·8	0
10	0+1·2	0
6	0+0·7	0
5	+0·13±0·5	+0·15
4	+0·46±0·4	+0·47
3	+0·83±0·3	+0·84
2	+1·59±0·2	+1·59
1	+4·61±0·1	+4·81

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[141] J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J.A.C.S.* 1939, **61**, 1874.

[142] E. Bright Wilson, *Chem. Rev.* 1940, **27**, 17.

[143] W. F. Edgell and G. Glackler, *J. Chem. Phys.* 1941, **9**, 375.

[144] K. S. Pitzer, L. Guttman, and E. F. Westrum, *J.A.C.S.* 1946, **68**, 2209.

[145] F. A. French and R. S. Rasmussen, *J. Chem. Phys.* 1946, **14**, 389.

[145a] E. N. Lassettre and L. B. Dean, ib. 1948, **16**, 151.

[146] For a formula relating the b.pts. of the paraffins to their structures see H. Wiener, *J.A.C.S.* 1947, **69**, 17.

[146a] A. W. Horton, ib. 182.

[146b] N. S. Osborne and D. C. Ginnings, *J. Res. Nat. Bur. Stand.* 1947, **39**, 453.

[147] G. S. Parks and R. D. Rowe, *J. Chem. Phys.* 1946, **14**, 507.

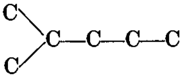
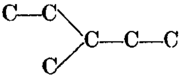
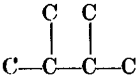
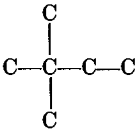
[148] F. C. Whitmore and G. H. Fleming, *J.A.C.S.* 1933, **55**, 3803.

[149] G. Calingaert, H. Soroos, V. Hnizda, and H. Shapiro, ib. 1944, **66**, 1389.

[150] For a comparison of the v.ps. of the isomeric hexanes see W. B. Kay, ib. 1946, **68**, 1336.

[151] W. F. Seyer, R. F. Patterson, and J. L. Keays, ib. 1944, **66**, 179.

Thus the energy content of methane is 4·6 k.cals. (1·15 per C—H) less than the calculated. This is no doubt due to the repulsions of the hydrogen atoms (or the C—H links), the crowding being less in methane than in ethane. Rossini *et al.*[161] have found that in the paraffins from C_4 to C_7 the normal (with only 2 CH_3 groups) is always the most stable isomer. The heats of combustion of all the 5 hexanes were determined,[162] and the differences (in k.cals. ±0·20) were:

		Diff. from normal
Normal hexane	C—C—C—C—C—C	(0)
2-me-pentane		+1·75
3-me-pentane		+1·07
2, 3-di-me-butane	 $\overset{C}{\overset{\mid}{C}}$	+2·55
2, 2-di-me-butane		+4·58

The heptanes behave in the same way[163]; the energy content is greater the more CH_3 groups there are, the mean difference (obtained from the heats of combustion) being:

No. of CH_3 Gps. . .	2	3	4	5
Mean diff., k.cals. . .	0	0·80	3·42	3·71

Similar results were obtained for the 18 isomeric octanes[155] and for the 8 C_9 alkyl benzenes.[165-6]

For examples of the influence of this effect on the heats of reaction of hydrocarbons see reference [167].

[152] G. Glockler and R. E. Peck, *J. Chem. Phys.* 1936, **4**, 624.

[153] F. D. Rossini, *Bur. Stand. J. Res.* 1934, **12**, 735.

[154] Id., ib. **13**, 21, 189.

[155] E. J. Prosen and F. D. Rossini, ib. 1944, **33**, 255.

[156] D. D. Wagman, J. E. Kilpatrick, K. S. Pitzer, and F. D. Rossini, ib. 1945, **35**, 467.

[157] E. J. Prosen and F. D. Rossini, ib. 1946, **36**, 269.

[158] W. H. Johnson, E. J. Prosen, and F. D. Rossini, ib. 463.

[159] J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, ib. 559.

[160] W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer, and F. D. Rossini, ib. **37**, 95.

[161] F. D. Rossini, E. J. Prosen, and K. S. Pitzer, ib. 1941, **27**, 529.

[162] F. D. Rossini and E. J. Prosen, *J.A.C.S.* 1940, **62**, 2250.

[163] G. F. Davies and E. C. Gilbert, ib. 1941, **63**, 2730.

[164] E. J. Prosen and F. D. Rossini, *J. Res. Nat. Bur. Stand.* 1945, **34**, 163.

[165] W. H. Johnson, E. J. Prosen, and F. D. Rossini, ib. **35**, 141.

[166] Id., ib. 1946, **36**, 455.

[167] J. R. Lacher, *J.A.C.S.* 1946, **68**, 526.

Solid hydrates are formed by some of the lower paraffins, especially methane.[168] More recently Roberts *et al.*[169] have examined the phase diagram for CH_4, H_2O and C_2H_6, H_2O from $-12°$ to $+16°$. The triple points found for ice, liquid water, and solid hydrate are

for CH_4, 7 H_2O . . 0° and 23 atm.
for C_2H_6, 7 H_2O . . 0° and 5 atm.

The heats of formation at 0° from gas+liquid water are

for CH_4, 7 aq. . . 14·5
and for C_2H_6, 7 aq. . . 16·3 k.cals./mole.

These are obviously crystal aggregates held together by van der Waals forces.

Unsaturated Hydrocarbons

The lengths, heats of formation[170] (for 170.4 k.cals. as the heat of atomization of solid carbon), and the valency angles for single and multiple carbon links are as follows:

		Heat of formation	
	Length A	*Abs.*	*Rel.*
C—C	1·542	81·6	1
C=C	1·326	146·1	1·79
C≡C	1·204	192·1	2·35

Angles: C—C—C 109·5°; C—C=C 125·25°;
C=C=C 180°; C—C≡C 180°.

Doubly Linked (Olefinic) Hydrocarbons

For the wave-mechanical theory of multiple links see Hückel (1930),[171-2] Penney (1934),[173] Penney and Kynch (1938),[174] Lennard-Jones (1939),[175] Mulliken (1939).[176]

The olefinic hydrocarbons are very similar in physical properties to the paraffins, and usually boil within 10° of the paraffin with the same carbon skeleton[177-9] (ethylene boiling at $-103·8°$ while ethane boils at $-84°$ is an exception). Chemically they are of course distinguished by their strong tendency to take up other atoms and become saturated.

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[168] R. de Forcrand, *C.R.* 1902, **135**, 959.

[169] D. L. Roberts, E. R. Brownscombe, and L. S. Howe, *Oil and Gas J.* 1940, **39**, Nos. 30, 37, 43.

[170] L. Pauling, *Chem. Bond*, 1942, 53, 131, 164.

[171] E. Hückel, *Z. Elektrochem.* 1930, **36**, 641.

[172] Id., *Z. Phys.* 1930, **60**, 423.

[173] W. G. Penney, *Proc. Roy. Soc.* 1934, **144**, 166.

[174] W. G. Penney and G. J. Kynch, ib. 1938, **164**, 409.

[175] J. E. Lennard-Jones and C. A. Coulson, *Trans. Far. Soc.* 1939, **35**, 811.

[176] R. S. Mulliken, *J. Chem. Phys.* 1939, **7**, 121, 339, 353, 356, 364.

[177] A. B. Lamb and E. E. Roper, *J.A.C.S.* 1940, **62**, 806.

[178] H. I. Waterman and W. J. C. de Kok, *Rec. Trav.* 1933, **52**, 251.

[179] Id., ib. 298.

Cis-Trans Relations

The differences in energy content between the isomeric *cis* and *trans* olefine derivatives are usually small, and sometimes very small; if there is no interaction between the attached groups, they should be of the same order as the rotation barriers discussed above (about 3 k.cals.). Accordingly it is found that with 2-butene $CH_3—CH=CH—CH_3$ the energy content of the *cis* is 1·3 k.cals. greater than that of the *trans*[180]; with *s*-dichloroethylene $C_2H_2Cl_2$ the difference is 0·6,[183-5] and with the dibromo-compound 0·33.[183] On the other hand, with tetramethyl butene diol $(CH_3)_4C_4H_2(OH)_2$ it is 4·4 k.cals.,[181] with angelic and tiglic acids 8·5, and with cinnamic and isocinnamic 7.[182]

The interconversion has, like other slow chemical reactions, a considerable heat of activation. The following values have been observed:

	Kistiakowsky[a]	*Taylor*[b]
Stilbene $\Phi\cdot CH=CH\Phi$[c]	42·8 k.cals.	36·7 kc.
$\Phi\cdot CCl=CH\Phi$	..	37·0 ,,
$\Phi\cdot CCl=CCl\cdot\Phi$	..	34·1 ,,
Methyl maleate	26·5 ,,	..
Methyl cinnamate	41·6 ,,	..

a = [186]; *b* = [187]; *c* = [192].

The mechanism of the reaction has been much disputed. The common view that the conversion of maleic into fumaric acid with an acid as catalyst occurs through the intermediate addition and removal of HX has been tested by Horrex[188]; it can easily be seen from the model that if this is true, the hydrogen atom which comes off in the second stage is not that which was added in the first. The reaction was therefore carried out in D_2O containing 2-normal DCl. The fumaric acid formed, after recrystallization from water to remove carboxylic deuterium, was found to be free from deuterium, so that this theory cannot be true.[189]

Harman and Eyring[190] have proposed a theory as to the orbital changes which occur in general in the conversion of an intermediate C—C into C=C; they show that this involves a catalytic hastening of the reaction by paramagnetic substances, and point out that this is known to occur with oxygen: thus styrene $\Phi:CH=CH_2$ polymerizes 10^6 times as quickly

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[180] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J.A.C.S.* 1935, **57**, 876.

[181] W. A. Roth and F. Müller, *Ber.* 1927, **60**, 643.

[182] See Freudenberg, *Stereochemie*, Leipzig, 1933, p. 737.

[183] A. R. Olson and W. Maroney, *J.A.C.S.* 1934, **56**, 1320.

[184] W. Maroney, ib. 1935, **57**, 2397.

[185] R. E. Wood and D. P. Stevenson, ib. 1941, **63**, 1650.

[186] G. B. Kistiakowsky and W. R. Smith, ib. 1935, **57**, 269.

[187] T. W. J. Taylor and A. R. Murray, *J.C.S.* 1938, 2078.

[188] C. Horrex, *Trans. Far. Soc.* 1937, **33**, 570.

[189] K. Nozaki and R. Ogg, *J.A.C.S.* 1941, **63**, 2583.

[190] R. A. Harman and H. Eyring, *J. Chem. Phys.* 1942, **10**, 557.

in oxygen as in nitrogen; in the same way the conversion of dichloroethylene is hastened by oxygen or nitric oxide, which do not affect the proportions at equilibrium.[191] Harman and Eyring suggest that this paramagnetic action may explain the 'peroxide effect' in the addition of hydrogen bromide to ethylenic compounds (see VII. 1178).

The *polymerization* of unsaturated carbon compounds has been the subject of much recent work, largely on account of its technical importance for the production of artificial rubber and of plastics; only references can be given here. Monographs have been published by Staudinger in 1932[193] and by R. E. Burk *et al.* in 1937[194]; a discussion on it was held by the Faraday Society in 1939[195]; for further work see references [196-204a].

Addition Reactions of $C=C$. The most characteristic property of molecules with a $C=C$ link is that of saturating themselves by taking up two monovalent atoms or groups, especially hydrogen, carbon (as in the polymerizations above), halogens and their hydrides, and radicals containing oxygen.

Hydrogenation. Olefines take up 2 atoms of hydrogen to form paraffins in the presence of many catalysts, such as platinum black, colloidal palladium, light in presence of mercury vapour,[205] or if heated in presence of chromic oxide,[206] etc. The heat of the reaction $C=C+H_2 = CH—CH$ has been determined (in the gaseous state) with great accuracy for many unsaturated hydrocarbons by Kistiakowsky and his co-workers; the results are summarized and discussed in the last of these papers.[207] The heat of this reaction (which on Pauling's values for the links should be 30 k.cals.) is for ethylene 32·8 k.cals.; but the successive replacement of the hydrogen atoms by methyl groups causes this to lessen, so that for tetramethyl ethylene it is only 26·6 k.cals. This result, which is shown to be quite

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[191] B. Tamamushi, H. Akiyama, and K. Ishii, *Z. Elektrochem.* 1941, **47**, 340.

[192] For the equilibrium of the two forms in the vapour see D. C. Downing and G. F. Wright, *J.A.C.S.* 1946, **68**, 141.

[193] H. Staudinger, *Die hochmolekulare organische Verbindungen*, Berlin, 1932.

[194] R. E. Burk, H. E. Thompson, A. J. Weith, and I. Williams, *Polymerisation*, A.C.S. monograph, New York, 1937.

[195] *Trans. Far. Soc.* 1939, **35**, 1022–89.

[196] O. K. Rice and D. V. Sickman, *J.A.C.S.* 1935, **57**, 1384.

[197] W. H. Carothers, *Trans. Far. Soc.* 1936, **32**, 39.

[198] H. Dostal and H. Mark, ib. 54.

[199] J. B. Harkness, G. B. Kistiakowsky, and W. H. Mears, *J. Chem. Phys.* 1937, **5**, 682.

[200] M. W. Perrin, *Trans. Far. Soc.* 1939, **35**, 1062.

[201] C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc.* 1941, **179**, 169.

[202] G. W. Wheland, ib. 1938, **164**, 397.

[203] J. D. Ferry and G. S. Parks, *J. Chem. Phys.* 1936, **4**, 70.

[204] A. V. Grosse and V. N. Ipatiev, *J. Org. Chem.* 1937, **1**, 559.

[204a] H. Mark, *Trans. Far. Soc.* 1947, **43**, 447.

[205] H. S. Taylor and G. D. Hill, *J.A.C.S.* 1929, **51**, 2922 (the first example of the use of mercury vapour as a catalyst).

[206] G. B. Kistiakowsky, *J. Chem. Phys.* 1942, **10**, 78.

[207] J. B. Conn, G. B. Kistiakowsky and E. A. Smith, *J.A.C.S.* 1939, **61**, 1868.

general with unsaturated compounds, must be due to the much greater steric effect ('rotation barrier') in the reduction products.

The addition of halogens and halogen hydrides to the double link is discussed under the halogens (VII. 1174, 1177).

Acetylenic Hydrocarbons

The triply linked hydrocarbons are in many ways like the other classes; acetylene boils at practically the same temperature as ethane (−83·8°, about 20° higher than ethylene); the homologues, if they have one unreplaced ≡C—H left, boil about 7°, if not, about 16° higher than the corresponding paraffins. As we should expect from the heats of formation they are very readily reduced or in other ways converted into compounds with no triple links.

Their most remarkable characteristic is the definitely acidic nature of the hydrogen attached to the triply linked carbon; this cannot be due to isomerization, as it is in the β-diketones, since it is already developed to the full in acetylene itself and its mono-alkyl derivatives. It is related to the heats of formation of the triple links. The ratio of the values for triple to those for single links are for C—C 2·35, for C—N 3·06, for N—N 5·86. In general the heats of formation of multiple links increase less rapidly than the multiplicity with C—C, at about the same rate with C—N and C—O, and much more rapidly with N—N and O—O. This is no doubt because in the C—C links all the valency electrons are shared, while in the C—N and N—N links the nitrogen atoms have a pair of unshared electrons which can accommodate themselves to the strain of the multiple links. This view is supported by the behaviour of the azides (V. 717), from which it can be shown that the heat of formation of the N≡N— link, where there is only one pair of shared electrons, is not more than about 3 times that of N—N, instead of 6 times as with N≡N.

Now when acetylene ionizes, H—C≡C—H becomes [H—C≡C]$^-$, which is isoelectronic with H—C≡N; we may thus assume that the heat of formation of —$\overset{-}{\mathrm{C}}$≡C is 3 times that of C—C, as C≡N is of —C—N, or is 245 k.cals. instead of the normal 192 of —C≡C—: i.e. that in the ionization there is from this source a gain of 53 k.cals., more than 50 per cent. of the energy needed to break the C—H link (98·8); this will obviously promote the ionization. (The corresponding calculation for ethylene gives a gain of only 17 k.cals.)

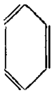
Aromatic Hydrocarbons

These include primarily benzene and its homologues containing one or more 6-carbon rings with 3 double bonds. The exceptional stability of these compounds has been recognized for the last century, and is now seen to be due to their unusually large resonance energy. Secondarily, the term can be applied to other ring-molecules with similar properties, such as thiophene, pyrrol, pyridine, etc. The resonance energies of such molecules can be found as the defect of the heat of combustion or of hydrogenation[208] compared with that calculated for the simple structures. Their values are considerable, of the order of 40 k.cals. per aromatic ring; examples are[209,210]:

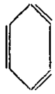
Benzene	41	k.cals.
Toluene	41	,,
Mesitylene	50	,,
Diphenyl methane	2 × 47	,,
Naphthalene	2 × 39	,,
Anthracene	3 × 39	,,
Phenanthrene	3 × 43	,,
Chrysene	4 × 41	,,
Furane	24	,,
Thiophene	29	,,
Pyrrol	24	,,
Pyridine	43	,,
Indol.	2 × 32	,,

The application of the theory of resonance to the aromatic compounds was primarily due to Pauling and his pupils; it is discussed in his *Chemical Bond*, pp. 134–54, and in greater detail, and with many valuable collections of data, by G. W. Wheland in his *Theory of Resonance and its Application to Organic Chemistry* (New York and London, 1944; see especially pp. 2-5, 27, 69, 88, 102, 108).

The main resonance forms of benzene are the two Kekulé structures



and



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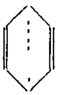
which account for some 80 per cent. of the resonance energy,[211] the rest being due to the three less stable Dewar structures,



The various spectra of benzene and its derivatives have been examined in great detail: see refs. [212–16]; for a summary of the conclusions, in which certain difficulties were removed, largely by the use of deuterobenzenes, see Ingold's Bakerian Lecture.[217–18] See also Ingold *et al.*[219]

It follows from this work that benzene has complete sixfold symmetry, as one would expect from the resonance: the 6 carbon atoms are at the

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[208] See Pauling, *Chem. Bond*, p. 134.

[209] Id., ib., p. 137.

[210] G. W. Wheland, *Theory of Resonance*, p. 69.

[211] L. Pauling and G. W. Wheland, *J. Chem. Phys.* 1933, **1**, 362.

[212] W. G. Penney, *Proc. Roy. Soc.* 1934, **146**, 223.

[213] F. London, *J. Chem. Phys.* 1937, **5**, 837.

[214] G. B. Kistiakowsky and A. K. Solomon, ib. 609.

[215] A. Klit and A. Langseth, ib. 925.

[216] H. C. Cheng, C. F. Hsueh, and T. Y. Wu, ib. 1938, **6**, 8.

[217] C. K. Ingold, *Proc. Roy. Soc.* 1938, **169**, 149.

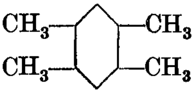
[218] See also C. K. Ingold *et al. J.C.S.* 1936, 912–71, 1211 (9 papers).

[219] Id., ib. 1946, 222–316.

corners of a regular plane hexagon, and all the 6 C—C links are equivalent. This is supported by measurements of X-ray[220] and electron[221] diffraction, and of dipole moments.[222] It has also been shown that all the atoms directly attached to the ring lie in its plane; thus all the 12 carbon atoms in hexamethyl benzene are coplanar[223]; this planar character extends as we have seen (p. 497) to all condensed ring compounds examined up to coronene with its 7 rings—and indeed up to graphite itself.

The C—C distance in benzene is 1·39 A (shortened from the mean of C—C 1·54 and C═C 1·33, i.e. 1·44, through resonance). The length of the external C—C links in C_6Me_6 is 1·53 A.[220,224]

The rigidity of the aromatic structure is remarkable. The repulsion of the methyl groups in durene



has been shown[225] to deflect them some 3° from one another, in the plane of the ring; and in hexamethyl benzene, where no such sideways deflexion is possible, it is found[220] that the methyl carbon atoms lie about 1° out of that plane; but such deflexions (especially out of the plane of the ring) occur rarely and only under great stress. Other determinations of aromatic structures (usually by X-rays, but some by electron diffraction) are numerous; some of the more important references are: naphthalene[226]; anthracene[227]; pyrene[228]: a very careful X-ray examination gives all the distances, which vary from 1·39 to 1·45 A. (See orig.); chrysene[229]; dibenzanthracene[230a]; coronene[230]; diphenyl[231-3]; terphenyl (*p*-diphenyl benzene)[234]; quarterphenyl (*p*, *p*′-di-diphenyl)[235]; dibenzyl[236]; stilbene[237]; tolane $\Phi:C\equiv C:\Phi$[238]; diphenylene: this has been shown by electron diffraction[239] and by X-ray analysis[242] to have the 4-ring structure, and not the

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[220] L. O. Brockway and J. M. Robertson, *J.C.S.* 1939, 1324.

[221] L. Pauling and L. O. Brockway, *J. Chem. Phys.* 1934, **2**, 867.

[222] J. W. Williams, *Fortschr. Chem. Phys.* 1930, **20**, 257.

[223] K. Lonsdale, *Proc. Roy. Soc.* 1929, **123**, 494; for C_6Cl_6 see id., ib. 1931, **133**, 536.

[224] L. Pauling and L. O. Brockway, *J.A.C.S.* 1937, **59**, 659.

[225] J. M. Robertson, *Proc. Roy. Soc.* 1933, **142**, 1223.

[226] Id., ib. 674.

[227] Id., ib. **140**, 79.

[228] J. M. Robertson and J. G. White, *J.C.S.* 1947, 358.

[229] J. Iball, *Proc. Roy. Soc.* 1934, **146**, 140.

[230] J. M. Robertson and J. G. White, *Nature*, 1944, **154**, 605.

[230a] Id., *J.C.S.* 1947, 1001.

[231] W. G. Penney and J. G. Kynch, *Proc. Roy. Soc.* 1938, **164**, 409.

[232] L. W. Pickett, *Nature*, 1933, **131**, 513.

[233] G. L. Clarke and L. W. Pickett, *J.A.C.S.* 1931, **53**, 167.

[234] L. W. Pickett, *Proc. Roy. Soc.* 1933, **142**, 333.

[235] Id., *J.A.C.S.* 1936, **58**, 2299.

[236] J. M. Robertson, *Proc. Roy. Soc.* 1935, **150**, 348.

[237] J. M. Robertson and I. Woodward, ib. 1937, **162**, 568.

[238] Id., ib. 1938, **164**, 436.

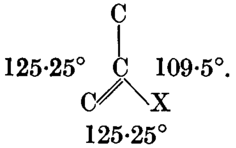
[239] J. Waser and V. Schomaker, *J.A.C.S.* 1943, **65**, 1451.

5-ring previously suggested[240-1]: the C—C distances between the 6-rings are 1·46 A.

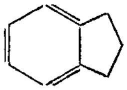
Cyclo-octatetrene, the 8-membered analogue of benzene, can be made by the polymerization of acetylene under pressure, in presence of tetrahydrofurane and nickel cyanide. It boils at 69·5°/66 mm., and melts at $-7·5°$. The heat of formation of the liquid from graphite and hydrogen gas at 25° is 59·1 k.cals.[243] Its Raman spectrum[244] suggests a puckered ring with alternate single and double links. For a discussion of its resonance see reference [244a].

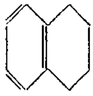
'Mills-Nixon' Effect

Mills and Nixon[245] pointed out that in a benzene ring with one fixed Kekule structure the external valencies do not radiate symmetrically from the centre of the hexagon. The normal valency angles in the grouping shown are as indicated.

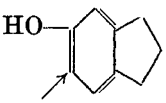


If these carbon atoms form part of a benzene ring, the internal angle must be 120° instead of 125·25°, but this will only slightly enlarge the external angles, which may be taken to be about 112° and 128° respectively. Now the angle of a regular pentagon is 108°, and of a regular hexagon 120°; we might therefore expect that if the benzene ring is fused in the ortho-position to a reduced 5-ring, as in hydrindene, the position of least strain would be that in which the link common to both rings is single (I, below), while if a 6-ring is joined on as in tetrahydronaphthalene (tetraline) it would be double (II) or at least that these forms

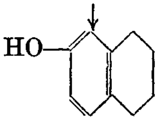

(I)


(II)

would predominate; the steric argument is weaker with the 6-ring, as this might relieve the strain by coming out of the plane. Mills and Nixon tested this conclusion by the positions taken up by substituents in the two phenols (III and IV). When an open-chain enol



(III)



(IV)

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[240] W. Baker, *Nature*, 1942, **150**, 211. [241] C. A. Coulson, ib. 577.

[242] J. Waser and C. S. Lu, *J.A.C.S.* 1944, **66**, 2035.

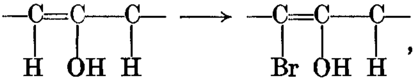
[243] E. J. Prosen, W. H. Johnson, and F. D. Rossini, ib. 1947, **69**, 2068.

[244] E. R. Lippincott and R. C. Lord, ib. 1946, **68**, 1868.

[244a] A. Maccoll, *Nature*, 1946, **157**, 695.

[245] W. H. Mills and I. G. Nixon, *J.C.S.* 1930, 2510.

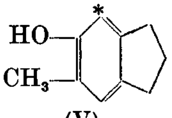
has a hydrogen atom replaced by a bromine or a diazo-group, it is found that the substituent always goes to the carbon atom which is doubly linked to the C·OH



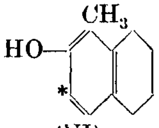
$$-\underset{\mathrm{H}}{\mathrm{C}}=\underset{\mathrm{OH}}{\mathrm{C}}-\underset{\mathrm{H}}{\mathrm{C}}- \longrightarrow -\underset{\mathrm{Br}}{\mathrm{C}}=\underset{\mathrm{OH}}{\mathrm{C}}-\underset{\mathrm{H}}{\mathrm{C}}-,$$

and the same should occur with the phenols, so that these substitutions should indicate the positions of the double-carbon bond. It was found that in the hydrindene and the tetraline phenols (III and IV) both the bromine and the diazo-group take up the positions required by this theory (indicated by arrows in III and IV), so that it would seem that the double bonds are fixed in this way in both types, and that there is no resonance in either. Fieser and Lothrop[246] then showed that when these preferred places were blocked with methyl groups (V and VI), the tetraline phenol was substituted in the alternative (β—, starred in the formula) position, while the hydrindene phenol would not react at all. Under energetic conditions of substitution, however,[247] the hydrindene derivative also was substituted in the alternative (starred) position. This indicated considerable fixation of the double bonds in the hydrindene compound, but much less in the tetraline.

So far the evidence was wholly derived from the reactivities, and Sutton and Pauling[248] showed that a difference of 6 per cent. in the ratio of the coefficients of the two Kekule forms, which as wave-mechanics indicated might well be caused by the side rings, was enough to account for the observed differences of reactivity. See further, Longuet-Higgins and Coulson.[249]

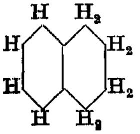


(V)



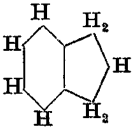
(VI)

The next attack was through the dipole moments.[250] These were measured for tetraline, hydrindene, and their symmetrical dibromo-derivatives (VII, VIII, IX, X); the values, with that for 4,5-dibromo-*o*-xylene (XI) are (in benzene at 25°):



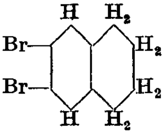
0·52

(VII)



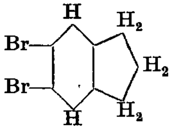
0·53

(VIII)



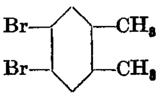
2·80

(IX)



2·48

(X)



2·86 D.

(XI)

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[246] L. F. Fieser and W. C. Lothrop, *J.A.C.S.* 1936, **58**, 2050.

[247] Id., ib. 1937, **59**, 945.

[248] L. E. Sutton and L. Pauling, *Trans. Far. Soc.* 1935, **31**, 939.

[249] H. C. Longuet-Higgins and C. A. Coulson, ib. 1946, **42**, 756.

[250] N. V. Sidgwick and H. D. Springall, *J.C.S.* 1936, 1532.

It is obvious that the angles between the two C—Br links (on which the moment depends) will be 70° with a fixed double link common to the two rings, 38° with a fixed single link, and 60° with complete resonance. The results show that the moments are those to be expected if in the hydrindenes the common link is fixed as single, while in the tetralines there is a full resonance as in the analogous *o*-xylene derivative. Moreover the moments obviously represent the normal states of the molecules, and are not complicated by questions of heat of activation.

The last stage of this curious story was reached when Kistiakowsky *et al.*[251] found that the heat of addition at 82° C. of 3 H_2 is to benzene 49·80, to *o*-xylene 47·25, and to hydrindene 45·80 k.cals.; in the absence of resonance this would be 85·77 k.cals., so that the resonance energies are: benzene 36·0, *o*-xylene 38·5, hydrindene 40·0 k.cals. These small differences of a few k.cals are not of importance here, as we have seen; but it is clear that the resonance is at least as great in hydrindene as in benzene itself, and that there can be no question of its bonds being 'fixed'. The differences in reactivity found by Mills and by Fieser are no doubt due to complicated effects on the heats of activation. The dipole moments are so far unexplained, but Kossiakoff and Springall[252] have measured the electron diffraction of the dibromo-derivatives of tetraline, hydrindene, and *o*-xylene (IX, X, and XI above), and find no trace of any difference in the angles between the C—Br valencies, the C—C—Br angle being 122° in all three compounds.

Organic Reactions

The direction and completeness of organic as of other reactions are determined by the energy changes they involve, which agree approximately with the heats of reaction. The velocities of the reactions depend on the heats of activation.

Since we know the heats of formation of all the ordinary links concerned (see table, p. xxxi) we can calculate to within a few kilocalories the heats of organic reactions. For example, the reduction of an ethylenic hydrocarbon to a paraffin involves changes of link with these heat values:

$$\begin{array}{ccccccc} \mathrm{C{=}C} & + & \mathrm{H{-}H} & = & \mathrm{C{-}C} & + & 2\,\mathrm{C{-}H} \\ 146{\cdot}1 & & 103{\cdot}4 & & 81{\cdot}6 & & 2\times 98{\cdot}8 \end{array}$$

If the atoms come together to form the links on the left-hand side (the compounds being gaseous) 249·5 k.cals. will be evolved: if on the right, 279·2. Hence the reduction of this link will normally evolve about 30 k.cals.[253] Experimental values may differ from this by a few k.cals.;

[251] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *J.A.C.S.* 1937, **59**, 831.

[252] A. Kossiakoff and H. D. Springall, ib. 1941, **63**, 2223.

[253] The latest Rossini values, as calculated by T. L. Cottrell and L. E. Sutton (*J. Chem. Phys.* 1947, **15**, 685) would make this difference 29·9 k.cals.

thus Kistiakowsky showed that the reduction of ethylene evolves 32·6, and that of trimethylethylene 26·9.

Again, in the hydrolysis of an organic chloride we have in the vapour:*

$$\text{C—Cl} + \text{H—OH} = \text{C—OH} + \text{H—Cl}$$

$$78{\cdot}5 \qquad 110{\cdot}2 \qquad\qquad 81{\cdot}5 \qquad 102{\cdot}7$$

This makes the gaseous reaction endothermic, absorbing 4 k.cals. per mole. If a reaction occurs in presence of a solvent, the difference between the heats of solution of the compounds on the two sides must be added. In this particular reaction, if water is present we may neglect the heat of solution in it of the alcohol (for methyl alcohol 1·6, for ethyl 2·4 k.cals.), but must add that of the hydrogen chloride (18 k.cals.), so that in presence of water this hydrolysis becomes exothermic (+14 k.cals.). If an alkaline solution is used, the heat of neutralization (14 k.cals.) must also be added, making +28 k.cals. in all.

The following are the heats of some of the commoner organic reactions (in the gaseous state) calculated in this rough way.

C—C + H—H	= 2 C—H	+ 12 k.cals.
C—C + F—F	= 2 C—F	+ 92 „
C—C + Cl—Cl	= 2 C—Cl	+ 17 „
C—C + Br—Br	= 2 C—Br	+ 3 „
C—C + I—I	= 2 C—I	− 4 „
C=C + H—H	= H—C—C—H	+ 29 „
C=C + F—F	= F—C—C—F	+ 109 „
C=C + Cl—Cl	= Cl—C—C—Cl	+ 34 „
C=C + Br—Br	= Br—C—C—Br	+ 20 „
C=C + I—I	= I—C—C—I	+ 13 „
C≡C + H—H	= H—C=C—H	+ 48 „
C≡C + F—F	= F—C=C—F	+ 127 „
C≡C + Cl—Cl	= Cl—C=C—Cl	+ 52 „
C≡C + Br—Br	= Br—C=C—Br	+ 39 „
C≡C + I—I	= I—C=C—I	+ 30 „
C—C + $\frac{1}{2}O_2$	= C—O—C	+ 22 „
C—H + $\frac{1}{2}O_2$	= C—O—H	+ 34 „
CH_2 + O_2	= C=O + HOH	+ 78 „

		In gas	*In water*	*In alkali*
C—H + F_2	= C—F + HF	+104	—	—
C—H + Cl_2	= C—Cl + HCl	+ 24	+41	+55
C—H + Br_2	= C—Br + HBr	+ 8	+27	+41
C—H + I_2	= C—I + HI	− 7	+12	+26
C—F + H_2O	= C—OH + HF	+ 0·3	+12	+28
C—Cl + H_2O	= C—OH + HCl	− 4	+13	+27
C—Br + H_2O	= C—OH + HBr	− 7	+13	+27
C—I + H_2O	= C—OH + HI	− 14	+ 5	+19

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* These reactions are always understood to be in the vapour unless otherwise stated.

Rates of Reaction

The velocity constant K of a bimolecular reaction is given by the equation

$$K = A \cdot P \cdot e^{-E/RT},$$

where A is the number of collisions, P is a factor which is often nearly 1; it seems to depend largely on the probability of one molecule hitting another in the right place, while it is also affected by the formation of addition products between the reactants: and E is the heat of activation, the energy the molecules must have if their collisions are to result in reaction. If we have two similar reactions proceeding simultaneously, such as ortho- and meta-substitution in a benzene nucleus, we may assume that both A and P are much the same for both. Hence if K and K' are the velocity constants, and ln the natural logs.,

$$\begin{aligned} \ln K \quad &= \text{Const.} - E/RT \\ \text{and } \ln K' \quad &= \text{Const.} - E'/RT \\ \text{or} \quad \ln K - \ln K' &= \frac{E' - E}{RT}. \end{aligned}$$

Now the experiments as a rule do not detect less than 1 per cent. of a product in such reactions, so that if one of our reactions went 100 times as fast as the other, we should usually say that the second did not occur at all. But if there is this ratio, then

$$\ln K - \ln K' = \ln 100 = 4{\cdot}6,$$

and so
$$E' - E = 4{\cdot}6\, RT = 4{\cdot}6 \times 600 = 2{,}800 \text{ cals.}$$

at the ordinary temperature, since $R = 2$ cals. That is to say, a change of 2·8 k.cals. in a heat of activation which is commonly 30 and may be 70 k.cals., a change that is of 4 to 10 per cent., will increase or diminish the rate 100 times, and may make us think that one of the reactions does not occur at all.

Modern Theories of Organic Reactivity

These theories have been developed in recent years mainly in this country by organic chemists, especially Flürscheim, Lapworth, Robinson, and Ingold (see especially Robinson[254-6]; Ingold[257-9]); this is no place to discuss them in detail, but something may be said about their physical background. They all agree in ascribing differences in reactivity to a displacement of the valency electrons in the molecule from their normal positions, and to the resulting distribution of positive and negative charges.

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[254] J. Allan, A. E. Oxford, R. Robinson, and J. C. Smith, *J.C.S.* 1926, 401.

[255] R. Robinson, *Outlines of an Electrochemical (Electronic) Theory of Organic Reactions*, Inst. of Chemistry, London, 1932.

[256] R. Robinson, *Journ. Soc. Dyers and Colourists*, 1934, 65.

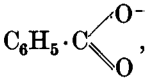
[257] C. K. and E. H. Ingold, *J.C.S.* 1926, 1310.

[258] C. K. Ingold, ib. 1933, 1120.

[259] Id., *Chem. Rev.* 1934, 15, 225.

There are two preliminary questions: (1) have we any evidence that the electrostatic state of the molecule has any influence on the course of its reactivity, and (2) is there anything in modern physics to suggest that this kind of 'electronic drift' is possible? The answer to both these questions is in the affirmative.

The most conclusive evidence that an electric charge has a direct effect on reactivity is given by the results of substitution in benzene. Aniline is substituted in the ortho- and para-positions; but if it is nitrated or brominated in concentrated sulphuric acid, so that the molecule that is reacting is really the anilinium ion $C_6H_5\text{-}NH_3^+$, then substitution occurs in the meta-position. Conversely benzoic acid substitutes in the meta-position; but in alkaline solution where the acid is of course replaced by its ion



$$C_6H_5\cdot C\begin{matrix}\nearrow O^- \\ \searrow O\end{matrix},$$

the substitution takes place in the ortho- and para-positions. This is evidence that an electric charge does largely influence the course, which implies the velocity, of the reaction.

A physical argument which comes closer to the question is the relation discovered by Sutton[260] between the effect of a substituent in benzene on the course of further substitution and its effect on the dipole moment. If the drift of electrons assumed in the organic theories is real, it is precisely the dipole moments which should show it. Now the moment of a compound Aryl—X is in general somewhat different from that of Alkyl—X. This in itself suggests that some kind of electron drift can occur in the aromatic ring. Sutton showed that if we call those moments of which the positive end is remote from the alkyl or aryl group positive, and those in the opposite direction negative, then if the value of μ(Ar—X)—μ(Alk—X) is positive, X directs further substitution to the ortho- and para-positions, but if this difference is negative, the direction is to the meta-position. This generalization has been found to hold in all the cases where it has been tested, which include some 15 of the ordinary substituents. Some examples are:

X	μ(Ar—X)	μ(Alk—X)	μ(ArX)—μ(AlkX)	*Orientation of product*
CH_3	+0·45	±0	+0·45	*o, p*
NH_2	+1·55	+1·23	+0·32	*o, p*
Cl	—1·56	—2·15	+0·59	*o, p*
CH_2Cl	—1·82	—2·03	+0·21	*o, p*
$CHCl_2$	—2·03	—2·06	±0	*o, m, p*
CCl_3	—2·07	—1·57	—0·50	*m*
C≡N	—3·89	—3·46	—0·43	*m*
NO_2	—3·93	—3·05	—0·88	*m*

Sutton's results show that the amount of this change of moment is far less than would be caused by the migration of an electron from one atom to

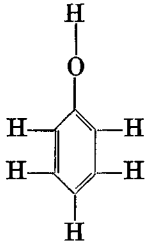
[260] L. E. Sutton, *Proc. Roy. Soc.* 1931, **133**, 668.

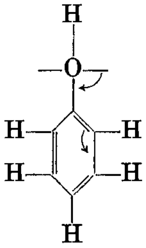
the next. Such a migration would involve the shift of a charge of $4{\cdot}80 \times 10^{-10}$ E.S.U. through a distance of the order of 1·5 A.U., that is, a change of moment of the order of $4{\cdot}8 \times 1{\cdot}5 = 7{\cdot}2$ Debye units: whereas the mean value of the observed change is 0·4 and its maximum 0·88, i.e. from 1/17 to 1/8 of this amount.

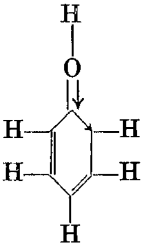
Thus we have good evidence that an electronic drift occurs, and that it has an important influence on reactivity.

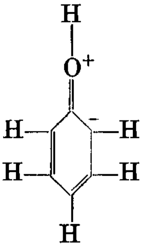
The second question is whether there is any physical mechanism that can account for the drift. This is provided by the theory of resonance.[261] In any of the examples which the organic theorists provide, if we carry the drift further, to the extent of a complete electron shift from one atom to the next, we shall arrive at another 'canonical' chemical formula. This second formula has the same atoms linked as the first one, and so does not require any serious change in the relative positions of the atoms (condition 2 of resonance); it also usually represents what on general grounds we should regard as a possible but often somewhat unstable structure. Thus according to the resonance theory the molecule will be in a state intermediate between the two, and will approach more nearly to the first structure, because that is the more stable. Hence the electronic distribution should be that of the first structure distorted to a small extent towards the second. This is precisely what the organic theory requires, and what the dipole results of Sutton indicate.

The point will be made clearer if we take one or two examples. The high reactivity of the ortho- and para-positions in phenol is expressed by the symbol I. B. The curved arrows indicate a partial shift of electrons from an atom to a link, or from a link to an atom, or from one link to another. If we carry them to an extreme, and imagine the shift to be complete, we arrive at formula II. A, which may also be written as II. B, which is identical with II. A, with the co-ordinate links written $\overset{+}{X}\text{—}\overset{-}{Y}$ instead of $X \rightarrow Y$.


(I. A.)


(I. B.)


(II. A)


(II. B.)

It will be observed that in II all the atoms have their full octets, but the ortho-carbon atom has only three covalencies (valency group 2, $\underline{6}$), and in consequence has a negative charge, since this valency group is the equivalent of $2+6/2 = 5$ electrons, instead of 4. The positions of the

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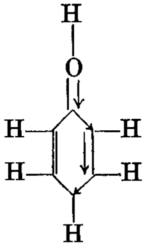
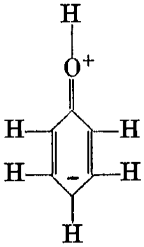
[261] See further, G. W. Wheland, *Theory of Resonance and its Applications to Organic Chemistry*, 1944.

atoms are practically unchanged, except that the C—O—H angle is altered from 110° to 125°, so that in the actual molecule we must suppose an intermediate and slightly strained position of the hydrogen. Thus the second resonance formula (II) differs from the first (I) in having a positive charge on the oxygen, which should facilitate ionization of the hydrogen, and perhaps explains why phenol is more acidic than alcohol: and in having a negative charge on the ortho-carbon atom. It is evident that the conditions for resonance are present, and that we should expect the phenol molecule to be in a state intermediate between I and II, and to be much nearer to I on account of its greater stability; so that the negative charge on the ortho-carbon will be much less than that of a whole electron. If we make the further assumption that a negative charge on an aromatic carbon atom increases its reactivity in bromination, nitration, sulphonation, etc., we have an explanation of the reactivity of the ortho-carbon atom in phenol.

If we carry the process a stage farther, as in III. A and III. B, the negative charge disappears from the ortho-carbon and appears on the para, and we know that these are the two active atoms in phenol.



(III. A)

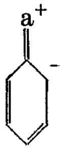


(III. B)

A third shift of the same kind would bring the negative charge to the other ortho-atom; but it will be seen that it is not possible on this mechanism for the negative charge to appear on the meta-atoms, which are the inactive atoms in phenol.

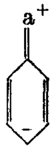
An exactly similar series of structures will account for the ortho-para substitution in chloro-benzene, if we assume the possibility of the halogen atom forming a double co-ordinated link $C\overset{\leftarrow}{=}Cl$ with the carbon. For this there is definite physical evidence, as we shall see later under silicon (p. 607).

(II. A)



(II. B)

(III. A)



(III. B)

Thus the general ideas which lie at the basis of the modern theories of organic reactivity are completely in accordance with modern physical conceptions.

Metallic and Semi-metallic Alkyls and Aryls

The references to the text for these compounds are:

Gp. I. Alkali metals 67; Cu, Ag, Au 114.
Gp. II. Be 200; Mg 224; Ca, Sr, Ba 246 ; Zn 265; Cd 267; Hg 299.
Gp. III. B 349, 369; Al 414; Ga 461; In 462; TlR_3 462.
Gp. IV. Si 560; Ge 568; Sn 577; Pb 587.
Gp. V. As 761; Sb 772; Bi 779.
Gp. VI. Se 953; Te 964; Cr 1001.
[Gp. VII. None.]
Gp. VIII. Pt. 1627.

The alkyls and aryls of the elements of the first three groups are all except those of boron, zinc, cadmium, and mercury polymerized through some obscure form of linkage; they are all except HgR_2 and $TlR_2[X]$ attacked by air or water, usually by both. The stannous and plumbous alkyls are readily oxidized, as are those of tellurium and chromium, but not those of platinum.

In general the aryls are much more stable than the corresponding alkyls.

*Binary Carbides**

These are very numerous, and very diverse in character. Though their structures are not always certain, they may be divided into three main classes, according as the links are to be regarded as (1) salt-like, (2) covalent, or (3) metallic.

1. Salt-like carbides are formed mainly by the elements of Groups I, II, and III. They can be further divided according to the number of carbon atoms in the anion, which can be 1 (1. A), 2 (1. B), or 3 (1. C).

1. A. Some of these carbides, which are presumably ionized, have all the carbon atoms far apart, and on hydrolysis give methane; such are Be_2C (II. 200), which has an anti-fluorite structure, and Al_4C_3 (III. 413); this last has a complicated lattice, but the carbon atoms are 3·16 A apart.

1. B. This is the large group of acetylides, which have the carbon atoms in pairs, forming the anion $[C{\equiv}C]^{--}$[262]. These are formed by the elements of Groups I–VI, especially I, II, and III.

Examples of these acetylides are:

Gp. I. Na_2C_2, K_2C_2, etc., 78; Cu_2C_2 112; Ag_2C_2 113; ? Au_2C_2 113.
Gp. II. BeC_2 199; MgC_2 223; CaC_2, SrC_2, BaC_2 246; ZnC_2, CdC_2 264.
Gp. III. Al_2C_6 413; Ce_2C_6, ref. [263]; YC_2, LaC_2, CeC_2, PrC_2, NdC_2, SmC_2, 440.†
Gp. IV. ThC_2: its structure is peculiar, but it is no doubt an acetylide (Wells, *S.I.C.* 457).
Gp. V. VC_2 (Wells, *S.I.C.* 458).
Gp. VI. UC_2 1071.

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* See A. F. Wells, *Structural Inorganic Chemistry*, pp. 455, 565.

† These carbides of the Rare Earth elements are noticeable because they seem to involve the metal being divalent, which among these metals has only been observed in Sm, Eu, Yb, and perhaps Tm—certainly not in La, Ce, Pr, or Nd.

1. C. The only example is Mg_2C_3 (II. 224) which has the anion $[C{=}C{=}C]^{--}$.

II. *Covalent carbides.* These are of two kinds, one (II. A) volatile, with small molecules, formed especially by hydrogen and the elements of Groups IV-VII; examples are CH_4, $(CN)_2$, CO_2, CS_2 (VI. 888), CSe_2 (979): CF_4, CCl_4, CBr_4, CI_4. The second kind (II. B) are giant molecules. The most familiar of these is carborundum SiC (555), a very hard solid decomposing above 2,200°, with a lattice very like that of diamond. $B_{12}C_3$ (III. 368) is another example: the carbon atoms are here arranged in linear groups of three, the boron atoms forming a continuous structure. Cr_3C_2 (VI. 1001) probably belongs to this class; it has continuous slightly stretched chains of carbon atoms.

To this class should perhaps be assigned the compounds formed by the insertion of other atoms between sheets of graphite, such as KC_8, KC_{16}, and 'carbon monofluoride' CF (496).

III. *Interstitial carbides.** In the close-packed lattices of metals (if their atoms are regarded as spheres in contact) are a series of holes into which other atoms, if small enough, can be fitted; these holes are of two kinds, (1) tetrahedral, with four tetrahedrally disposed metallic neighbours, and (2) octahedral, with six. In (1) there are two holes for every metallic atom, and if all are filled (giving MC_2) a fluorite lattice results;† but here the radius of the inserted atoms must be between 0·23 and 0·41 of that of the metallic atoms, and no carbides of this type are known. For octahedral holes the ratio must be from 0·41 to 0·59, so that carbon can be inserted if the radius of the metallic atom for 12-fold co-ordination is greater than 1·3 A. In a (cubic) close-packed structure the number of octahedral holes is equal to the number of spheres, and if all are filled a sodium chloride lattice is formed. If the metallic lattice is hexagonal, similar rules apply.

Compounds of this interstitial type (which occur with hydrogen, boron, carbon, and nitrogen in the holes) have properties—opacity, conductivity, metallic lustre, and variable composition—like those of metallic alloys, and it is assumed that the forces between the metallic atoms are much the same as in the pure metal; but this must not be interpreted too strictly. The insertion of the carbon atoms is found to result in an increase in volume, the intermetallic distances being increased on the average by some 9 per cent. (e.g. TiC 11·3 per cent., ZrC 4·3 per cent.). The bonds formed by the carbon with the metal must therefore evolve more energy than is required (1) to strain the metallic links to this extent, and (2) to atomize

* See Wells, *S.I.C.* 455, 565.

† If half are filled the most symmetrical structure is that of wurtzite.

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[262] See further, J. Schmidt, *Z. Elektrochem.* 1934, **40**, 171.

[263] A. Damiens, *Bull. Soc.* 1914, **15**, 370.

[264] H. A. Bahr, and T. Bahr, *Ber.* 1928, **61**, 2177.

[265] B. Jacobson and A. Westgren, *Z. physikal. Chem.* 1933, **B 20**, 361.

[266] J. Schmidt and E. Ostwald, *Z. anorg. Chem.* 1933, **216**, 85.

the carbon; and it seems probable that these bonds are covalent. Another result of the new bonds is that these carbides are as a rule harder and less fusible than their metals, as the following values show. (The hardness is given on Mohs's scale, on which diamond is 10, and very few metals as much as 7.)

Compound	*M.pt.* ° C.	*M.pt. metal*	*Hardness*
TiC	3,137°	1,800°	8–9
HfC	3,890°	2,220°	. .
W_2C	2,850°	3,380°	9–10
NbC	3,490°	1,950°	. .

The following list includes the more certainly interstitial carbides, with Goldschmidt's radii for 12-co-ordination (the page references are prefixed):

Gp. IV	211	TiC	1·47	211	ZrC	1·60
				211	HfC	1·59
Gp. V	324	VC	1·35	324	V_2C	1·35
	467	NbC	1·47			
	508	TaC	1·47			
Gp. VI	646	MoC	1·40			
	647	WC	1·41	647	W_2C	1·41

There are other carbides with a similar structure but of a more complicated type, in which the metallic atoms have radii less than 1·4; examples are:

Compound	*Metallic radius*	*Ref.*
Mn_3C	1·37	VII. 1266
Fe_3C	1·26	VIII. 1324, refs. [4,5]
Co_3C	1·25	ref. [282]
Ni_3C	1·25	refs. [284–6]

[Compounds of Carbon and Nitrogen: see under Nitrogen, Gp. V.]

Carbon and Oxygen[267–8]*: Oxides of Carbon*

Three or perhaps four of these are known: carbon monoxide (described later under divalent carbon, p. 545): carbon dioxide: carbon suboxide C_3O_2: and perhaps pentacarbon dioxide C_5O_2.

Carbon Dioxide, CO_2

The solid has a v.p. of 1 atm. at −78·5°[269]; the triple point is −56·6° at 5·01 atm.[270] and the critical temperature +31·0 at 73 atm.

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[267] For a general discussion on the oxidation of carbon see *Trans. Far. Soc.* 1946, **42**, 99–395.

[268] For the kinetics of the reaction of carbon with steam (formation of carbon monoxide) see (*a*) J. Gadsby, C. N. Hinshelwood, and K. W. Sykes, *Proc. Roy. Soc.* 1946, **187**, 129; (*b*) R. F. Strickland-Constable, ib. 1947, **189**, 1.

[269] W. F. Giauque and C. J. Egan, *J. Chem. Phys.* 1937, **5**, 45.

[270] C. H. Meyers and M. H. van Dusen, *Bur. Stand. J. Res.* 1933, **10**, 381.

The molecule is a resonance hybrid of three forms[271] which, with their calculated and observed O to O distances and heats of formation, are:

	$O=C=O$	$O—C\equiv O$	$O\equiv C—O$	*Observed*
O· ·O calc.	2·44	2·53	2·53	2·30 A.
Heat of formation, H_a . .	346	*ca.* 338	*ca.* 338	380 k.cals.

Liquid carbon dioxide is not a good solvent. Water dissolves in it up to 0·02 per cent. at −29°, and 0·10 per cent. at +22·6°.[272] According to Büchner[273] it practically does not dissolve salts, but ether, benzene, pentane, and the like are miscible with it; many organic substances form two layers with it, often with an inferior critical solution temperature.

Carbon Suboxide, C_3O_2

This was first made in 1906 by Diels and Wolf,[274-6] by dehydrating malonic acid with phosphorus pentoxide *in vacuo* at 140—50°:

$$HO·CO·CH_2·CO·OH \quad = \quad O=C=C=C=O + 2\,H_2O.$$

The linear structure which this formula involves is confirmed by electron diffraction,[277] which shows the distances to be C—O 1·20, C—C 1·30 (theory C=O 1·22, C=C 1·33); this is supported by the ultra-violet, the Raman, and the infra-red spectra.[278-80] This suggests that there is a resonance between structures like those of carbon dioxide

$$O=C=C=C=O, \qquad \overset{+}{O}\equiv C—C\equiv C—\overset{-}{O}, \qquad \overset{-}{O}—C\equiv C—C\equiv\overset{+}{O}.$$

Carbon suboxide is an evil-smelling gas, boiling at −6·8°; it combines very readily with water to malonic acid, and with ammonia and amines to malonamides.

What is presumably the sulphur analogue of this, C_3S_2, has been made in minute yield by the action of the zinc arc on carbon bisulphide.[281] It takes up bromine to give a stable substance $C_3S_2Br_6$.

Pentacarbon Dioxide C_5O_2 or $O=C=C=C=C=C=O$.

According to Wagner[282] this is formed in about 3 per cent. yield by passing pure carbon suboxide through a glass tube at 200°. It is relatively

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[271] R. S. Mulliken, *Rev. Mod. Phys.* 1942, **14**, 204.

[272] H. W. Stone, *Ind. Eng. Chem.* 1943, **35**, 1284.

[273] E. H. Büchner, *Z. Physikal. Chem.* 1906, **54**, 665.

[274] O. Diels and B. Wolf, *Ber.* 1906, **39**, 689.

[275] O. Diels and P. Blumberg, ib. 1908, **41**, 82.

[276] A. Klemenc, R. Wechsberg, and G. Wagner, *Mon.* 1935, **66**, 337.

[277] L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.* 1933, **19**, 860.

[278] H. W. Thompson and N. Healey, *Proc. Roy. Soc.* 1936, **157**, 331.

[279] H. W. Thompson, *Trans. Far. Soc.* 1941, **37**, 249.

[280] R. C. Lord and N. Wright, *J. Chem. Phys.* 1937, **5**, 642.

[281] A. Stock, A. Brandt, and H. Fischer, *Ber.* 1925, **58**, 643.

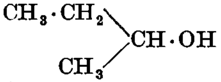
[282] A. Klemenc and G. Wagner, ib. 1937, **70**, 1880.

stable; the extrapolated boiling-point is +105°, the melting-point being below −100°; it reacts with water to form carbon dioxide and a complicated acid of doubtful structure. Its existence has been disputed by Diels,[283a] and seems to be somewhat uncertain; see further Klemenc.[283] It should be noticed that the type of resonance shown by carbon dioxide and carbon suboxide is possible for a compound C_nO_2 only when *n* is odd—for CO_2, C_3O_2, C_5O_2, etc., but not for C_2O_2 or C_4O_2.

Organic Oxygen Compounds

The discussion of these compounds belongs mainly to organic chemistry, but a few points of general interest may be mentioned here.

Alcohols. The following table shows that additional methyl groups lower the boiling-points almost as much as CH_2 raises them, and that the effect of the tertiary butyl group in raising the melting-point is even more marked:

	B.pt.	*M.pt.*
$CH_3 \cdot OH$	64·7°	−97·7°
$CH_3 \cdot CH_2 \cdot OH$	78°	−114°
$CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$	97°	−127°
$(CH_3)_2CH \cdot OH$	82·7°	−85·8°
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$	117°	−79·9°
 $(CH_3 \cdot CH_2)(CH_3)CH \cdot OH$	99·5°	..
$(CH_3)_3C \cdot OH$	82·3°	+25·1°
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$	137°	..
$(CH_3)_3C \cdot CH_2 \cdot OH$	113°	+52°

The alcohols are of course associated liquids with high Trouton constants (usually about 26). From the vapour densities de Fries and Collins[284] find that at 120° and 2 atm. pressure methyl alcohol is 12·5 per cent. dimeric. For the nature of the 'hydrogen bond' by which the molecules are held together, see I. 25.

Aldehydes and Ketones. Electron diffraction measurements[285] have shown that the distances in formaldehyde are C=O 1·21, C—H 1·09 (theory 1·22, 1·07); combined with the spectrum results this gives the H—C—H angle as 120°. Trioxymethylene $(CH_2O)_3$ is found by X-ray analysis to have a symmetrical 6-ring (C_3O_3).[286]

In acetaldehyde electron diffraction[287] gives the C—C distance as 1·50; it is definitely shortened (theory 1·54), probably through resonance; the C=O has the normal value 1·21, and the C—C—O angle is 121±2°.

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[283] A. Klemenc, ib. 1938, **71**, 1625. [283a] O. Diels, ib. 1197.

[284] T. de Vries and B. T. Collins, *J.A.C.S.* 1941, **63**, 1343.

[285] D. P. Stevenson, J. E. LuValle, and V. Schomaker, ib. 1939, **61**, 2508.

[286] N. F. Moerman, *Rec. Trav.* 1937, **56**, 161.

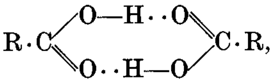
[287] D. P. Stevenson, H. D. Burnham, and V. Schomaker, *J.A.C.S.* 1939, **61**, 2922.

Paraldehyde and metaldehyde were formerly supposed to be steric isomers of the trimeric $(CH_3\cdot CHO)_3$; but while Brockway has shown[288] by electron diffraction that this is the structure of paraldehyde (C—O 1·43, C—C 1·54: theory the same), Pauling[289] finds in metaldehyde by X-ray analysis a non-planar 8-ring $(CH_3\cdot CHO)_4$, with alternate carbon and oxygen atoms, and the methyl groups nearly level with the ring; C—O and C—C are 1·43 and 1·54 as in paraldehyde.

For the kinetics of the decomposition of aldehydes see references [290-2]; for that of acetone see reference [293].

Carboxylic Acids

These acids, especially the lower members, are largely dimeric in the solid, in the vapour, and in non-ionizing solvents. The carboxyl group forms a relatively stable dimer



(the dotted lines indicate a hydrogen bond),* whose structure does not allow of further association.[297] With formic and acetic acids the dimer forms over 90 per cent. of the vapour at the ordinary temperature,[294,296] and from 7 to 9 per cent. at 303° and 22 mm. With benzoic acid in 3·5 per cent. benzene solution the dimer is found by the v.p. to be 94 per cent.[298] The heat of association of carboxylic acids is usually about 15 k.cals.,[296,300] but from certain infra-red measurements values of about 8 k.cals. have been got.[294-5,299,301-2]

From the infra-red spectrum of the monomeric form of formic acid these distances and angles have been deduced[297a]: O—H 0·96; C—H 1·08; C=O 1·23; C—O 1·41 (theory O—H 0·96: C—H 1·07); angles O—C=O 125±1°; C—O—H 107±5°; H—C=O 122±5°.

* Chelate 8-rings are usually rare, owing to strain; but the O—H··O angle being 180°, the other angles are the same as in a 6-ring.

[288] D. C. Carpenter and L. O. Brockway, *J.A.C.S.* 1936, **58**, 1270.

[289] L. Pauling and D. C. Carpenter, ib. 1274.

[290] K. B. Krauskopf and G. K. Rollefsen, ib. 1935, **57**, 590.

[291] C. A. Winkler and C. N. Hinshelwood, *Proc. Roy. Soc.* 1935, **149**, 355.

[292] R. E. Smith and C. N. Hinshelwood, ib. 1940, **175**, 131.

[293] C. A. Winkler and C. N. Hinshelwood, ib. 1935, **149**, 340.

[294] L. G. Bonner and R. Hofstadter, *J. Chem. Phys.* 1938, **6**, 531.

[295] For values from the entropy of the force constants of the association bond in dimeric formic and acetic acids see J. O. Halford, ib. 1946, **14**, 396.

[296] J. Karle and L. O. Brockway, *J.A.C.S.* 1944, **66**, 574.

[297] The v.d.'s are, however, said to indicate the formation of a certain amount of a higher polymer as well: H. L. Ritter and J. H. Simons, ib. 1945, **67**, 757.

[297a] Van Zant Williams, *J. Chem. Phys.* 1947, **15**, 232.

[298] F. T. Wall and P. E. Rouse, *J.A.C.S.* 1941, **63**, 3002.

[299] R. C. Herman and R. Hofstadter, *J. Chem. Phys.* 1938, **6**, 534.

[300] F. H. MacDougall, *J.A.C.S.* 1936, **58**, 2585.

[301] M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Phys.* 1938, **6**, 767.

[302] Id., ib. 755.

The structure of the dimeric form has been examined by electron diffraction by Karle and Brockway[296] (see also [302]). With formic and acetic acids they find:

	Formic acid		*Acetic acid*	
	Monomer.	*Dimer.*	*Dimer.*	*Theory*
C—O	1·42 [1·37]	1·36	1·36	1·37 A.
C=O	1·24 [1·21]	1·25	1·25	1·21
C—C	. .	. .	1·54	1·54
O—H··O	. .	2·73	2·76	1·92

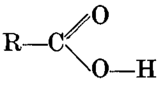
The values in brackets were obtained by Schomaker and O'Gorman in a very detailed electron diffraction measurement.[302a]

The observed difference between the two links of carbon to oxygen is important. In monomeric formic acid they have the normal (ether and ketone) values. In the dimers the longer link becomes 0·06 A less, while the shorter remains much the same, but there is still a difference of 0·1 A between them. Hence in the hydrogen bond —O—H··O= the two distances from oxygen to hydrogen must be different.

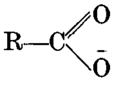
Le Fevre and Vine[303] examined the polarization of several fatty acids in benzene solution, and conclude that the dimeric form has a moment of about 1·1 D. This may well be due to atomic polarization, as in the metallic acetylacetonates.[304]

The carboxyl group has two resonance forms, which give equivalent ions[305]

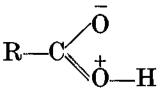
A.



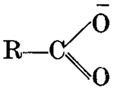
A'.



B.



B'.



The heats of combustion show the resonance energy to be 28 k.cals./mole (24 for the esters).

From the crystal structure of sodium formate Zachariasen has shown[306] that in the ion there is complete resonance between the two C—O groups, the distance being 1·27 A (theoretical mean for C—O+C=O 1·32; resonance shortening 0·05 A), and the O—C—O angle 124°.

The acidity is mainly due to the effect of the resonance form B, in which the positive charge on the hydroxyl oxygen repels the hydrogen. The increase of acidity caused by the introduction of halogens (the dissociation constants of the three chloracetic acids are about 80, 3,000, and

[302a] V. Schomaker and J. M. O'Gorman, *J.A.C.S.* 1947, **69**, 2638.

[303] R. J. W. Le Fevre and H. Vine, *J.C.S.* 1938, 1795.

[304] L. E. Coop and L. E. Sutton, ib. 1284.

[305] L. Pauling, *Chem. Bond.* ed. 2, 202.

[306] W. H. Zachariasen, *J.A.C.S.* 1940, **62**, 1011.

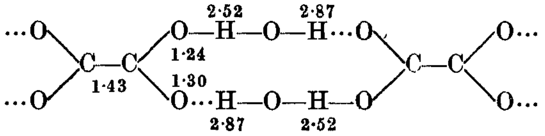
100,000 times that of acetic acid itself)[307] is presumably due to the inductive effect, the negative halogen drawing electrons towards itself and away from the hydroxyl hydrogen. The way in which this increase dies away as the halogen gets farther from the hydroxyl is shown by the following figures[308] for the thermodynamic dissociation constants $\times 10^5$ at 25°:

	$X\cdot CH_2COOH$	$X\cdot CH_2\cdot CH_2COOH$	$X\cdot CH_2\cdot CH_2\cdot CH_2COOH$
X = H	1·75	1·34	1·50
F	213·0	. .	. .
Cl	139·7	10·1	3·0
Br	138	9·8	2·6
I	71	9·0	2·3
CN	342	10·2	3·7
COOH	149	6·4	4·5

The second resonance form (B) also explains why the carbonyl group in acids and esters differs so much from that in aldehydes and ketones, for example in not forming oximes or hydrazones.

Carbonic Acid. In the hydration of carbon dioxide equilibrium is not reached at once (this is important in the preparation of ^{18}O and ^{13}C), but the reaction is catalysed by solids such as glass fibres, alumina, carbon, etc., as well as by enzymes (carbonic anhydrase).[309,310] The dissociation constants of the acid have been the subject of much work; the most probable value of K_1 (therm.) at 25° is $4\cdot4 \pm 0\cdot1 \times 10^{-7}$ [311-14]; that of K_2 is $2\cdot29 \times 10^{-11}$ at 0° and $4\cdot01 \times 10^{-11}$ at 18°.[315]

Oxalic acid. Accurate measurements of the crystal structure of the dihydrate[316] $(CO\cdot OH)_2$, 2 H_2O give the distances:



This O—H··O distance of 2·52 A is the shortest known. The dihydrates of acetylene dicarboxylic acid and diacetylene dicarboxylic acid[317,317a] are formed on exactly the same plan.

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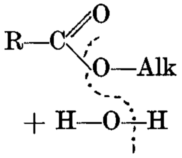
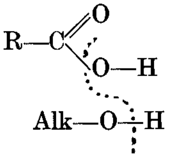
[307] H. O. Jenkins, *Nature*, 1940, **145**, 625.
[308] D. J. G. Ives and K. Sames, *J.C.S.* 1943, 513.
[309] A. F. Reid and H. C. Urey, *J. Chem. Phys.* 1943, **11**, 403.
[310] H. C. Urey, A. H. W. Aten, and A. S. Keston, ib. 1936, **4**, 662.
[311] D. A. McInnes and D. Belcher, *J.A.C.S.* 1935, **57**, 1683.
[312] T. Shedlovsky and D. A. McInnes, ib. 1705.
[313] J. Curry and C. L. Hazelton, ib. 1938, **60**, 2773.
[314] H. S. Harned and R. Davis, ib. 1943, **65**, 2030.
[315] O. Weider, *Ber.* 1935, **68**, 1423.
[316] J. D. Dunitz and J. M. Robertson, *J.C.S.* 1947, 142.
[317] Id., ib. 148.
[317a] Id., ib. 1145.

Esters. By the use of heavy oxygen it has been shown that in the saponification of esters,[318] in the esterification of acids,[319] and in the reaction of acid anhydrides with alcohols[320] the same oxygen atom remains attached to the alkyl group throughout:





In the formation of halide esters

$$R—O—H + H—Cl = R—Cl + H—O—H$$

the alcohol must obviously lose its oxygen, which explains why this reaction is so slow, and why changes in R which promote esterification by organic acids hinder the formation of halides.

For recent work on the hydrolysis of esters see Hinshelwood *et al.*,[321-3] Ingold *et al.*,[324-5] Roberts and Urey.[326]

The effect of ring strain on the rate of hydrolysis of *acid anhydrides* is very marked; the relative rates at 25°[327] and the heats of hydration are[328]:

	Acetic	*Succinic*	*o-Phthalic*	*Maleic*
Rel. rates . .	0·99	1	3·99	9·96
Heats . . .	14·0	11·2	. .	8·33 k.cals.

Binary compounds of carbon with sulphur, selenium, and tellurium are described under Group VI (pp. 888, 953, 964).

[The organic halogen compounds are discussed under Group VII; fluorides, p. 1116: chlorides, bromides, and iodides, p. 1174.]

Co-ordination Compounds of Carbon

Owing to the great stability of a carbon atom with a fully shared octet, which cannot co-ordinate either as donor or as acceptor, co-ordination compounds of carbon are relatively rare. There are, however, certain well-marked classes, especially those formed by divalent carbon in carbon monoxide and the iso-cyanides (these are discussed under divalent carbon below, p. 546); by olefines; and by aromatic hydrocarbons. The structures of these compounds are not always clear. The most instructive

[318] M. Polanyi and A. L. Szabo, *Trans. Far. Soc.* 1934, **30**, 508.

[319] I. Roberts and H. C. Urey, *J.A.C.S.* 1938, **60**, 2391.

[320] N. I. Dedusenko and A. I. Brodski, *Acta Phys. Chem. U.R.S.S.* 1942, **17**, 314.

[321] C. N. Hinshelwood and A. R. Legard, *J.C.S.* 1935, 587.

[322] W. B. S. Newling and C. N. Hinshelwood, ib. 1936, 1357.

[323] E. Tommila and C. N. Hinshelwood, ib. 1938, 1801.

[324] C. K. Ingold and H. G. G. Mohrhenn, ib. 1935, 1482.

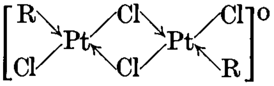
[325] C. K. Ingold and W. S. Nathan, ib. 1936, 222.

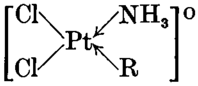
[326] I. Roberts and H. C. Urey, *J.A.C.S.* 1939, **61**, 2584.

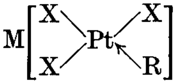
[327] A. C. D. Rivett and N. V. Sidgwick, *J.C.S.* 1910, **97**, 1677.

[328] J. B. Conn, G. B. Kistiakowsky, R. M. Roberts, and E. A. Smith, *J.A.C.S.* 1942, **64**, 1747.

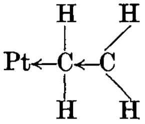
perhaps are those formed by palladium and platinum (see VIII. 1585) with the simpler olefines, such as



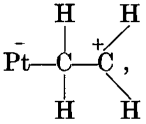




in which X = Cl, Br, or I, and R is either carbon monoxide or ethylene. As there is no doubt that the carbon monoxide is attached in the form $\mathrm{M}\leftarrow\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$, the ethylene also must act as donor and fill one co-ordination place. This gives us the structure



or



in which the remoter carbon has only a sextet of electrons; this is not a very satisfactory solution, but no other seems possible.

A similar replacement of carbon monoxide by ethylene occurs with the cuprous compounds (I. 130), though here the ethylene compound could not be isolated, but was only established in solution by the absorption of the ethylene. The strong affinity of palladium for ethylene is shown by the fact that if the gas is passed through a solution of the mixed chlorides of all the platinum metals, the palladium alone is reduced to the metal.[329]

Similar olefine compounds are formed by silver, as Lucas has shown (I. 130) by measuring the partition of the olefine between carbon tetrachloride and an aqueous solution of (*a*) potassium nitrate and (*b*) silver nitrate, the excess with the latter being assumed to be co-ordinated with the silver ion; in this way equilibrium constants were established, and it was shown, for example, that the heat of co-ordination of the silver with cyclohexene and with trimethyl ethylene was about 6 k.cals. In the same way a solution of aluminium chloride in benzene will absorb olefines and acetylene (III. 429), after which by a further reaction alkyl benzenes are formed; in presence of alcohol a solid of the composition $\mathrm{AlCl_3,C_2H_2}$, 2 EtOH separates out.

The aromatic nucleus also can form co-ordination compounds. The definite dipole moments of aluminium bromide and iodide (5·2 and 2·5 D: III. 426) and of iodine in benzene solution, while they are non-polar in solvents like hexane and carbon disulphide, are good evidence of this, and support the view that the carbon acts as a donor here, as it does in the co-ordination of carbon monoxide and olefines. But often the complexity is doubtful. Benzene and other aromatic hydrocarbons form solid compounds with a variety of solutes, such as hexaphenyl digermane $\Phi_3\mathrm{Ge}$—$\mathrm{Ge}\Phi_3$ and its tin and lead analogues (IV. 574), silver perchlorate (VII. 1234), antimony trichloride (V. 798), the alkaline periodides MI_x (VII. 1197), and

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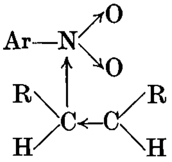
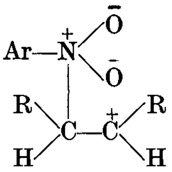
[329] S. C. Ogburn and W. C. Brastow, *J.A.C.S.* 1933, **55**, 1307.

the amine of nickel cyanide (VIII. 1434: this last is a very stable compound); but the evidence for co-ordination in solution is usually weak.[*]

Another series of solids are formed with nitro-compounds (V. 697: and see D. Ll. Hammick in Taylor and Baker's *Organic Chemistry of Nitrogen*, p. 261). Here again, except with picric acid, which has other possibilities of its own, the evidence for the formation of complexes is weak, though the solutions are often coloured (see refs. [330-1]). In some cases where the crystal structure of the solid has been examined, as with the compound of picryl chloride with hexamethyl benzene, it has been found that there is no co-ordination, the nearest distances between the atoms of the components being 3·5 A (Powell and Huse: see V. 698 and ref. [332]) The effect does not depend on the nitro-compound being aromatic, or on the hydrocarbon having nuclear hydrogen, since tetranitromethane and hexamethyl benzene will act as components. If we suppose that when there is co-ordination the carbon acts as donor, the nitro-group can easily become an acceptor:



or as it may be written



TRIVALENT CARBON COMPOUNDS

This group comprises those compounds in which a carbon atom on the ordinary formulation has a valency group of only seven electrons, one unshared and six shared. They are generally known as free radicals. Comprehensive papers and monographs on this subject are quoted in references [333-41].

These substances are of two kinds:

I. Transient or shortlived molecules, which only exist until they meet one another, and then react. They include the free methyl and ethyl radicals of Paneth. They are of great interest, especially from the light they throw on the mechanism of many chemical reactions; but they show the instability which we should expect from their structure.

[*] The surprising difference between the solubility of silver perchlorate at 25° in benzene (5·3) and toluene (101) certainly suggests solvation in the solutions.

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[330] K. Brass and K. Fanta, *Ber.* 1936, **69**, 1.

[331] G. Briegleb, *Z. physikal. Chem.* 1935, B **31**, 58.

[332] D. H. Saunder, *Proc. Roy. Soc.* 1946, **188**, 31; 1947, **190**, 508.

[333] J. Schmidlin, *Das Triphenyl-methyl*: vol. vi of 'Chemie in Einzeldarstellungen', Enke, Stuttgart, 1914.

[334] P. Walden, *Chemie der freien Radikale*, Hirzel, Leipzig, 1924.

[335] Id., *Angew. Chemie*, 1926, **39**, 601.

[336] Id., *Solvay Report*, 1928, 431.

[337] K. Ziegler, *Angew. Chemie*, 1930, **43**, 915.

[338] W. Schlenk, *Solvay Report*, 1931, 515.

II. Permanent substances, which remain unchanged indefinitely long in the absence of other reagents; such are many triaryl methyls, Ar_3C. The fact that the trivalent atom does not complete its octet by polymerization indicates the action of a new influence and obviously needs explanation.

Free Alkyl Radicals

We owe our knowledge of these mainly to Paneth and his collaborators.[342-7] He obtained them by passing hydrogen or helium at about 2 mm. pressure, charged with a minute concentration of lead tetra-alkyl (or, less effectively, of the alkyls of some other metals such as antimony and bismuth) through a heated quartz tube. A mirror of lead is deposited just beyond the heated place, and the gas which passes on was shown to be able to remove similar mirrors of such metals as lead, zinc, and bismuth, if they had been deposited not too far from the point of decomposition of the original metallic alkyl. That this active vapour contains methyl or ethyl was proved by condensing in liquid air the product from, say, a zinc mirror, and identifying it by its boiling-point and melting-point as zinc methyl or ethyl; other products were identified later. The activity dies away rapidly with time, showing the instability of the free radicals, but is still perceptible, with a gas velocity of about 20 metres per second (48 miles per hour) 40 cm. beyond the heated spot. The yield of zinc alkyl in the earlier experiments was very small, about 1 mg. in 5 hours, but later yields of several mg. per hour were got. It was shown that if the gas is not passed over a metallic mirror with which the alkyls can combine, it nearly all polymerizes, methyl giving ethane, and ethyl butane. This reaction, like all gaseous polymerizations, involves a triple collision to carry off the large heat of combination, and accordingly it was found to be largely a wall reaction; there was also a small amount of combination with hydrogen to give methane or ethane.* The half-life of the radical in a narrow tube in hydrogen is about 1/200 second; but in a wide tube and in helium it may be as long as a tenth of a second. From the size of the metallic mirror required to destroy the reactivity it was shown that every CH_3 molecule

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* Wave-mechanical calculations show[348] that the heat of the reaction

$$CH_3+H = CH_4$$

is 117 k.cals. (normal C—H 98·8), whence it follows that $CH_3+\frac{1}{2}H_2$ evolves 54·3 k.cals.

[339] General discussion on free radicals, *Trans. Far. Soc.* 1934, **30**, 3–248.

[340] W. Hückel, *Theoret. Grundlagen der organischen Chemie*, ed. 2, Leipzig, 1934, vol. i, pp. 111–33.

[341] W. A. Waters, *J.C.S.* 1946, 409; a lecture on free radicals.

[342] F. A. Paneth and W. Hofeditz, *Ber.* 1929, **62**, 1335.

[343] F. A. Paneth and W. Lautsch, ib. 1931, **64**, 2702.

[344] F. A. Paneth and K. Herzfeld, *Z. Elektrochem.* 1931, **37**, 577.

[345] F. A. Paneth and H. Loleit, *J.C.S.* 1935, 366.

[346] F. A. Paneth, W. Hofeditz, and A. Wunsch, ib. 372.

[347] F. A. Paneth and W. Lautsch, ib. 380.

which strikes it combines with the metal; but the mirror must be formed by the decomposition of a metallic alkyl or by distillation of the metal; a smooth surface of metallic foil has no action on the radical.

Methyl and ethyl are very similar, but it is impossible to get free propyl from lead tetrapropyl in this way, because at the temperature of its formation propyl decomposes into free methyl and ethylene; both of these were identified in the product. Ethyl itself behaves in the same way if it is passed through a strongly heated tube; it yields free methyl, and the CH_2 groups presumably polymerize to ethylene. Free propyl can, however, be made by the action of light on dipropyl ketone.[349]

With the help of these free radicals Paneth has been able to prepare a number of methyl and ethyl derivatives of arsenic, antimony, and bismuth, some of which cannot be made in any other way, such as antimony cacodyl $(CH_3)_2Sb—Sb(CH_3)_2$, which has the singular property of forming bright red crystals which melt at 17·5° to a pale yellow oil.

These free radicals can also be made[350] in small amounts by other methods, as by heating the vapour of azomethane $CH_3 \cdot N{=}N \cdot CH_3$[351]; also by the action of ultra-violet light on acetone, methyl ethyl ketone, and diethyl ketone, wherein various products such as mercury dimethyl, dimethyl telluride, and triethyl arsine were identified.[352] An interesting method of production is that of Polanyi and his collaborators,[353–63] by the action of sodium vapour on alkyl iodides at 200–300°; the formation of free alkyls is proved (1) by their starting reaction chains when the gas is introduced into a mixture of hydrogen and chlorine, and (2) by their conversion by iodine into methyl or ethyl iodide; the two methods of estimation agree. The rate of the reaction

$$\text{Alk—hal} + \text{Na} = \text{Na[hal]} + \text{Alk}$$

is determined by measuring the distance to which the sodium vapour extends by its light absorption. The relative life of R·hal with different halogens in presence of a constant concentration of sodium is $R \cdot F\ 10^6$:

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[348] W. G. Penney, *Trans. Far. Soc.* 1935, **31**, 734.

[349] T. G. Pearson and R. H. Purcell, *Nature*, 1935, **136**, 221.

[350] For the conditions of formation and stability of free radicals produced in the thermal decomposition of paraffins see A. Kossiakoff and F. O. Rice, *J.A.C.S.* 1943, **65**, 590.

[351] J. A. Leermakers, ib. 1933, **55**, 4508.

[352] T. G. Pearson and R. H. Purcell, *J.C.S.* 1935, 1151.

[353] M. Polanyi and D. W. G. Style, *Naturwiss.* 1932, **20**, 401.

[354] H. v. Hartel, N. Meer, and M. Polanyi, *Z. physikal. Chem.* 1932, B **19**, 139.

[355] N. Meer and M. Polanyi, ib. 164.

[356] J. Curry and M. Polanyi, ib. 1933, B **20**, 276.

[357] E. Bergmann, M. Polanyi, and A. Szabo, *Z. physikal. Chem.* 1933, B **20**, 161.

[358] E. Horn, M. Polanyi, and D. W. G. Style, ib. B **23**, 291.

[359] Id., *Trans. Far. Soc.* 1934, **30**, 189.

[360] E. Horn and M. Polanyi, *Z. physikal. Chem.* 1934, B **25**, 151.

[361] L. Frommer and M. Polanyi, *Trans. Far. Soc.* 1934, **30**, 519.

[362] R. A. Ogg and M. Polyani, ib. 1935, **31**, 482.

[363] Id., ib. 604.

R·Cl 104: R·Br 50: R·I 1. For molecules of the formula $C_nH_{2n+1}\cdot Cl$ they find

$n =$	1	2	3	4	5	Isopr.	Tert. Bu.	2ry n–Bu
Life	10,000	7,000	4,400	3,300	2,200	3,300	1,500	2,200

$H_2C{=}CH\cdot Cl$	$H_2C{=}CH\cdot CH_2Cl$	$C_6H_5\cdot CH_2\cdot Cl$
11,000	250	1

Phenyl radicals can be made in the same way from phenyl iodide[360]; they behave of course like the alkyls and not like triphenyl methyl

Diradicals

So-called diradicals like methylene $H:\ddot{C}:H$, though they contain divalent carbon, may be discussed here. Pearson, Purcell, and Saigh[364] give a review of the subject. Methylene can be made by the thermal or photo-dissociation of diazomethane CH_2N_2 or ketene $H_2C{=}C{=}O$; it can be detected by its forming with mirrors of selenium or tellurium $H_2C{=}Se$ and $H_2C{=}Te$ (these can be isolated and analysed, but their constitution does not seem to have been further established). Methylene reacts further with diazomethane to give ethylene and nitrogen, and so when made from diazomethane has only a short life; but when made from ketone its life can be lengthened to 0·23 sec. Thus it is definitely more stable than the trivalent carbon alkyls, and in behaviour is in a way intermediate between them and ordinary reactive molecules.

Methylene diradical can be made from methylene bromide and sodium vapour,[365] but it seems to polymerise and react in other ways at once. The same is true of the diradicals with two trivalent carbon atoms got by the action of sodium on trimethylene bromide $Br\cdot CH_2\cdot CH_2\cdot CH_2\cdot Br$.[366] Thus there seems no doubt about the existence of these diradicals, but they have not been so satisfactorily identified as the alkyls.

For aromatic diradicals (with 2 trivalent carbons) see refs. [367-8].

Triaryl Methyls

The triaryl-methyl radicals were discovered by Gomberg in 1900.[369] In order to obtain hexaphenyl ethane he treated triphenyl methyl chloride $(C_6H_5)_3C\cdot Cl$ with silver. When this reaction was carried out in the complete absence of air, a colourless solid was obtained of the composition $(C_6H_5)_6C_2$ but of a very peculiar behaviour. It formed a yellow solution in benzene, and in this solvent was at once oxidized by air to the peroxide $\Phi_3C{-}O{-}O{-}C\Phi_3$, whose structure was established by its synthesis from triphenyl methyl chloride and sodium peroxide. The solution was also decolorized at once by bromine or even iodine, with the formation of triphenyl methyl bromide or iodide. These reactions could only be

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[364] T. G. Pearson, R. H. Purcell, and G. S. Saigh, *J.C.S.* 1938, 409.

[365] C. E. H. Bawn and J. Milsted, *Trans. Far. Soc.* 1939, **35**, 889.

[366] C. E. H. Bawn and R. F. Hunter, ib. 1938, **34**, 608.

[367] W. Theilacker and W. Ozegowski, *Ber.* 1940, **73**, 898.

[368] E. Müller and E. Tietz, ib. 1941, **74**, 807.

[369] M. Gomberg, ib. 1900, **33**, 3150.

explained by supposing that in solution the hexaphenyl ethane is partly dissociated into triphenyl methyl molecules, a conclusion supported by the later observation of Schmidlin[370] that if the benzene solution was shaken with a limited amount of air the colour at once disappeared with precipitation of the peroxide; on standing the colour reappeared, and could again be removed by air and again returned on standing, until the whole had been oxidized; this showed that the solution contained the monomeric and dimeric forms in equilibrium, and that if the monomeric triphenyl methyl was removed by oxidation, this equilibrium was gradually restored.

With hexaphenyl ethane itself the dissociation is very small,[371] but if the phenyls are replaced by certain other aryl groups both the dissociation and the colour can be greatly increased.

This behaviour, which occurs with other elements such as tin, lead, and nitrogen as well as with carbon, obviously means that the energy of the (endothermic) reaction

$$R_3C{-}CR_3 = 2\,R_3C'''$$

is much reduced by the presence of the aryl groups; it can in fact be shown (see p. 540) that the heat absorbed, instead of being as it normally is, 81·6 k.cals., is only about 11. This may arise from two causes: the hexa-aryl ethane may be unusually unstable and its central C—C link unusually weak (presumably owing to steric effects), or the Ar_3C radical may be abnormally stable, presumably through resonance; or both.

The more important of the methods used for the preparation of these compounds are (1) the removal of the halogen atoms from triaryl-methyl halide with a metal such as silver, zinc, or mercury (Gomberg), or with the Grignard reagent[372] or with vanadous or chromous chloride[373]; (2) the removal of the metal from sodium triaryl-methyl $Ar_3C{\cdot}Na$ by means of oxygen or certain alkyl halides; (3) the action of heat on azo-triaryl-methane[374] $Ar_3C{-}N{=}N{-}CAr_3$ or benzene-azo triphenyl methane $\Phi{\cdot}N{=}N{=}CAr_3$.[375]

Most of the compounds so produced are primarily of the dimeric type $Ar_3C{-}CAr_3$, but are capable of dissociation, especially in solution, to an extent ranging from almost nothing to 100 per cent. into the free radicals.

Reasonably concordant values for the dissociation have been got by various methods, of which the more important are the (usually cryoscopic) determination of the molecular weights,[370,374,376-7] or the measurement of

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[370] J. Schmidlin, ib. 1908, **41**, 2471.

[371] The earliest determinations of this dissociation, whether by freezing-point or by colour, are inaccurate: C. B. Wooster, *J.A.C.S.* 1929, **51**, 1163.

[372] J. Schmidlin, *Ber.* 1910, **43**, 1141.

[373] J. B. Conant and A. W. Sloan, *J.A.C.S.* 1923, **45**, 2466.

[374] H. Wieland, *Ber.* 1909, **42**, 3020.

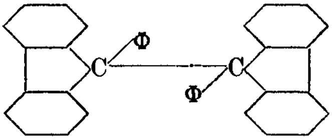
[375] H. Wieland, E. Popper, and H. Seefried, ib. 1922, **55**, 1816.

[376] S. T. Bowden, *J.C.S.* 1939, 33.

[377] S. T. Bowden, W. E. Harris, and D. I. Roberts, ib. 302.

the colour,[378-82] since the radicals are coloured and the associated forms colourless. Magnetic measurements[383-7] have given results at least in qualitative agreement with the others. When the concentration of free radicals is too small to be determined by these physical methods, their presence can often be detected by the formation of the peroxide $Ar_3C—O—O—CAr_3$. Thus ethane derivatives with only four aryls have been shown by this test to dissociate; for example, tetraphenyl succinic ethyl ester[388] and various dialkyl compounds of the type of $Ar_2AlkC—CAlkAr_2$[389]: and even a compound with only two such aryls, tetra-cyclohexyl diphenyl ethane.[389-90] This test evidently detects a very small and transient production of the radical, since it has been shown[391] that a solution of triphenyl methyl bromide forms the peroxide if it is exposed to sunlight in the presence of air.

The degree of dissociation is not greatly affected either by the temperature or by the solvent; it depends essentially on the groups attached to the two carbon atoms that are to be separated. With hexaphenyl ethane there is general agreement that the dissociation in a normal benzene solution at 20° is about 2 per cent.[379,386,392]; if any of the phenyls are replaced by alkyl groups the dissociation usually vanishes (see, however, p. 537); much the same happens if two of the phenyls on each carbon are replaced by a biphenylene group.[393-4]



On the other hand, the dissociation of hexaphenyl ethane is increased by almost any substituent on the phenyls.[395] The following figures[383] show the large effect of an ortho-methyl group on the percentage dissociation

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[378] J. Piccard, *Ann.* 1911, **381**, 347.

[379] K. Ziegler and L. Ewald, ib. 1929, **473**, 163.

[380] L. C. Anderson, *J.A.C.S.* 1935, **57**, 1673.

[381] J. W. Copenhaver, M. F. Roy, and C. S. Marvel, ib. 1311.

[382] J. B. Conant, *J. Chem. Phys.* 1933, **1**, 427.

[383] R. Preckel and P. W. Selwood, *J.A.C.S.* 1941, **63**, 3397.

[384] C. S. Marvel, J. W. Shackleton, C. M. Himel, and J. Whitson, ib. 1942, **46**, 1824.

[385] C. S. Marvel, F. C. Dietz, and C. M. Himel, *J. Org. Chem.* 1942, **7**, 392.

[386] M. F. Roy and C. S. Marvel, *J.A.C.S.* 1937, **59**, 2622.

[387] C. S. Marvel, J. Whitson, and H. W. Johnston, ib. 1944, **66**, 415.

[388] B. Whitten and F. Y. Wiselogle, *J. Org. Chem.* 1941, **6**, 584.

[389] K. Ziegler, *Ann.* 1942, **551**, 127 ff.

[390] S. S. Rossander, L. H. Bock, and C. S. Marvel, *J.A.C.S.* 1930, **52**, 2976.

[391] J. O. Halford and L. C. Anderson, *Proc. Nat. Acad. Sci. Wash.* 1933, **19**, 759.

[392] W. Schlenk, T. Weichel, and A. Herzenstein, *Ann.* 1910, **372**, 1.

[393] W. Schlenk and H. Mark, *Ber.* 1922, **55**, 2285.

[394] H. E. Bent and J. E. Cline, *J.A.C.S.* 1936, **58**, 1624.

of a 0·03-molar solution in toluene at 20° as the phenyls are replaced by ortho-tolyl groups: the degree of dissociation was determined magnetically:

$\Phi_3C—C\Phi_3$	$tol\Phi_2C—C\ tol\Phi_2$	$tol_2\Phi C—C\ tol_2\Phi$
2·8	19·7	90·8

Marvel *et al.* found that in the para-compounds $(R \cdot C_6H_4)_6C_2$, where R was ethyl, propyl, butyl, amyl, and hexyl, the colour was deeper the larger the alkyl; it may be taken that this implies an increase in dissociation. This was confirmed later[386] by a magnetic measurement of the dissociation in benzene, which showed them to be (in per cent. at 25°) phenyl 2·1; *p*-ethyl-phenyl 3·5; *n*-propyl 4·2; *n*-butyl 4·9; isobutyl 6·7.

Other substituents behave in the same way, nitro- and methoxy-groups being especially effective. Tri(*p*-nitrophenyl) methyl[396] is almost completely dissociated. Methoxy-groups have the same effect or rather more[397-9]; this has been confirmed by Bowden.[376] In the same way it has been found[400] that *p*-nitrophenyl-di-*p*-methoxyphenyl methyl is highly dissociated.

Halogens behave in the same way. Marvel *et al.*,[385] measuring the dissociation magnetically, have shown that the order of effectiveness in promoting dissociation is $o > m > p$, and among the halogens is Br > Cl > F. One halogen atom has about as much effect as two alkyls.[401]

A remarkable extension of the triphenyl-methyl structure is to pentaphenyl ethyl $\Phi_3C—\overset{*}{C}\Phi_2$. Schlenk and Mark[393] made this in two ways: (1) from sodium triphenyl methyl and benzophenone dichloride Φ_2CCl_2, giving octophenyl propane $\Phi_3C—C\Phi_2—C\Phi_3$, which breaks up into pentaphenyl ethyl and triphenyl methyl, and (2) from triphenyl methyl chloride and disodium tetraphenyl ethylene, $\Phi_3C \cdot Cl + Na \cdot C\Phi_2—C\Phi_2 \cdot Na$, which gives primarily decaphenyl butane $\Phi_3C—C\Phi_2—C\Phi_2—C\Phi_3$. This last forms a red solution in ether, from which large red-brown crystals separate which have the composition and (by the f.pt. in benzene) the molecular weight of pentaphenyl ethyl; this conclusion was further supported by its conversion into the already known chloride and carbinol. The reactions of pentaphenyl ethyl are very like those of triphenyl methyl, except that the dissociation is complete.

Schlenk and Mark showed later[402] that the replacement of the two phenyls of the $C\Phi_2$ group by biphenylene, a replacement which practically

[395] A tertiary butyl group in the para position has an exceptionally large effect (C. S. Marvel, H. W. Johnston, J. W. Meier, T, W. Mastin, J. Whitson, and C. M. Himel, ib. 1944, **66**, 914).

[396] K. Ziegler and E. Boye, *Ann.* 1927, **458**, 248.

[397] M. Gomberg and D. Nishida, *J.A.C.S.* 1923, **45**, 190.

[398] M. Gomberg and C. C. Buchler, ib. 207.

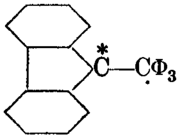
[399] M. Gomberg and G. C. Forrester, ib, 1925, **47**, 2373.

[400] K. Ziegler and W. Mathes, *Ann.* 1930, **479**, 111.

[401] For the effects of substituents on the dissociation see further, C. M. Himel and M. B. Mueller, *J.A.C.S.* 1943, **65**, 1654.

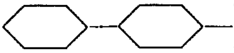
[402] W. Schlenk and H. Mark, *Ber.* 1922, **55**, 2299.

abolishes the dissociation of triphenyl methyl, has little effect on pentaphenyl ethyl, the compound



forming large violet crystals, which give a deep red solution in benzene, in which the compound is shown by the freezing-point to be monomeric.

The replacement of the phenyl groups in triphenyl methyl by a different aromatic system, such as that of naphthalene or diphenyl, has a very marked effect. For diphenyl we have the results of Schlenk *et al.*,[392] who found by the freezing-point the following values of the percentage dissociation in 1-5 per cent. solution in benzene; the dissociations found magnetically by Marvel *et al.*[384] are added, to show that there is at least a qualitative agreement; the colour will be seen to deepen as the dissociation increases:

(the symbol B stands for *p*-biphenyl )

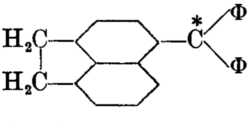
	$\Phi_3C—C\Phi_3$	$B\Phi_2C—CB_2\Phi_2$	$B_2\Phi C—CB_2\Phi$	$B_3C—CB_3$
% dissn. (Schlenk)	*ca.* 2	15	80	100
„ Marvel, magn.	. .	. .	18	26
Colour of solution	Yellow	Orange	Red	Violet

In the crystalline state all these compounds are colourless except the last, which is dark green.

The α- and β-naphthyl groups have a similar effect in increasing the dissociation. Marvel[384] found in 0·1-molar benzene solution at 25° the following percentage dissociations (aN = α-naphthyl; bN = β-naphthyl; B = *p*-diphenylyl):

$bN\Phi_2C—C\Phi_2bN$	$bN_2\Phi C—C\Phi bN_2$	$bN_3C—CbN_3$	$aNB\Phi C—C\Phi BaN$
6	13	21	54

Ziegler and Ewald[379] found by colour measurements that the dissociation of tetraphenyl-di-α-naphthyl ethane in normal solution in cyclohexane at 20° is 80 per cent. When the naphthyl in this compound is replaced by acenaphthyl



giving the radical above, the dissociation is about the same.[403]

According to Pauling and Wheland[404] the order of dissociation among

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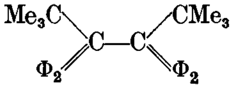
[403] S. T. Bowden and W. E. Harris, *J.C.S.* 1939, 307.

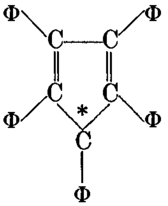
[404] L. Pauling and G. W. Wheland, *J. Chem. Phys.* 1933, **1**, 362.

the compounds $Ar_3C—CAr_3$, where Ar is phenyl, α- or β-naphthyl (aN, bN), and biphenylyl (B) is: less than 6 aryls, none; then in increasing order come Φ_6C_2; $\Phi_4bN_2C_2$; $\Phi_4aN_2C_2$ approx. = $\Phi_2B_4C_2$. Their first statement, that if one of the 6 aryls is replaced by an alkyl there is no dissociation, is not quite true. Not only do many such compounds give evidence of some (though slight) dissociation by forming peroxides (see p. 534) but Conant has shown that especially tertiary alkyl groups can occur in free radicals along with two aryls. Thus[405] di-tert. butyl-tetraphenyl ethane



shows by its colour and reactivity that it is considerably dissociated, though it decomposes further too quickly for its molecular weight to be determined. The corresponding tetra-biphenylyl compound $B_4(CMe_3)_2C_2$[406] is a pale orange solid giving an orange-red solution which darkens on heating; in 0·5 per cent. benzene solution it was found cryoscopically to be 70 per cent. dissociated.

The aromatic groups so far considered have had the nucleus directly attached to the trivalent carbon of the radical. But indirectly attached aryl groups can also be very effective if the attachment is through a chain with double links conjugated with the aromatic nucleus. This is especially true of two such groups. The first is di-phenyl-vinyl $\Phi_2C{=}CH—$. Ziegler has shown[407-8] that this causes high dissociation; in particular, the dianisyl compound $(CH_3\cdot O\cdot C_6H_4)_2\overset{*}{C}—CH{=}C\Phi_2$ is a green solid, and largely dissociated. An even more remarkable compound is pentaphenyl-cyclopentadienyl, which Ziegler and Schnell[409] have shown to be completely dissociated. This conclusion has been confirmed by the magnetic measurements of Müller,[410] which indicate that it is wholly monomeric at the ordinary temperature.



A consideration of the effect of various groups on the dissociation should throw light on the question whether this is caused by steric repulsion in the dimer, or resonance in the monomer—whether the smallness of the

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[405] J. B. Conant and N. M. Bigelow, *J.A.C.S.* 1928, **50**, 2041.

[406] J. B. Conant and R. F. Schultz, ib. 1933, **55**, 2098.

[407] K. Ziegler and K. Ochs, *Ber.* 1922, **55**, 2257.

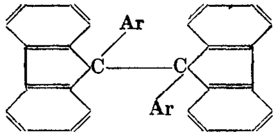
[408] K. Ziegler, *Ann.* 1923, **434**, 34.

[409] K. Ziegler and B. Schnell, ib. 1925, **445**, 266.

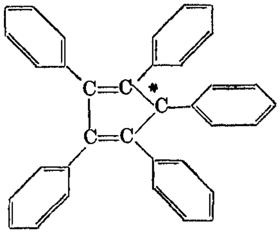
[410] E. Müller and I. Müller-Rodloff, *Ber.* 1936, **69**, 665.

energy difference between the two is due to exceptionally small stability in the hexa-substituted ethane, or the exceptionally great stability in the trivalent carbon radical. On this point, however, the experimental evidence is not simple. Some of the effects that have been mentioned cannot be due to steric causes. Thus para-di-phenylyl groups cannot have a greater steric effect than phenyls, and the diphenyl-vinyl group $\Phi_2C{=}CH-$ must have far less; yet both of these cause greater dissociation. The same is true of para-substituted phenyl groups—nitro-, methoxy-, halide, alkyl-phenyls. All these facts point to a 'chemical' influence, an influence independent of the space-filling properties of the groups, and no doubt due to an increase in the extra resonance energy of the radical.

On the other hand, certain of the results indicate the presence of a steric influence; the effect of the halogens on the dissociation is in the order $o > m > p$, which is characteristic of a steric as opposed to a chemical influence. Further evidence of this is that the replacement of two phenyls by a biphenylene group—i.e. the introduction of a tie between two of the phenyls in the ortho-position—practically stops the dissociation. It is interesting to contrast this with another radical in which also the trivalent carbon is contained in a 5-ring, the cyclopentadiene:



No dissociation
(6 continuously conjugated double links.)



High dissociation
(14 continuously conjugated double links.)

We can scarcely doubt the presence of a steric effect in the first of these compounds, and as little that of a resonance effect in the second. In the light especially of the thermal evidence brought forward by Bent and his co-workers (p. 540) of the weakening of the central link in hexaphenyl ethane, we must conclude that both causes are operative, and that the stability of the ethane is unusually small, and that of the radical unusually large.

Properties of the Triaryl-methyl Radicals

These are of course manifested more clearly the more the dimers are dissociated. The radicals are all coloured, and the colour can be used to measure the dissociation. It has been found[411] that both hexa-phenyl ethane and hexa-biphenylyl ethane have zero dipole moments in benzene solution. The dimeric form is sure to be non-polar, but since the biphenylyl

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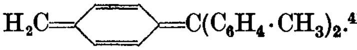
[411] G. Karagunis and T. Jannakopoulos, *Z. physikal. Chem.* 1940, B **47**, 343.

compound is highly dissociated, its non-polarity shows that the trivalent radical is also non-polar, as it should be if it has the expected configuration (p. 543) with the C—C links in a plane and at 120° to one another.

Magnetism. While the dimeric hexa-aryl ethanes must be diamagnetic, we should expect the trivalent radical with its unpaired electron to be paramagnetic. This has been found to be so. It was established by Allen and Sugden[412] for tri-*p*-nitrophenyl methyl; Müller[410] found that tri-biphenylyl methyl, both in the solid state and in solution at all the temperatures examined, had the moment required for one unpaired electron, and so must be almost wholly dissociated. Schwab and Agallidis[413] confirm these results by measuring the effect of these radicals in converting para-hydrogen into the equilibrium mixture. Marvel and his colleagues,[384-6] as we have seen, have used the magnetic properties with fair success to measure the degree of dissociation.

The chemical properties are practically all those of the radicals, and they take the form of extreme unsaturation. Some tri-aryl methyls can disproportionate into two 'even' molecules, tri-*p*-tolyl methyl, for example, on warming into tritolyl methane and (in the first instance)



[414]

The oxygen of the air adds on with great ease to form the peroxide $Ar_3C—O—O—CAr_3$, colourless and only slightly soluble. Halogens, even iodine, readily form the halides $Ar_3C \cdot hal$. Alkali metals add on to form the bright red alkaline compounds such as $Ar_3C \cdot Na$ and $Ar_3C \cdot K$* (see I. 73).

Nitric oxide is taken up, no doubt with the formation of nitroso-compounds $Ar_3C—N{=}O$, which, however, decompose further; carbon monoxide has no action. Diazomethane reacts thus:[421]

$$Ar_3C + CH_2N_2 + CAr_3 = Ar_3C—CH_2—CAr_3 + N_2.$$

Water curiously has no action on the triaryl methyls. Hydrogen chloride converts them into triaryl methane and triaryl methyl chloride. Triaryl methyls, and in particular triphenyl methyl, form addition compounds with many kinds of organic molecules—ethers, ketones, esters, nitriles,

* The free energy of combination of the radicals Ar_3C with sodium for various aryl groups has been examined by Bent and his collaborators.[415-20]

[412] F. L. Allen and S. Sugden, *J.C.S.* 1936, 440.
[413] G. M. Schwab and E. Agallidis, *Z. physikal. Chem.* 1938, B **41**, 59.
[414] P. W. Selwood and R. F. Preckel, *J.A.C.S.* 1943, **65**, 895.
[415] H. E. Bent and M. Dorfman, ib. 1932, **54**, 1393.
[416] H. E. Bent, M. Dorfman, and W. F. Bruce, ib. 3250.
[417] H. E. Bent and M. Dorfman, ib. 1935, **57**, 1452.
[418] M. Dorfman, ib. 1455.
[419] E. Swift, ib. 1938, **60**, 1403.
[420] H. E. Bent and R. G. Gould, ib. 1935, **57**, 1217.
[421] W. Schlenk, *Ann.* 1912, **394**, 183.

aromatic hydrocarbons, and even paraffins. Little is known about the products.

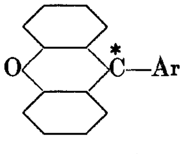
Rate of Dissociation of Hexa-aryl Ethanes

Ziegler[422-3] has examined this, by determining the rate of reaction of hexa-aryl ethanes with some reagent which will combine with the radical practically instantaneously; oxygen is probably not quick enough, but iodine is; at 0° the rate of reaction with iodine is independent of the concentration of the latter.[422] He finds the half-life of the hexaphenyl ethane to be 2·75 minutes at 0° and about 1 minute at 10°. In a later paper[423] Ziegler uses the rate of absorption of nitric oxide at pressures above an atmosphere, which gives a half-life of 3·3 minutes at 0° in chloroform; the value is very little affected by the solvent (he used 16 solvents); from −20° to +10° the heat of reaction is from 10 to 12 k.cals., and the heat of activation 19 to 20. These values are probably more correct than those in the first paper.[422] Bachmann *et al.*[424] measured the rate of dissociation of penta-aryl ethanes by titration with iodine, the dissociation being the slow step. They thus found the effect of the aryl group R in $C_2H\Phi_4R$. These examples (out of 20) give the half-life in minutes:

R = *o*-biphenyl	10·8′	R = phenyl	56·0′
R = *α*-naphthyl	15·9	R = *o*-tolyl	22·2
R = *o*-anisyl	20·2	R = *m*-tolyl	41·1
R = *m*-anisyl	39·6	R = *p*-tolyl	52·8
R = *p*-anisyl	41·8	R = o-F·C_6H_4	63·3
		R = p–F·C_6H_4	66·6

Heat of Dissociation

This has been determined for several of the compounds concerned. For hexaphenyl ethane Ziegler *et al.*[379,422-3] have obtained from the dissociation at various temperatures a value for the heat of the reaction $\Phi_3C—C\Phi_3 = 2\,\Phi_3C$ of 11±1 (endothermic) depending on the solvent used.



Conant[382] examined a series of xanthyl-aryl methyls, and with various aryls found a mean value of 8·7. Bent and Ebers,[426] by determining the equilibrium between $Ar_3C—CAr_3$ and $Ar_3C{\cdot}Na$ in presence of sodium amalgam (the heat of formation of the sodium compound from the radical being practically independent of the nature of the aryl group), confirmed the conclusions of Ziegler and of Conant. We can thus take it that the

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[422] K. Ziegler, L. Ewald, and P. Orth, ib. 1930, **479**, 277.

[423] K. Ziegler, P. Orth, and K. Weber, *Ann.* 1933, **504**, 131.

[424] W. E. Bachmann, R. Hoffman, and F. Whitehead, *J. Org. Chem.* 1943, **8**, 320.

[425] E. Hückel, *Z. physikal. Chem.* 1936, B **34**, 335.

[426] H. E. Bent and E. S. Ebers, *J.A.C.S.* 1935, **57**, 1242.

difference of energy between $Ar_3C—CAr_3$ and 2 Ar_3C instead of being, as it normally is, 81·6 k.cals., is reduced to about 11, owing either to defective stability in the dimer, or to excessive stability (defective energy content) in the monomers, or both.

These are the two possible explanations of the dissociation of compounds such as hexa-aryl ethane: either (1) the steric repulsion of the aryl groups prevents the full union of the two ethane carbon atoms, or (2) some process of resonance which becomes possible in the radical absorbs or neutralizes the extra energy of the unsaturated valency. According to (1) the energy content of the radical is normal, and that of the ethane excessive; according to (2) the energy content of the ethane is normal, and that of the radical abnormally small. The problem can be attacked in two ways, either from the relation between the steric properties of the aryl groups and their observed effect on the dissociation, or by determinations of the thermal strength of the ethane C—C link in these compounds, and of the energies or heats of formation of the ethane molecules and the radicals. The evidence of the first kind has already been discussed above (p. 538), and it has been shown that while the dissociation is in some cases related to the space-filling properties of the groups, in many it cannot be due to this, and must be caused by a stabilizing influence exerted by the aryls on the radicals.

We come next to the thermal evidence on the weakening of the central C—C link in the hexa-aryl ethanes. The difficulty here is that if we determine the heat of transformation of $Ar_3C—CAr_3$ into some compound or compounds in which the C—C link is broken, we need some assurance that the products are not themselves abnormal. This difficulty is emphasized by E. Hückel,[425] who says that the heats of conversion of hexa-aryl ethane into the peroxide or into triaryl methane $Ar_3C \cdot H$ throw no light on the strength of the C—C link, because these products may be as abnormal as the original ethanes. This, however, is an overstatement; such evidence, though perhaps not conclusive, is of considerable force, especially if several reactions of this kind give concordant results. A further though smaller difficulty is that the thermal data should be for the vapour, and this is not practicable with substances of such high boiling-points. The actual data must be obtained for the solids or their solutions, and cannot at present be corrected for the vapour. The corrections will no doubt cancel out to some extent, but not wholly; thus it is found that the heat of hydrogenation of hexaphenyl ethane to triphenyl methane is in the solid 40·5 and in benzene solution 34·8.[426] This indicates the kind of errors to be expected.

The thermal work that has been done on these lines is mainly due to Bent and his colleagues.[394,426–8] The most important of their results are these. They show[426] that the heat of combustion of hexaphenyl ethane is

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[427] H. E. Bent, G. R. Cuthbertson, M. Dorfman, and R. E. Leary, ib. 1936, **58**, 165.

[428] H. E. Bent and G. R. Cuthbertson ib. 170.

4,757 k.cals., while that calculated from the equations of Kharasch,[429] which fit the other phenyl ethanes, is 4,720; the difference of 37 k.cals. may be taken to be the reduction in the strength of the C—C link. Again, the difference between the heat of combustion of hexaphenyl ethane and 2 moles of triphenyl methane, with the ordinary values for the C—C and C—H bonds, should be 56 k.cals., while it is found experimentally to be only 20 k.cals., indicating a weakening of 36 k.cals. Later they determine the heat of oxidation of hexaphenyl ethane to the peroxide $\Phi_3C—O—O—C\Phi_3$, and find it to be 39·3 k.cals. On the 'theoretical' values we have for the change of links:

$$\begin{array}{ccccccc} C—C & + & O{=}O & = & 2\,C—O & + & O—O \\ 81·6 & & 118·2 & & 163 & & 34·9 \\ & 199·8 & & & & 197·9 & \end{array}$$

i.e. an absorption of 1·9 k.cals. so that the C—C link in the ethane (assuming the C—O to be normal) should be weakened by 41·2 k.cals.

Bent and Cuthbertson[428] measure the heat of the reaction

$$\Phi_3C—C\Phi_3 + H_2 = 2\,\Phi_3C\cdot H$$

and find that this is in the solid state 40·5 and in benzene solution 34·8 k.cals. (exothermic). According to the more recent values of Rossini[430] for the heats of combustion of the paraffins this reaction should evolve 7·9 k.cals. It thus appears that the weakening of the C—C link as calculated from the heat of hydrogenation in the solid state is $40·5-7·9 = 32·6$, and from that in benzene solution $34·8-7·9 = 26·9$. We may take the mean value of 30 k.cals. as the most probable. Bent and his collaborators thus get the following four values for the weakening of the C—C link—for the difference between its heat of formation in hexaphenyl ethane and in a normal hydrocarbon:

By heat of combustion of Φ_8C_2 compared with phenyl ethanes .	37 k.cals.
The same, compared with $\Phi_3C\cdot H$	36 ,,
By heat of oxidation to peroxide	41 ..
By heat of hydrogenation to triphenyl methane	30 ,.
Mean value	36 ,,

All these results are independent of the value assumed for the heat of atomization of carbon, since this always comes in equally on both sides. But if we want to know the absolute value of the C—C link, or its relative weakening, we must take this heat of atomization (H_{at}), 170·4 k.cals., into account. We then get for a weakening of 36 k.cals.:

Normal C—C	*Reduced* C—C	*Red./Norm.*	*Extra res. energy of* Φ_3C
81·6	45·6	0·56	17·3

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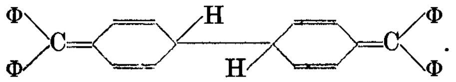
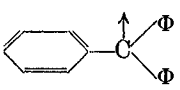
[429] M. S. Kharasch, *Bur. Stand. J. of Res.* 1929, **2**, 359.

[430] F. D. Rossini, ib. 1934, **13**, 21, 189.

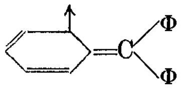
The heat of conversion of hexaphenyl ethane into 2 molecules of triphenyl methyl is 11 k.cals. If there were no extra resonance energy in the radicals it would (with this weakening) be 45·6 k.cals., so that the extra resonance stability of each radical must be 17·3 k.cals. Hence we may conclude with Bent that the dissociation of hexaphenyl ethane is about half due to the steric weakening of the C—C link, and about half to the resonance stabilization of the two resulting radicals. It must be remembered that these values are worked out for the hexaphenyl compound where the dissociation is small. It is evident that in such compounds as the diphenyl-vinyl derivatives the disappearance of the steric effect is more than compensated by an increase in the resonance.

The nature of the resonance in the radicals has been discussed by E. Hückel,[431] and in more detail by Pauling and Wheland.[432] The calculations are given in the original papers; but it must be remembered that the amount of resonance energy to be accounted for is only about half what it would be if the steric effect could be neglected. Resonance between the monomer Φ_3C and the dimer $\Phi_3C—C\Phi_3$ is of course impossible, since the former has an unpaired electron which is paired in the dimeric form. The possible resonance formulae given by Pauling and Wheland are A and B below (the vertical arrow shows the atom which has only 7 valency electrons); it would seem, however, that we should add the paraform C, especially as it has been shown that triphenyl methyl can be transformed into the para-compound





A



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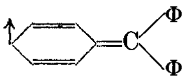

C

The resonance must obviously occur with each of the three phenyl groups, making seven resonance forms in all that are possible only in the radical. These are very much the ideas of Ingold.[433]

Stereochemistry. The central carbon atom must have a tetrahedral distribution of valencies in $Ar_3C—CAr_3$, and in the anion $[Ar_3C]^-$; in the cation $[Ar_3C]^+$, where it has a valency sextet, we should expect a plane arrangement of the valencies, with angles of 120°. The neutral radical on the analogy of chlorine dioxide and (probably) diborane should also have a tetrahedral arrangement. The experimental evidence does not take us far. Adams and Wallis[434] prepared the optically active 12-phenyl-12 benzoxanthracene thioglycollic acid; sodium converts this into the salt $[Ar—C{=}Ar']Na$, which is reduced by ammonium bromide in liquid

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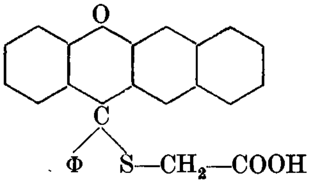
[431] *Trans. Far. Soc.* 1934, **30**, 40.

[432] L. Pauling and G. W. Wheland, *J. Chem. Phys.* 1933, **1**, 362.

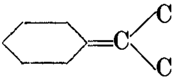
[433] C. K. Ingold, *Trans. Far. Soc.* 1934, **30**, 52.

[434] F. H. Adams and E. S. Wallis, *J.A.C.S.* 1932, **54**, 4753.

ammonia to the methane derivative [Ar—C=Ar′]H. When this has been carried out the product is found to be optically active, showing that the trivalent radical is so too. In these reactions, however, there is no evidence that a neutral radical of the Ar_3C type is ever formed; it occurs as the anion in the sodium salt, but as this has a complete octet the tetrahedral disposition is bound to be maintained.



The suggested resonance forms B and C for the trivalent carbon radical require that the group



should be planar, and since all three aryl groups must partake equally in the resonance, all the carbon atoms in triphenyl methyl must lie in a plane, with all the valencies of the central carbon at 120° to one another. But when the two triphenyl methyl radicals polymerize to hexaphenyl ethane this plane arrangement is no longer possible; the methyl carbons now have fully shared octets and their valencies must be tetrahedrally disposed; also it is easy to see that for steric reasons two neighbouring 6-rings could not then lie in the same plane. The resulting loss of resonance energy must offset all but 11 k.cals. of the heat evolved by the saturation of the fourth valencies of the methyl carbons.

Comparison of the Trivalent Radicals of Carbon with those of other Elements, especially of Group IV

In the series silicon, germanium, tin, lead, the strength of the A—A bond falls off with a rise of atomic weight, and so less resonance energy is required to reduce it to zero. We should therefore expect these elements to form trivalent radicals with increasing ease. This is on the whole true, but it is curious that *silicon*, unlike its neighbours on both sides, cannot become trivalent any more than it can become divalent. There are no signs of dissociation in the $R_3Si—SiR_3$ compounds: $\Phi_3Si—Si\Phi_3$ gives no sign of it and melts undecomposed at 354°.[435]

With germanium there are no trivalent radicals Ar_3Ge; hexaphenyl digermane $\Phi_3Ge—Ge\Phi_3$ gives no indication of dissociation in benzene; but the sodium salts of these radicals, such as $Li[Ge\Phi_3]$ and even $Na[GeEt_3]$ are known.

With *tin* the hexa-aryl and even the hexa-alkyl compounds (including the hexa-cyclohexyl distannanes) seem undoubtedly to be largely dissociated, although this has been denied on the ground that they are diamagnetic. The sodium compound $Na\cdot SnMe_3$ exists and even Na_2SnMe_2.

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[435] **W. Schlenk, J. Renning, and G. Racky, *Ber.* 1911, 44, 1178.**

With *lead* the position is much the same as with tin; all the evidence, other than the magnetic, points to great dissociation not only of the hexa-aryl compound $Ar_3Pb—PbAr_3$, but almost as much of the alkyls $Alk_3Pb—PbAlk_3$.

A different kind of comparison can be made between the positive, neutral, and negative triaryl methyl molecules and the corresponding derivatives of *boron* on the one side and *nitrogen* on the other. We have $[Ar_3C]^+$ with the valency group $\underline{6}$: the neutral $[Ar_3C]^\circ$ with a septet 1, $\underline{6}$: and the negative $[Ar_3C]^-$ with 2, $\underline{6}$. Isoelectronic with these are the triaryl boron derivatives $[Ar_3B]^\circ$ ($\underline{6}$), $[Ar_3B]^-K$ (1, $\underline{6}$), and $[Ar_3B]^{--}K_2$ (2, $\underline{6}$): and with nitrogen the 'tetravalent' derivatives such as the salt $[Ar_3N]^+(ClO_4)^-$ (1, $\underline{6}$) with its hydrazyl analogues, and of course triarylamine $[Ar_3N]^\circ$, with an octet 2, $\underline{6}$.

We thus have the series:

Val. group	B	C	N
$\underline{6}$	Ar_3B	$[Ar_3C]^+$	..
1, $\underline{6}$	$[Ar_3B]^-$	Ar_3C	$[Ar_3N]^+$
2, $\underline{6}$	$[Ar_3B]^{--}$	$[Ar_3C]^-$	Ar_3N

COMPOUNDS OF DIVALENT CARBON

All the elements of the series from carbon to lead, with the probable exception of silicon, can occur in the divalent state, but the changes in the stability of that state are peculiar. This stability is very great in lead, but it dies away as we ascend the series until it has almost if not quite disappeared in silicon. This is to be expected from the behaviour of the B elements of others of the later groups. But the divalency reappears in considerable force in carbon, where obviously some new factor comes in. This is in fact the greater stability of multiple links, making such structures as $\overset{-}{C}\equiv\overset{+}{O}$ stable, which they are not with the heavier elements. The most important compounds of divalent carbon are the monoxide and the isonitriles or carbylamines.

Carbon Monoxide

This is formed when carbon is burnt in defect of air,[268] and so is a considerable constituent of producer gas (about 25 per cent.) and of water gas (about 40 per cent.). It is commonly made in the laboratory by the action of sulphuric acid on formic or (together with carbon dioxide) on oxalic acid. The purest is made by decomposing nickel carbonyl at 200°.[436]

Carbon monoxide boils at $-190°$ and freezes at $-205{\cdot}1°$.[437] It is very stable in the cold, but at higher temperatures behaves as unsaturated.

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[436] G. Meyer, R. A. Henkes, and A. Slooff, *Rec. Trav.* 1935, **54**, 797.

[437] R. Kaischew, *Z. physikal. Chem.* 1939, B **40**, 273.

On heating, especially in the presence of a catalyst, it undergoes the reversible reaction

$$2\,CO \rightleftharpoons C + CO_2$$

which evolves 38·8 k.cals.; at equilibrium the percentage of the dioxide is 90 at 550° C. and about 1 at 1,000°.[446] Hence carbon monoxide can act as a reducing agent, and does so in many metallurgical processes; it can also take up chlorine to give phosgene $COCl_2$ and sulphur to give the oxysulphide COS, etc. Though it has the formula of an anhydride of formic acid it has no action on alkali until it is heated, when it gives the formate. Its most remarkable power is that of forming compounds, often volatile (the carbonyls) with a variety of metals. These compounds are described in the next section (p. 547), although strictly the carbon in them is tetravalent.

Carbon monoxide is a powerful poison, since it forms a compound with haemoglobin which is more stable than oxy-haemoglobin, and prevents it from carrying oxygen.

Structure. The older doubly linked formula $C{=}O$ is in many ways unsatisfactory, and Langmuir[438] suggested the triply linked structure $\overset{-}{C}\equiv\overset{+}{O}$, which is undoubtedly in close agreement with the properties of the substance, though the first must occur as a resonance form (see Pauling, *Chem. Bond*, p. 139). Langmuir's structure is supported by the dipole moment which is nearly zero (0·10 D)[439,440]; since the carbonyl group in aldehydes and ketones has a moment of about 2·3 D, $C{=}O$ itself should be highly polar, and there must be some opposing moment present, which is obviously that of the co-ordinate link. The interatomic distance and the heat of formation from the atoms confirm this view.*

	Calculated for			*Obs. Carbon Monoxide*
	C—O	C=C	$C\equiv O$	
Distance	1·43	1·21	1·10	1·13[a]
Heat of formation H_a . .	81·5	173	256	256[b]

$a = {}^{441}$; $b = {}^{442}$.

The triple link is further supported by the diamagnetic susceptibility.[443]

Similarly the structure of the isocyanides must be $R—\overset{+}{N}\equiv\overset{-}{C}$.[444] The —NC group in the aryl compounds was shown to have a moment of 3·6 D

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* It should be noticed that the resonance itself will shorten the interatomic distance and increase the heat of formation, thus bringing both these values nearer to those of the triple link, and exaggerating the apparent importance of the latter.

[438] I. Langmuir, *J.A.C.S.* 1919, **41**, 1543.

[439] C. T. Zahn and J. B. Miles, *Phys. Rev.* 1928, **32**, 497.

[440] H. E. Watson, G. G. Rao, and K. L. Ramaswamy, *Proc. Roy. Soc.* 1934, **143**, 558.

[441] L. Gerö, G. Herzberg, and R. Schmid, *Phys. Rev.* 1937, **52**, 467.

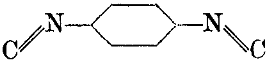
[442] Bichowsky and Rossini, *Thermochemistry*.

[443] R. J. Jaanus and J. A. Shur, *Phys. Z. Soviet-union*, 1935, **7**, 19.

[444] D. Ll. Hammick, R. G. A. New, N. V. Sidgwick, and L. E. Sutton, *J.C.S.* 1930, 1876.

with the negative end away from the nucleus; in Ar—N═C it would be in the opposite direction. Further, *p*–di-isocyanobenzene has been found[445] to have zero moment, showing that the —NC atoms lie on the line joining the two para-positions, which again implies a triple link, as in I, not II.

(I)



(II)

Metallic Carbonyls

These are discussed in detail under the various metals, the references being:

Gp. I. Cu′ 131; Ag′ 132; Au′ 133.
Gp. II. Hg 306.
Gp. VI. Cr 1026; Mo, W 1066.
Gp. VII. Re 1314.
Gp. VIII A. Fe 1369; Ru 1482; Os 1509.
,, B. Co 1422; Rh 1528; Ir 1548.
,, C. Ni 1451; Pd 1577; Pt 1627.

They are compounds in which the CO group is attached to a metallic atom. It must occupy one co-ordination place, since it replaces, for example, one CN radical in forming $K_3[Fe(CN)_5CO]$. The metal must be attached to carbon and not to oxygen, since carbon is normally, and oxygen only rarely, 4-covalent. The M—C—O atoms are always found by X-ray analysis or electron diffraction to be linear, so that the group must be written $\overset{-}{\mathrm{M}}\text{—}\mathrm{C}\equiv\overset{+}{\mathrm{O}}$ or $\mathrm{M}\leftarrow\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$. The M—C distance is, however, as a rule abnormally short, in nickel carbonyl, for example, 1·82 (theory 2·16: for Ni″), and the C—O distance between the value for a double and a triple link (theory C═O 1·21, C≡O 1·10: observed in carbon monoxide 1·13, in the metallic carbonyls 1·14–1·15 A). This indicates that the structure M═C═O occurs as a resonance form.*

The carbonyl compounds are confined to Groups VI A, VII A, and VIII, with a few of a peculiar kind in I B and II B. The valencies of the central atoms can be calculated in the usual way when the structures are known, but they do not seem to have much relation to the ordinary valencies. Apart from the $M_2(CO)_9$ compound of iron (and presumably those of ruthenium and osmium also), where the metal has been shown to have a valency of 4, they have the values 0, 1, and 2. But evidently the determining factor is not so much the valency as a very peculiar relation of the E.A.N. (effective atomic number) to the atomic number of the next

* See L. Pauling, *Chem. Bond*, ed. 2, p. 251.

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[445] R. G. A. New and L. E. Sutton, ib. 1932, 1415.

[446] For the exchange of isotopic oxygen in this reaction see J. D. Brandner and H. C. Urey, *J. Chem. Phys.* 1945, **13**, 351.

higher inert gas. In the simple 'binary' carbonyls $M(CO)_y$, with one metallic atom in the molecule, the E.A.N. of M (which obviously is its at. no. $+2y$) is always the inert gas number: 36 in $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$; 54 in $Mo(CO)_6$, $Ru(CO)_5$; and 86 in $W(CO)_6$ and $Os(CO)_5$. In the odd groups VII and VIII B no such arrangement is possible, and there are no simple 'binary' carbonyls. Where there are several M atoms in the molecule a similar relation holds. If $M_x(CO)_y$ is the compound, and m the at. no. of M, and G that of the next higher inert gas, then:[447]

$$G-\frac{xm+2y}{x}=x-1.$$

If the E.A.N. (calculated as before for 2 electrons added per CO) is, say, 35 instead of 36, there are found to be 2 M's in the molecule (by polymerization or otherwise): if 34, then 3 M's and so on. Among the binary carbonyls this is supported by the following compounds, whose molecular weights are known, $(Re(CO)_5)_2$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_4(CO)_{12}$; together with a great many more complicated carbonyl derivatives, such as the hydrides $Fe(CO)_2(CO\cdot H)_2$ and $Co(CO)_3(COH)$ and their metallic derivatives, as well as many carbonyl halides and carbonyl ammines. In fact the majority of the carbonyl compounds (though not all) agree with this rule, which presumably means that the E.A.N.s of the metallic atoms are still those of the next inert gas; in the only complicated carbonyl whose structure is known, $Fe_2(CO)_9$, this is certainly true. The same rule can be extended to the nitrosyl compounds (see V. 686) if the NO group is assumed to add 3 electrons to the central atom, as the CO adds 2.

The carbonyl compounds comprise (1) 'binary' carbonyls $M_x(CO)_y$; (2) carbonyl halides, such as $Fe(CO)_4hal_2$; (3) ammines of the carbonyls and carbonyl halides, as $Re(CO)_3py_2$ and $Re(CO)_3py_2$ hal; (4) carbonyl hydrides, such as $H_2Fe(CO)_4$—really $Fe(CO)_2(CO\cdot H)_2$—and their metallic derivatives, and (5) compounds with only one CO group on the metal. Mixed carbonyl-nitrosyl compounds are described under Nitrogen (V. 687).

Class 1 has already been discussed; class 2 (the carbonyl halides) occurs with chlorine, bromine, and iodine; they are especially easily made by Hieber's method of treating the metallic halides with carbon monoxide under high pressure. They contain per metallic atom 1 or 2 halogen atoms and from 1 to 5 carbonyls. Their properties are those of covalent halides, and the halogen is evidently attached to the metal. While many, such as $Re(CO)_5X$ and $Os(CO)_4X_2$, conform to the inert gas rule, or can be made to do so by a probable assumption as to their polymerization (such as $Os(CO)_3Cl_2$ and $Ir(CO)_2X_2$, which should be tri- and tetrameric respectively), others depart widely from it, such as $Rh(CO)_2Cl_2$, which should be tetrameric and is found to be dimeric, and $Au(CO)Cl$, which is monomeric though the simple E.A.N. is 82, so that the rule would require 5-fold polymerization.

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[447] N. V. Sidgwick and R. W. Bailey, *Proc. Roy. Soc.* 1934, **144**, 521.

Ammines. Carbonyl compounds can have one or two groups replaced by as many amine molecules, as in $Re(CO)_3py_2$ (presumably dimeric) and $Re(CO)_3py_2X$; this leaves the E.A.N. unaffected. Other donors can replace the amines, as in $(CO)_4Fe \leftarrow SbCl_5$ and $(CO)_4Fe \leftarrow SnCl_4$ (monomeric). Some of the ammines are difficult to formulate, such as $Fe(CO)_5$, 4 $EtNH_2$, in which the iron seems to have the E.A.N. of 44.

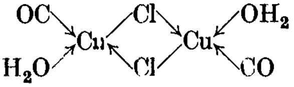
Carbonyl hydrides. These remarkable compounds, which are made by the direct or indirect reduction of the carbonyls, are highly volatile substances which have one or two hydrogen atoms in addition to the metal and the CO groups. Two of them have been isolated, of the compositions $H_2Fe(CO)_4$ and $H \cdot Co(CO)_4$, and two more, of rhodium and iridium, presumably $H \cdot Rh(CO)_4$ and $H \cdot Ir(CO)_4$, have been shown to exist. Their structure follows from the fact that electron diffraction shows that the iron and cobalt hydrides have the 4 CO groups tetrahedrally arranged, with M—C—O linear. Hence the hydrogen cannot be on the metal, but must be attached to the oxygen in the form $M—C \equiv O—H$; the oxygen atom, since it has 4 covalencies and can only carry 8 valency electrons, must transfer 2 to the metal, giving $\overset{-}{M}—C \equiv \overset{+\cdot}{\overset{+}{O}}\cdot—H\cdot$. The structure is unusual, but is exactly like that of the nitrosyls, which is shown (V. 686) to be $\overset{=}{M}—\overset{+}{N} \equiv \overset{+}{O}$; both of these groups can increase the E.A.N. of the central atom by one more than CO can (3 instead of 2), and so in combination with the metals of the series nickel—cobalt—iron they can make up for the fall in the atomic number: as is shown in the series of similar compounds—all volatile—which they form:

$Ni(CO)_4$	$Co(CO)_3COH$	$Fe(CO)_2(COH)_2$
	$Co(CO)_3NO$	$Fe(CO)_2(NO)_2$

The hydrogen atoms in these hydrides can be replaced by metals or complex cations, the products sometimes being apparently true salts, as in $[Zn(NH_3)_3](Fe(CO)_4)$ and $[Co(NH_3)_6] \cdot [Fe(CO)_3COH]_3$; but remarkably often covalent, especially the cobalt hydride compounds of B elements—Zn, Cd, Hg, (Et_2Pb) In, Tl, and Sn: the last compound being $Sn(Co(CO)_4)_4$, the only known molecule with 16 CO groups. These compounds are crystalline, insoluble in water, soluble and monomeric in benzene; with hydrochloric acid they regenerate the hydride. The derivatives of the iron hydride are similar.

Finally, we have a rather miscellaneous series of compounds with only one CO in the molecule. Many of these show the peculiarities of the ordinary carbonyls. For example, the ferrous pentacyano ('prusso') complex salts $M_2[Fe(CN)_5CO]$ are much less easily oxidized to the ferric state than the ferrocyanides, since this would lower the E.A.N. from 36 to 35, which is usually impossible for a true carbonyl. Among the few compounds of monovalent nickel is the salt $K_2[Ni(CN)_3CO]$. To this class belong also the only known carbonyl compounds of Groups I and II.

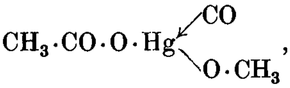
Cuprous chloride solutions (in hydrochloric acid, aqueous ammonia or potassium chloride solution) absorb carbon monoxide in the cold, and colourless crystals will separate out of the composition CuCl, CO, H_2O; in the same way solid cuprous chloride will absorb carbon monoxide if wet, but not if dry. The compound may probably be written



(E.A.N. 36).

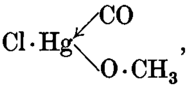
Silver sulphate in concentrated and especially fuming sulphuric acid absorbs carbon monoxide up to nearly 1 CO/Ag_2SO_4, and may form a similar compound, but it has not been isolated. Finally, aurous chloride in the *dry* state absorbs the monoxide to give Cl—Au ← CO, soluble and monomeric in benzene; the low co-ordination number is characteristic of aurous gold, but it is to be noticed that the E.A.N. is only 82.

Mercuric acetate in methyl alcohol takes up carbon monoxide readily, giving



$$\mathrm{CH_3\cdot CO\cdot O\cdot Hg}\begin{matrix}\swarrow \mathrm{CO}\\ \diagdown \mathrm{O\cdot CH_3}\end{matrix},$$

(E.A.N. 84) converted by potassium chloride into the chloride



$$\mathrm{Cl\cdot Hg}\begin{matrix}\swarrow \mathrm{CO}\\ \diagdown \mathrm{O\cdot CH_3}\end{matrix},$$

and on treatment with hydrochloric acid at once evolving carbon monoxide to form a complex mercuric halide, a sign that the CO is co-ordinated to the mercury.

GROUP IV B

SILICON, GERMANIUM, TIN, LEAD

THE difference in properties between carbon and silicon is very marked; the main causes are (1) the increase of the covalency maximum from 4 to 6, (2) the change in the relative affinities for hydrogen and oxygen, the heat of linkage of carbon being 17·3 k.cals. greater to hydrogen than to oxygen, while that of silicon is 14·2 k.cals. less; (3) multiple links, especially to oxygen, are much less stable than with carbon. The first two of these combine to make silicon chains unstable, the first diminishing the heat of activation by allowing further co-ordination to 4-covalent silicon, and the second increasing the heat of oxidation.

The heat of linkage of carbon and silicon, and their differences, are given here:

	A—A	A—H	A—O	A—S	A—F	A—Cl	A—Br	A—I
A = C	81·6	98·8	71·5	66·0	103·4	78·0	65·5	57·0
A = Si	42·5	75·1	89·3	60·9	127·9	85·8	69·3	51·1
Diff.: (C—X)—(Si—X)	+39·1	+23·7	−17·8	+5·1	−24·5	−7·8	−3·8	+5·9

Heat of formation of Si—C is 57·6 k.cals.

The chemistry of the two elements has been discussed in detail by Stock,[448] who points out that compared with that of carbon the affinity of silicon for hydrogen is weak, for silicon itself is not strong, especially in chains, for nitrogen is weak, while that for oxygen is the strongest except that for fluorine, though the double link Si=O is unstable. All these points are illustrated in what follows.

The abundance of these elements in the earth's crust is in g per ton

C	Si	Ge	Sn	Pb
800	276,000	7	40	16

(Compare the values Ga 15, Nd 24, Th 11.)

The Elements

These five elements occur in three different lattices, which are distributed thus:

	C	Si	Ge	Sn	Pb
Diamond lattice	+	+	+	+	
Graphite lattice	+				
Metallic lattice				+	+

The boiling-points and melting-points are:

	Carbon	*Silicon*	*Germanium*	*Tin*	*Lead*
B. pt.	3,470° sbl.	2,355°	2,700°	2,362°	1,755° C.
M. pt.	3,570°	1,414°	958·5°	231·8°	327·5°

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[448] A. Stock, *Ber.* 1917, 50, 170.

The metallic lattice becomes more stable with rise of atomic number, and is the only form with lead.

Silicon

This is the commonest element (27·6 per cent.) after oxygen (49·4 per cent.) in the earth's crust. Silicates form the main constituents of igneous rocks; silica (quartz, sandstone, etc.) is the result of their weathering, being slowly expelled by carbon dioxide at lower temperatures.

Silicon is relatively inactive; it is attacked by halogens and even by dilute alkali, but by scarcely any acids other than hydrofluoric.

Germanium

This is ekasilicon, one of the elements whose properties were predicted by Mendeleeff from the Periodic Table in 1871; it was discovered in 1886 by Winkler in a new mineral argyrodite, 4 Ag_2S, GeS_2.

It occurs up to 0·17 per cent. in certain American zinc oxide ores[449] and in minute quantities (on the average 6 parts per million)[450] in nearly all silicates.[451-2]

Germanium is more reactive than silicon; it dissolves in concentrated nitric or sulphuric acid, though not in dilute alkali except in presence of hydrogen peroxide, which is the best solvent for it.[453]

It is remarkable that of its five isotopes (70, 72, 73, 74, 76) three are isobars (70 Zn, 74, 76 Se).

Tin

There is a marked change in properties when we pass from germanium to tin; this has the electrical conductivity of a true metal, and it forms monatomic ions in solution, which germanium does not. It occurs in two or perhaps three allotropic forms: grey tin (density 5·765), which on warming changes at 13·2°[454] into white tin (tetragonal: density 7·285), the ordinary form; this probably[455-6] changes at 161° to a third rhombic form, stable up to the m.pt. 232°[455-6] The change from white to grey tin at low temperatures is very slow, and is catalysed by grey tin or stannic solutions; this change is the cause of 'tin pest'.

Grey tin has a diamond lattice (hence the low density) and white a metallic.

Tin is slowly attacked by dilute acids and readily by strong, nitric acid forming tin dioxide SnO_2; also by chlorine and bromine: boiling alkali converts it into a stannate.

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[449] L. M. Dennis and J. Papish, *J A.C.S.* 1921, **43**, 2131.

[450] V. M. Goldschmidt and C. Peters, *Nachr. Ges. Wiss. Gott.* 1933, 141.

[451] J. Papish, *Econ. Geol.* 1929, **24**, 470.

[452] I. and W. Noddack, *Z. physikal. Chem.* 1931, **154**, 214.

[453] L. M. Dennis, *Z. anorg. Chem.* 1928, **174**, 137.

[454] E. Cohen and A. K. W. A. van Lieshout, *Z. physikal. Chem.* 1935, **173**, 32.

[455] See P. Saldau, *Z. anorg. Chem.* 1930, **194**, 1.

[456] But see C. W. Mason and G. E. Pellissier, *Amer. Inst. Min. Met.* 1930, 1043.

Lead

This is more reactive still, though with the massive metal reaction is often stopped by a protective layer on the surface. Thus finely divided lead is pyrophoric, but ordinary lead is only superficially oxidized in air. Its high overvoltage makes it seem more noble than it really is: the true electrode potential to normal hydrogen is −0·1 volt. but the overvoltage may amount to 0·64 volt.

It dissolves in water and in ordinary acids owing to the presence of dissolved oxygen: water containing acid carbonates (ordinary hard water) stops the action by forming a layer of basic carbonate.

Lead is the final product of each of the three radioactive series, the atomic weights being: from radium 206, from thorium 208, and from actinium 207. Hence the atomic weight of lead from radioactive minerals will vary, and the value indicates its origin. For recent work on this subject see references [457-61].

Hydrides

All the typical and B elements of this group, as of the succeeding groups, form volatile hydrides, but with increasing difficulty as the atomic number increases. The boiling- and melting-points of some of the simpler are:

		Carbon	*Silicon*	*Germanium*	*Tin*	*Lead*
AH_4	b.pt.	−161·3°	−111·9°	−90°	−52°	(*ca.* −13°)
	m.pt.	−182·7°	−185°	−165°	−150°	?
A_2H_6	b.pt.	−88·7°	−14·5°	+29°		
	m.pt.	−183·7°	−132·5°	+109°		
A_3H_8	b.pt.	−44·5°	+52·9°	+110·5°		
	m.pt.	−189·9°	−117·4°	−105·6°		
A_4H_{10}	b.pt.	+0·5°	107·4°[a]			
	m.pt.	−135°	−84·3°			

a = [470].

Silicon. The main work is that of Stock,[462] who used methods similar to those for the boron hydrides, the action of hydrochloric acid on magnesium silicide Mg_2Si, followed by fractionation at low temperatures. The yield is about 25 per cent., much larger than with boron. In the absence of other substances they are relatively stable; they are decomposed by the electric discharge,[463] by ultraviolet light,[464] and by heating to temperatures of 300° above[465-6]; the products are hydrogen, silicon, and a solid hydride of composition about SiH. They are spontaneously inflammable in air

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[457] F. Hecht and E. Kroupa, *Z. anorg. Chem.* 1936, **226**, 248.

[458] G. P. Baxter, J. H. Faull, and F. D. Tuemmler. *J.A.C.S.* 1937, **59**, 702.

[459] J. P. Marble, ib. 653.

[460] J. Mattauch and V. Hauk, *Naturwiss.* 1937, **25**, 763.

[461] A. O. Nier, R. W. Thompson, and B. F. Murphey, *Phys. Rev.* 1941, ii. **60**, 112.

[462] See A. Stock, *Hydrides of Boron and Silicon*, Cornell, 1933.

[463] R. Schwarz and F. Heinrich, *Z. anorg. Chem.* 1935, **221**, 277.

[464] H. J. Emeleus and K. Stewart, *Trans. Far. Soc.* 1936, **32**, 1577.

[465] T. R. Hogness, T. L. Wilson, and W. C. Johnson, *J.A.C.S.* 1936, **58**, 108.

[466] H. J. Emeleus and C. Reid, *J.C.S.* 1939, 1021.

(there is also a low pressure explosion range[467-9]); they are chlorinated by hydrogen chloride with formation of hydrogen (this is characteristic of the hydrides of boron and silicon), and the merest trace of alkali in presence of water decomposes them into hydrogen and the silicon hydroxide.[470a]

The *germanium* hydrides can be made in the same way (Dennis, 1924),[471] or by the electrolytic reduction of germanium dioxide in concentrated sulphuric acid with lead electrodes (Paneth).[472] Later Kraus and Carney[473] showed that they can be made by the action of ammonium bromide in liquid ammonia (which behaves like hydrogen bromide in water) on magnesium germanide Mg_2Ge; up to 70 per cent. of hydride, mainly GeH_4, can thus be obtained.

The germanes are much less stable to heat than the silicanes, but they are less reactive with oxygen or water. Emeleus and Gardner[474] find that germane GeH_4 does not react with oxygen below 230° or explode below 330°; it is less explosive than digermane Ge_2H_6 (the same is true of SiH_4 and Si_2H_6).[474-5]

Pauling *et al.*[476] find by electron diffraction that the Ge—Ge distance in Ge_2H_6 and Ge_3H_8 is 2·41 A; in elementary germanium it is 2·44.

A solid hydride $(GeH_2)_x$, made from calcium germanide Ca_2Ge and hydrochloric acid, has been described[477-8]; it is a yellow solid which gives off GeH_4 and some of the lower hydrides on heating, and is ultimately converted by alkalis into the germanite Na_2GeO_2 and hydrogen.

Tin hydride or stannane SnH_4 was obtained by Paneth in 1919[479-82] by the electrolytic reduction with a lead cathode (utilizing the overvoltage of lead) of a solution of stannic sulphate in sulphuric acid; the yield is only some 2-3 mg. per hour.

Lead hydride, plumbane, presumably PbH_4. This was the most difficult hydride of all to make. It was prepared by Paneth in 1920.[480,483] He first showed that the gas evolved by the action of hydrochloric acid on magnesium lead alloy Mg_2Pb containing radioactive lead (thorium B) carried the active element with it, and so must contain lead hydride: but there was not enough to give a visible deposit of lead on heating. Electrolytic reduction, as with tin, was no use, nor the dispersion of lead fog by the arc

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[467] H. J. Emeleus and K. Stewart, *Nature*, 1935, **135**, 397.

[468] Id., *J.C.S.* 1935, 1182.

[469] Id., ib. 1936, 677.

[470] H. J. Emeleus and A. G. Maddock, ib. 1946, 1131.

[470a] F. P. Price, *J.A.C.S.* 1947, **69**, 2600.

[471] L. M. Dennis, R. B. Corey, and R. W. Moore, ib. 1924, **46**, 657.

[472] F. Paneth and E. Rabinovitsch, *Ber.* 1925, **58**, 1138.

[473] C. A. Kraus and E. S. Carney, *J.A.C.S.* 1934, **56**, 765.

[474] H. J. Emeleus and E. R. Gardner, *J.C.S.* 1938, 1900.

[475] H. J. Emeleus and H. H. G. Jellinek, *Trans. Far. Soc.* 1944, **40**, 93.

[476] L. Pauling, A. W. Laubengayer, and J. L. Hoard, *J.A.C.S.* 1938, **60**, 1605.

[477] P. Royen and R. Schwarz, *Z. anorg. Chem.* 1933, **211**, 412.

[478] Id., ib. **215**, 295.

[479] F. Paneth and K. Fürth, *Ber.* 1919, **52**, 2020.

[480] F. Paneth, *Z. Elektrochem.* 1920, **26**, 452.

[481] Id., ib. 1923, **29**, 97.

[482] See also F. Paneth, *Radioactive Elements as Indicators*, Cornell, 1928, p. 97.

[483] F. Paneth and O. Nörring, *Ber.* 1920, **53**, 1693.

n an atmosphere of hydrogen. Finally, he used a method which combined he last two, and effected the electrolytic reduction of the finely divided ead. The lead solution was electrolysed with a small lead cathode at 220 volts in a kind of little Kipp apparatus with a capillary delivery tube, so that as soon as the evolution of hydrogen began, the liquid was depressed and the electrode began to arc. This stopped the stream of hydrogen, and the liquid rose again, and so on. Thus the fine lead dust sputtered by the arc was continuously reduced. In this way enough hydride was formed for the gas to give a visible deposit of lead when passed through a hot tube. The plumbane could even be condensed with liquid air and re-evaporated. It was found to decompose fairly rapidly at or below the ordinary temperature; the boiling-point of −13° was arrived at only by extrapolation.

The chemical properties of these hydrides show how the affinity of the element for hydrogen falls off with rise of atomic number (C—H 98·8; Si—H 75·1); the temperatures at which, when heated alone, they break up into the element and hydrogen are approximately

CH_4	SiH_4	GeH_4	SnH_4	PbH_4
800°	450°	285°	150°	0°

The order of reactivity with oxygen, depending partly on the heat of oxidation and partly on the heat of activation, is more complicated. Methane does not catch fire in air below 500°; silicane is spontaneously inflammable in the cold; germane is scarcely oxidized below 300°. The tin and lead hydrides have not been fully examined.

Carbides

The carbides of the elements of this group other than silicon seem to be almost unknown.

Silicon carbide SiC is carborundum. It can be made by heating carbon with silicon (Moissan) or with silica (Acheson) to 2,000° in the electric furnace. It is almost as hard as diamond, and is widely used as a grinding and polishing material. It occurs in three very similar forms, closely related to diamond, zinc blende, and wurtzite respectively[484]; they are obviously giant molecules, and are like diamond in which every alternate carbon atom has been replaced by silicon. It does not break up into its elements below 2,200°, and is only attacked by chemical reagents at high temperatures.

ORGANIC COMPOUNDS OF GROUP IV B

A very large number of alkyl and aryl compounds of silicon, germanium, tin, and lead are known. The idea that silicon has an organic chemistry of its own, rivalling that of carbon, is now realized to be untrue, owing to the instability of the Si—Si and Si—H links. But compounds in which the atoms of any of these elements have all their valencies occupied by hydrocarbon radicals are numerous and stable, and give rise to various derivatives.

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[484] Wells, *S.I.C.*, p. 460.

These compounds have the A atoms (A = Si, Ge, Sn, Pb) linked to carbon, either alone or along with other links to hydrogen, to oxygen, to halogens, or to other A atoms. All these links get weaker as the atomic weight of A increases: a few have been measured and may be quoted here.

Heats of Linkage in k.cals.

C—C	Si—C	Si—Si	Ge—Ge	C—H	Si—H
81·6	69·1	42·5	42·5	98·8	75·1

Qualitative evidence of the weakening of the A—C link is abundant. In $SiAlk_4$ chlorine and bromine attack the C—H rather than the Si—C link; in $GeAlk_4$ they attack one of the Ge—C links, while from the tin and lead compounds they remove two alkyl groups at once. The preparation of tetra-alkyl compounds with four different alkyl groups, which is possible with silicon, cannot be effected with tin or lead. In the same way silicon tetra-phenyl boils undecomposed above 530°, and can be nitrated, sulphonated, or halogenated, while lead tetraphenyl decomposes at 270°, and has all its phenyl groups removed by heating with glacial acetic acid.

Among the various hydrocarbon radicals the aryls are on the whole less firmly attached than the alkyls; an example is given by diethyl germanium diphenyl, which with bromine loses its phenyls but not its ethyls, giving Et_2GeBr_2 and bromobenzene.

While the change of properties of any type of compound is continuous as we go from silicon to lead—the compound of an intermediate A is intermediate in properties—there is a much greater gap between germanium and tin than elsewhere;* this of course applies to all the compounds, and not only to the organic.

A brief survey of the organic derivatives of all four elements may be given first, followed by a more detailed account.

1. *Tetra-alkyls and Tetra-aryls*

These, as we have seen, are exceptionally stable, but as A gets heavier their stability, though still considerable, diminishes. This is shown by the

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* The following enumeration of the chief points in which the organic compounds of tin and lead differ from those of silicon and germanium may be useful. Stability of the types R_2AX_2 and $[R_2A]^{++}$; steric difficulties in the formation of certain tetra-alkyls and aryls; ease of oxidation in tetra-alkyls with secondary and tertiary alkyls; the halides only partially hydrolysed by water in absence of alkali (as with $SnCl_4$); mono- and difluorides ionized while the chlorides, bromides, and iodides are covalent (as in SnF_4); the monols $R_3A\cdot OH$ and diols $R_2A(OH)_2$ are much less like alcohols, and are definite bases, forming salts; when the monols lose water they form not ethers but the tetra-alkyl and the oxide AR_4+R_2AO; the halides form ammines such as $Alk_3SnX, 2\,NH_3$ or $\Phi_2SnCl_2, 2\,NH_3$, instead of reacting with the NH_3 to give amines and imines; they form complex halogen acids; the A—A compounds give signs of dissociation of R_3A radicals; the monohalides have a violent physiological action.

It will be remembered that the formation of tetravalent A^{4+} ions, and likewise that of divalent A^{++} ions (with the inert pair of electrons) also begin with tin.

increasing attack by halogens, and by the relative instability of the compounds of tin and lead with secondary and tertiary alkyls, which are less easy to make and are oxidized by air; the tertiary alkyl lead compounds are too unstable to be purified. Again with the aryl compounds of tin and lead steric effects (e.g. of ortho methyl groups) make the preparation difficult; this does not happen with silicon or germanium, though their smaller atoms should cause more steric hindrance.

2 A. *Hydrogen Compounds* $R_3A \cdot H$, R_3AH_3, $R \cdot AH_3$

These are all more or less unstable, though far less so than the AH_4 compounds, and like them are less stable the heavier A is; none of them is formed by lead. Only with silicon are all three types known, but the monohydrides are known with all but lead, and the dihydrides (as well as with silicon) in the aryl tin compounds.

The di- and tri-hydrides, though not spontaneously inflammable as SiH_4 is, are readily oxidized by air. Of the monohydrides $Ar_3Si \cdot H$ is not oxidized by air at all; $Ar_3Ge \cdot H$ only slowly, $Ar_3Sn \cdot H$ rapidly, while $Ar_3Pb \cdot H$ is too unstable to exist.

Trimethyl stannane $Me_3Sn \cdot H$ is 'back-substituted' by hydrogen chloride, giving the chloride $Me_3Sn \cdot Cl$ and hydrogen (like the boron and silicon hydrides).

2 B. *Alkaline Salts*, $R_3A[M]$

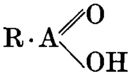
All the elements of the subgroup from carbon to lead give compounds of the type $R_3A \cdot M$, where M is an alkali metal atom, and R may be an alkyl or an aryl, or with carbon and germanium even hydrogen. With carbon as we have seen (I. 68) these compounds are of two kinds, one, like $K \cdot CH_3$, colourless, insoluble in ether, and giving no sign of ionization, and the other, like $\Phi_3C \cdot Na$ or $\Phi \cdot CH_2 \cdot Na$, bright red, giving a conducting solution in ether. With the other A elements no such sharp distinction is found; the compounds are all somewhat coloured, there is no great difference between the alkyls and the aryls, and nearly all dissolve in liquid ammonia to give coloured solutions, which conduct about as well as those of an ordinary binary salt, the aryls a good deal better than the alkyls. The compounds may probably be written as salts $[R_3A]M$, but perhaps are resonance hybrids between these and covalent molecules.

They are usually made by the action of the alkali metal in liquid ammonia or ethylamine either on the monohalide $R_3A \cdot Cl$ or on the di-compound $R_3A—AR_3$. They are fairly stable alone, but are readily oxidized by air (though not so violently as some of the carbon analogues), and they very easily exchange the alkali atom for other groups such as hydrogen (with NH_4Br in NH_3), $-AR_3$, etc.

2 B*. *Nitrogen Compounds*

With silicon the amines and imines of the trialkyl radicals have been obtained.

2 C. *Oxy-compounds: Monols* $R_3A \cdot OH$, *Diols* $R_2A(OH)_2$, *Triols* $R \cdot A(OH)_3$ *and their Derivatives*

All three types occur with every IV. B element. Two hydroxyl groups on the same A atom always tend, as they do with carbon, to lose water,* so $R_2A(OH)_2$ goes (usually at once) to $R_2A{=}O$, and $R \cdot A(OH)_3$ always at once to  $R \cdot A \begin{smallmatrix} {=}O \\ -OH \end{smallmatrix}$; but the strain which always occurs in the $A{=}O$ link except where A is carbon is relieved by polymerization to open-chain and ring-polymers.

The *monols* $R_3A \cdot OH$ change sharply in character when we pass from germanium to tin. With silicon and germanium they more or less resemble alcohols, and give covalent ethers (very stable), and esters (very easily hydrolysed). The silicon monols lose water reluctantly, the aryl Ge monols at the melting-point and the alkyl Ge monols at once, giving ethers $R_3A{-}O{-}AR_3$.

The tin and lead monols are very different; they are weak bases and form salts; the tin monols when they lose water (at their melting-points) are converted not into the ethers but into the disproportionation products $R_2SnO + SnR_4$.

The *diols* $R_2A(OH)_2$ lose water readily, all except the aryls $Ar_2Sn(OH)_2$ and the alkyls with tertiary alkyl groups at once, to form the oxide or 'ketone' $R_2A{=}O$ which immediately changes into open-chain and ring-polymers. The tin and lead diols are weakly basic and give salts such as $Et_2Sn[SO_4]$ and $\Phi_2Pb[NO_3]_2$. These $[R_2A]^{++}$ salts, in which the A has a shared valency quartet (as in HgR_2 and $[TlR_2]^+$) are formed with great ease by tin and lead, by the last, for example, from $Pb\Phi_4$ and nitric acid.

Triols $R \cdot A(OH)_3$ go at once to (polymerized) 'onic acids' $R \cdot AO \cdot OH$, which form salts, but are weaker than carbonic acid; they also very readily form various polymeric anhydrides.

2 D. *Halides* $R_3A \cdot X$, R_2AX_2, $R \cdot AX_3$

All three types are known with nearly every A and every halogen; they become less stable as either A or X gets heavier. The tin and lead fluorides are peculiar; all the other halides are covalent low-melting solids or liquids, volatile, more soluble in organic solvents than in water; so are the fluorides of the silicon and germanium compounds, which (like SiF_4 and GeF_4) are similar to and more volatile than the chlorides; but the fluorides of the tin and lead compounds are (like SnF_4) non-volatile salts, with melting-points high if any, which are more soluble in water.

The halides all hydrolyse with water to hydroxy-compounds, and more easily the lighter A is; those of tin and lead (like $SnCl_4$) only hydrolyse partially with water.

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* The loss of water seems to be easier in presence of primary or secondary alkyls than of tertiary alkyls or aryls.

The tin and lead halides form complexes: either ammines such as $R_3AX, 2\,NH_3$ (silicon and germanium alkyl or aryl halides react with ammonia to give imines) or complex acids of the type $H_2[RAX_5]$.

All the Group IV alkyl and aryl compounds are poisonous, and most of them have unpleasant smells; but the monohalides (including the fluorides) of tin and lead are exceptionally powerful in this respect, having an extremely violent action on the eyes and mucous membrane; this is not shared by the dihalides, nor by the monohalides of silicon and germanium.

3. A—A *Compounds*

These are of special interest owing to the proved dissociation of many carbon compounds $Ar_3C—CAr_3$ into free trivalent carbon radicals Ar_3C'''.

The other A—A links are in general more readily broken than C—C, not only because their heats of formation are smaller (C—C 81·6, Si—Si 42·5, Ge—Ge 42·5 k.cals.) but probably for other reasons as well. In particular the Si—Si link in inorganic compounds is very easily broken, especially by dilute alkali (p. 567) with evolution of hydrogen:

$$\text{Si—Si} + H_2O = \text{Si—O—Si} + H_2.$$

But the fully alkylated or arylated compounds Si_nR_{2n+2} are extremely stable, and quite indifferent to air or alkali, perhaps because the presence of the hydrocarbon groups prevents co-ordination. The same is true of the germanium compounds.

The Sn—Sn and Pb—Pb compounds are less stable; they are oxidized slowly by air or in other ways to the oxides $R_3Sn—O—SnR_3$ (not to peroxides) or to monols $R_3Pb\cdot OH$. All A—A compounds are decomposed by chlorine or bromine, and by alkali metals in liquid ammonia solution.

The question of the dissociation of the $R_3A—AR_3$ compounds of lead and tin into R_3A radicals (there is no sign of its occurrence with silicon or germanium) is very obscure. Freezing- and boiling-points indicate high dissociation in dilute solution, and little in strong. Magnetic measurements, however, show none at all. The chemical evidence does not help. The colour suggests that the dissociation is greater with the lead compounds than with those of tin; but it is surprising that there is no evidence that the hexa-aryl compounds $R_3A—AR_3$ are more highly dissociated than the hexa-alkyl.

The maximum number of A atoms that have been linked together in open-chain molecules of the normal paraffin type is so far 4 with silicon, 3 with germanium, 5 with tin, and 2 with lead; rings of 4 A atoms are probably formed by silicon germanium and tin. But these limits could no doubt be extended.

ORGANIC COMPOUNDS OF SILICON[485]

The original work on the organic compounds of silicon is due to Friedel and Crafts, and to Ladenburg (mainly 1863–74); the later chiefly to

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[485] See Krause and v. Grosse (1937), pp. 254–90.

Kipping and his collaborators, who have published over fifty papers on the subject since 1900.

1 *a*. *Silicon Tetra-alkyls*

Many types of alkyl derivatives are known, including the alkyl-hydrides such as Alk_2SiH_2, and compounds in which the silicon forms a ring with carbon atoms. Any hydrogen that is attached to the silicon is very easily oxidized, and can also be replaced by halogens, which then hydrolyse very readily.

The original methods of preparation of these substances (Friedel and Crafts, 1865; Ladenburg, 1872) was by the action of zinc alkyls (or for the aryls, of mercury aryls) on the silicon halides or the silicic esters. The best method[487-9] is to treat the tetrachloride with the Grignard reagent. The reaction goes very easily with the earlier replacements, but that of the last chlorine needs heating to 100°. By adjusting the proportions of the reagents, 1, 2, 3, or 4 halogens may be replaced.

Electron diffraction[486] gives these values of the Si—C distance: $SiMe_4$ 1·93; Si_2Me_6 1·90; Me_2SiCl_2 1·83 (in SiC it is 1·90 A; theory 1·94).

The following are some of the boiling- and melting-points of these compounds:

	$SiMe_4$	$SiEt_4$	$SiPr_4$	$Si\Phi_4$
B.pt. . . .	26·6°	153·7°	213°	over 530°
M.pt. . . .	—99·1°	. .	. .	237·5°

By means of the Grignard reagent different alkyls can be introduced (as in $SiMe_2Et_2$, b.pt. 96°), if necessary four different groups. This is not possible with tin or lead, as the attachment of the alkyls to these metals is not firm enough; on the other hand, the method used with tin and lead of expelling an alkyl group with bromine or chlorine will not work with silicon, as the Si—C link is so strong that the halogen often goes by preference to the carbon.

The silicon tetra-alkyls are in every way very stable. They are unaffected in the cold by air or water, or by concentrated potassium hydroxide or sulphuric acid (which last can be used to separate $SiMe_4$ from the ether used in its preparation), or normally by the halogens, which, if they are made to react, replace the hydrogen on the carbon, silicon tetra-ethyl giving, for example, $Et_3Si \cdot C_2H_4Cl$.[490]

Silicon tetramethyl boils at 26·6° C. and is dimorphic, the stable β-form melting at —99·1° and the unstable α- at —102·2°: the Trouton constant

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[486] R. L. Livingston and L. O. Brockway, *J.A.C.S.* 1944, **66**, 94.

[487] F. S. Kipping, *Proc. C. S.* 1904, **20**, 15.

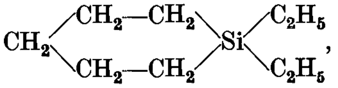
[488] W. Dilthey, *Ber.* 1904, **37**, 319, Anm. 1.

[489] F. C. Whitmore, L. H. Sommor, P. A. Di Giorgio, W. A. Strong, R. E. Van Strien, D. L. Bailey, H. K. Hall, E. W. Pietrusza, and G. T. Kerr, *J.A.C.S.* 1946, **68**, 475.

[490] C. Friedel and J. M. Crafts, *Ann.* 1866, **138**, 20; *Ann. de Chim. Phys.* 1870, [4] **19**, **348**.

is 19·3.[492] A study of its calorimetry down to 12° K. showed[491] that the rotation of the methyl groups is hindered by a potential barrier of 1·28 k.cals., compared with 4·80 for $C(CH_3)_4$. If the barrier were due, as has been suggested, to a lack of symmetry in the bonds owing to the interaction of other electrons, we should expect it to be greater with silicon than with carbon, as this has more electrons; hence it is probably caused by hydrogen repulsion, and so is less when the central atom is larger.

Among the compounds in which silicon forms part of a ring is the 6-ring compound



b.pt. 190°, which is made from pentamethylene bromide.[493]

1 *b*. *Silicon Tetra-aryls*

Silicon tetraphenyl can be made by treating silicon tetrachloride with chlorobenzene and sodium (Polis, 1885),[494] or better from the Grignard reagent with either the tetrachloride or the fluorosilicate Na_2SiF_6.[495–6] X-ray analysis of the crystals shows that the Si—C distance in $Si\Phi_4$ is 1·88 A[497] (theory 1·94).

Silicon tetraphenyl is quite extraordinarily stable, boiling undecomposed above 530°, and not being acted on when heated at 450° for 200 hours with hydrogen at 75 atmospheres. The melting-points of the tetraphenyl derivatives of this subgroup of elements have been determined by Drew and Landquist[498]; the results are these, the radii of the central atoms being added:

	$C\Phi_4$	$Si\Phi_4$	$Ge\Phi_4$	$Sn\Phi_4$	$Pb\Phi_4$
M.pt. . . .	285°	237·5°	233·4°	229·2°	227·8°
Rad. of A . .	0·77	1·17	1·22	1·40	1·46 A

They form an almost complete series of solid solutions; the small difference in melting-points shows how entirely the effect of the central atom is masked by that of the phenyl groups.

Both bromine and phosphorus pentachloride will split off phenyl groups on heating, but nitric acid does not, and gives the tetranitro-compound $Si(C_6H_4 \cdot NO_2)_4$. If the tetraphenyl is nitrated in acetic anhydride no ortho nitro-compound is formed, but a mixture of meta and para; with the

[491] J. G. Aston and R. M. Kennedy, *J.A.C.S.* 1940, **62**, 2567.

[492] J. G. Aston, R. M. Kennedy, and G. H. Messerly, ib. 1941, **63**, 2343.

[493] G. Grüttner and M. Wiernik, *Ber.* 1915, **48**, 1474.

[494] A. Polis, ib. 1885, **18**, 1540.

[495] Z. Manulkin and F. Jakubova, *J. Gen. Chem. Russ.* 1940, **10**, 1300.

[496] E. M. Soschestvenskaja, ib. 1938, **8**, 294.

[497] G. Giacomello, *Gaz.* 1938, **68**, 422.

[498] H. D. K. Drew and J. K. Landquist, *J.C.S.* 1935, 1480.

mixed silicon alkyl-aryls there is more meta the more phenyl groups are present, the proportions being:[499]

	$\Phi\cdot SiEt_3$	Φ_2SiEt_2	Φ_3SiEt	Φ_4Si
% meta	17	30	60	76
% para	83	70	40	24

The nitro-compound can be reduced to the amine, which can be acetylated, diazotized, etc.[500] The introduction of the NH_2 group in the para- but not in the meta-position weakens the Si—C link.

Tetrabenzyl silicon $Si(CH_2\cdot C_6H_5)_4$[496,501] is also very stable (which is unusual in benzyl compounds); it boils undecomposed above 550° and is very resistant to hydrogen under pressure.[501]

The following are some boiling- and melting-points of mixed and pure aryl-silicons:

	$Et_3Si\Phi$	$Et_2Si\Phi_2$	$Et\cdot Si\Phi_3$	$Si\Phi_4$	Si(*m*-tol)$_4$	Si(*p*-tol)$_4$
B.pt.	238·4°	310°	..	530+°	..	..
M.pt.	..	..	76°	237·5°	150·8°	228°

2 A. *Hydrogen Compounds*

The compounds in which the hydrogen of SiH_4 is only partly replaced by alkyls or aryls are much less stable, though much more so than SiH_4 itself. The compounds can be made from the hydride-halides such as SiH_2Cl_2 and the Grignard reagent.[502] They can also be made[501a] by the action of lithium aluminium hydride $LiAlH_4$ on the (Si, Ge, or Sn) halides in presence of ether. Examples of their boiling- and melting-points are:

	SiH_4	SiH_3Me	SiH_2Me_2	$SiHMe_3$[a]	$SiHEt_3$	$SiMe_4$	$SiEt_4$
B.pt.	−111·9°	−57°	−20°	+10°	+107°	27°	153·7°
M.pt.	−185°	−156·5°	−149·9°	..	..	−99·1°	..

a = [503]

The hydrogen attached to the silicon in these compounds is very readily attacked, especially by oxygen and the halogens. Methyl silane $CH_3\cdot SiH_3$ is not spontaneously inflammable, but it explodes if shaken with mercury and oxygen. It is insoluble in water, but it dissolves in alkali with evolution of hydrogen:

$$MeSiH_3 + 3\,H_2O = Me\cdot Si(OH)_3 + 3\,H_2.$$

[499] F. S. Kipping and N. W. Cuss, *J.C.S.* 1935, 1088.

[500] F. S. Kipping and J. C. Blackburn, ib. 1085.

[501] W. Ipatieff and B. Dolgow, *Ber.* 1929, **62**, 1220.

[501a] A. E. Finholt, A. C. Bond, K. E. Wilzbach, and H. I. Schlesinger, *J.A.C.S.* 1947, **69**, 2692.

[502] A. Stock and C. Somieski, *Ber.* 1919, **52**, 706.

[503] A. G. Taylor and B. V. de G. Walden, *J.A.C.S.* 1944, **66**, 842.

The dialkyl compounds $Alk_2Si \cdot H_2$ are similar. The trialkyl compound Et_3SiH is stable to air and to concentrated sulphuric acid, but it is oxidized by the fuming acid to the ether $Et_3Si—O—SiEt_3$, and it is at once converted by bromine into the bromide Et_3SiBr and HBr; it reacts with lithium methyl to give $SiMeEt_3+LiH$; triphenyl silicon hydride behaves in the same way.[504]

It has been found[505] to have this remarkable reaction with potassamide KNH_2 in liquid ammonia:

$$2\,Et_3SiH + KNH_2 = 2\,H_2 + (Et_3Si)_2NK.$$

This 'potassium silyl amide' forms colourless crystals easily soluble in liquid ammonia, and in that solvent is converted by ammonium bromide into the liquid secondary amine $(Et_3Si)_2NH$.

The only aryl hydrogen silanes seem to be of the type $Ar_3Si \cdot H$. Triphenyl silane $\Phi_3Si \cdot H$ was made by Reynolds, Bigelow, and Kraus[506] from silico-chloroform $SiHCl_3$ and the Grignard reagent. It melts at 36°: it reacts with sodium in liquid ammonia to give the very stable imine $(\Phi_3Si)_2NH$, which is hydrolysed by hydrochloric acid to ammonium chloride and triphenyl silicol $\Phi_3Si \cdot OH$. The tribenzyl compound $(\Phi_2CH_2)_3Si \cdot H$, m.pt. 91°, is also known.[507]

2 B. *Alkaline Compounds* $R_3Si \cdot M$

These compounds are less known with silicon than with any of the succeeding IV B elements, but they certainly exist. If the monochloride Et_3SiCl is treated in benzene solution with $Na \cdot Ge\Phi_3$, it gives the Si—Ge compound $Et_3Si—Ge\Phi_3$. In ethylamine solution this reacts[505] with lithium without any evolution of hydrogen, so that the Li compound $Li \cdot SiEt_3$ must be present in the liquid; this has been confirmed by its giving silicon tetraethyl when it is treated with ethyl iodide.

The aryl compound $Li \cdot Si\Phi_3$, got[508] by the action of lithium on Φ_6Si_2 in ethylamine, is a white crystalline solid.

2 B*. *Nitrogen Compounds*

Chloroalkyl silanes, such as Me_3SiCl, react with ammonia and amines in the same way as chlorosilanes, giving amines such as $(Me_3Si)_2NH$, b.pt. 126° and $Me_3Si \cdot NHMe$, b.pt. 71°; they are easily hydrolysed to the amine and the silicol.[509]

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[504] H. Gilman and S. P. Massie, ib. 1946, **68**, 1128.

[505] C. A. Kraus and W. K. Nelson, ib. 1934, **56**, 195.

[506] H. H. Reynolds, L. A. Bigelow, and C. A. Kraus, ib. 1929, **51**, 3067.

[507] W. E. Evison and F. S. Kipping, *J.C.S.* 1931, 2830.

[508] C. A. Kraus and H. Eatough, *J.A.C.S.* 1933, **55**, 5008.

[509] R. O. Sauer and R. H. Hasek, ib. 1946, **68**, 241.

2 C. *Oxygen Compounds* $R_3Si \cdot OH$, $R_2Si(OH)_2$, *and* $R \cdot Si(OH)_3$

These include the silicols $R_3Si \cdot OH$ and their derivatives, such as the ethers $R_3Si—O—Alk$, the esters $R_3Si—O—CO—Alk$ and the silico-ethers $R_3Si—O—SiR_3$: the disilicols (diols) $R_2Si(OH)_2$, which in the alkyl series at once lose water (they can be isolated in the aromatic series) to form silicoketones $R_2Si{=}O$ which immediately polymerize (the $Si{=}O$ bond being much more strained than the $C{=}O$): and finally, the trisilicols (triols) $R \cdot Si(OH)_3$, which again lose water at once to give the so-called silicoacids (or siliconic, or silonic acids) $R \cdot SiO \cdot OH$, which really are highly polymerized and except for a feeble acidity have scarcely any resemblance to the carboxylic acids.

The simple silicols $R_3Si \cdot OH$ can be made[510–11] by the hydrolysis of the corresponding halides. They are colourless liquids which distill without decomposition: b.pts.[512–13] $Et_3Si \cdot OH$, 154°; $n\text{-}Pr_3Si \cdot OH$, 207°.

They lose water not spontaneously but over phosphorus pentoxide, giving the silico-ethers $R_3Si—O—SiR_3$. They react, but rather slowly (the aromatic still more slowly) with sodium to give the compounds R_3SiONa, which are soluble in ether and in aromatic hydrocarbons,[512,514] and so would seem to be covalent. With acids such as acetic they form esters[515] which are very readily saponified, even by atmospheric moisture; an example is the triethyl-silicol acetate $Et_3Si \cdot O \cdot CO \cdot CH_3$, which boils at 168°.[516] Covalent sulphates, such as $(Me_3Si)SO_4$, m.pt. 57°, and $(Et_3Si)_2SO_4$, b.pt. 170°/12 mm., can be made by the action of oleum on the ethers $(R_3Si)_2O$.[517,517a]

The 'silyl' ethers, both those with two silicon atoms like $R_3Si—O—SiR_3$ and those with one, as $R_3Si—O—Alk$, are very resistant to hydrolysis, and in general very stable. For the preparation and properties of these siloxanes $R_3Si—O—SiR_3$ see Emeléus.[522a–b] The ethyl ether $Et_3Si—O—Et$ (b.pt. 153°) is not attacked by alcoholic ammonia even at 250°, and $Et_3Si—O—SiEt_3$ (b.pt. 231°)—which can be made by the action of phosphorus pentoxide on the silicol, or of aqueous potash on the chloride $Et_3Si \cdot Cl$, or by the oxidation of the hydride $Et_3Si \cdot H$ with fuming sulphuric

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[510] See especially F. S. Kipping, *J.C.S.* 1901-7-8-9-11.

[511] R. O. Sauer, *J.A.C.S.* 1944, **66**, 1707.

[512] A. Ladenburg, *Ann.* 1872, **164**, 318.

[513] G. Gruttner and M. Cauer, *Ber.* 1918, **51**, 1288.

[514] W. Schlenk, J. Renning, and G. Racky, ib. 1911, **44**, 1180.

[515] A. Ladenburg, ib. 1907, **40**, 2275.

[516] C. Pape, *Ann.* 1884, **222**, 366.

[517] L. H. Sommer, E. W. Pietrusza, G. T. Kerr, and F. C. Whitmore, *J.A.C.S.* 1946, **68**, 156.

[517a] L. H. Sommer, G. T. Kerr, and F. C. Whitmore, ib. 1948, **70**, 445.

[518] F. S. Kipping, *J.C.S.* 1907, **91**, 209.

[519] Id., ib. 1908, **93**, 457.

[520] W. Dilthey and F. Eduardoff, *Ber.* 1904, **37**, 1140.

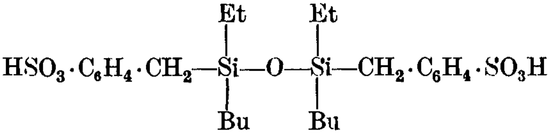
[521] H. Marsden and F. S. Kipping, *J.C.S.* 1908, **93**, 198.

[522] F. S. Kipping and L. L. Lloyd, ib. 1901, **79**, 449.

[522a] H. J. Emeléus and D. S. Payne, ib. 1947, 1590.

[522b] H. J. Emeléus and S. R. Robinson, ib. 1592.

acid—dissolves in cold concentrated sulphuric acid, and if the solution is not allowed to get warm, can be reprecipitated by water unchanged. A substituted ether of this type



$$\begin{array}{c}\mathrm{Et}\qquad\quad\mathrm{Et}\\ |\qquad\qquad|\\ \mathrm{HSO_3\cdot C_6H_4\cdot CH_2—Si—O—Si—CH_2\cdot C_6H_4\cdot SO_3H}\\ |\qquad\qquad|\\ \mathrm{Bu}\qquad\quad\mathrm{Bu}\end{array}$$

was resolved by Kipping[518-19] into its optical antimers as evidence of the tetrahedral arrangements of the silicon valencies.

The triaryl silicols (silanols, monols) $Ar_3Si\cdot OH$ are solids, and so are easily purified. Triphenyl silicol $\Phi_3Si\cdot OH$[515,520-1] melts at 151° and sublimes undecomposed. Nitric acid nitrates it, and sulphuric sulphonates it.

The silico-ether $\Phi_3Si—O—Si\Phi_3$ is made[522] by treating the silicol with a solution of hydrogen chloride in acetic acid.

The *diols* $R_2Si(OH)_2$ are only known as such in the aromatic series (see below); in the alkyl series they at once lose water to form compounds of the composition of ketones, R_2SiO; these have no other resemblance to ketones; they are syrupy liquids which are obviously polymerized. It has been shown[523-6] by the freezing-point in benzene solution[525] that the polymer formed by treating the dichloride Et_2SiCl_2 with water is trimeric; it can be distilled without decomposition above 300°. See further ref. [527].

The aryl diols $Ar_2Si(OH)_2$, on the other hand, can be isolated; they are fairly stable solids which melt if quickly heated between 70° and 150°, for example, $\Phi_2Si(OH)_2$ at 139°. On further heating they lose water, changing partly to such compounds as the silico-ether $HO\cdot Si\Phi_2—O—Si\Phi_2\cdot OH$ and partly (like the alkyl compounds) to polymers of the silico-ketones $Ar_2Si{=}O$, some of which have been isolated. According to Kipping (*J.C.S.* 1901–12) these include ring-polymers with 3 and 4 Si atoms. Hyde and DeLong[525] have isolated from the hydrolytic products of the dichloride Φ_2SiCl_2 a triple polymer $(\Phi_2SiO)_3$, m.pt. 200°, whose mol. weight was determined by the freezing-point in benzene. On further heating all these products turn into resins, as happens also with their alkyl analogues. The dibenzyl and benzyl-ethyl diols behave in the same way.[528] Many of these polymerized silicon oxides, especially derivatives $\mathrm{Me_2Si}\begin{smallmatrix}\diagup\mathrm{O}—\\ \diagdown\mathrm{O}—\end{smallmatrix}$, have been prepared, partly on account of their promise as plastics.[529-34]

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[523] R. Robinson and F. S. Kipping, ib. 1908, **93**, 439.

[524] G. Martin and F. S. Kipping, ib. 1909, **95**, 302.

[525] J. F. Hyde and R. C. DeLong, *J.A.C.S.* 1941, **63**, 1194.

[526] C. A. Burkhard, ib. 1945, **67**, 2173.

[527] P. A. DiGiorgio, L. H. Sommer, and F. C. Whitmore, ib. 1946, **68**, 344.

[527a] E. W. Pietrusza, L. H. Sommer, and F. C. Whitmore, ib. 1948, **70**, 484.

[528] F. S. Kipping, *J.C.S.* 1912, **101**, 2106.

[529] C. A. Burkhard, B. F. Decker, and D. Harker, *J.A.C.S.* 1945, **67**, 2174.

[530] L. K. Frevel and M. J. Hunter, ib. 2275.

[531] M. J. Hunter, J. F. Hyde, E. L. Warrick, and H. J. Fletcher, ib. 1946, **68**, 667.

Triols $R\cdot Si(OH)_3$. The alkyl triols[535,536] are presumably produced by the hydrolysis of the alkyl-trihalides $Alk\cdot SiX_3$ or of the tri-esters $Alk\cdot Si(O\cdot Alk)$, but they at once lose water to form the so-called silico-organic acids (siliconic acids) $R\cdot SiO\cdot OH$, which are obviously polymerized like the silico-ketones, and have no resemblance to the fatty acids beyond the formula. The lower members are amorphous insoluble powers, and though the higher will dissolve in ether or benzene they separate as glasses. They are all very weak acids; their salts are hydrolysed by water and decomposed by carbon dioxide; on heating, the acids lose water at about 100° to give the (also polymerized) anhydrides $[(Alk\cdot SiO)_2O]_n$.

The aromatic 'silonic acids' $Ar\cdot SiO\cdot OH$ are similar. The phenyl compound melts at 92° to a viscous liquid, which at 100° begins to lose water and go over to a mixture of infusible anhydrides. But many of these acids begin to lose water before they melt, and so have no sharp melting-points.

2 D. *Halogen Derivatives*

These again are of three classes, $R_3Si\cdot X$, R_2SiX_2, and $R\cdot SiX_3$. Alkyl groups attached to silicon are only very slowly replaced by halogens, and these compounds are best made by treating the tetrahalide with a limited amount of the Grignard reagent, and fractionating the product (see refs. [518,542-5]). The mono-alkyl trihalides $R\cdot SiCl_3$ can be made by the direct addition of $SiHCl_3$ to alkylenes in presence of acetyl peroxide or ultra-violet light.[527a] The chlorine can be replaced by fluorine[540] by the method of Swarts, by treatment with antimony trifluoride and pentachloride (Booth *et al.*[546-51]). The dihalides are readily made by passing the alkyl or aryl halides over elementary silicon at 300°, best in presence of a copper catalyst, which may act through the formation of a cuprous alkyl.[537-9] Electron diffraction[541] shows that the distances in Me_3SiCl are Si—C 1·89, Si—Cl 2·09 A (theory 1·94, 2·16); angle C—Si—C 113°. The halides are all unpleasant-smelling substances, but they have not the violent physiological effects of their stannic analogues. The following are some boiling-points.

$MeSiCl_3$	+65·7°
$MeSiFCl_2$	+29·5°
$MeSiF_2Cl$	—0·5°
$MeSiF_3$	—30·2°
Me_2SiCl_2	70·0°
Me_2SiFCl	36·4°
Me_2SiF_2	2·7°
Me_3SiCl	57·3°
Me_3SiF	16·4°

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[532] W. Patnode and D. F. Wilcock, *J.A.C.S.* 1946, **68**, 358.

[533] R. O. Sauer and D. J. Mead, ib. 1794.

[534] D. W. Scott, ib. 356.

[535] W. Melzer, *Ber.* 1908, **41**, 3390.

[536] G. Martin and F. S. Kipping, *J.C.S.* 1909, **95**, 309.

[537] E. G. Rochow, *J.A.C.S.* 1945, **67**, 963.

[538] D. T. Hurd and E. G. Rochow, ib. 1057.

[539] E. G. Rochow and W. F. Gilliam, ib. 1772.

[540] For the fluorides see J. A. Gierut, F. J. Sowa, and J. A. Nieuwland, ib. 1936, **58**, 897.

[541] R. L. Livingston and L. O. Brockway, ib. 1946, **68**, 719.

The aryl compounds resemble the alkyls in their preparation and in many of their properties. The fluorides can be made by treating silicon tetrafluoride with aryl magnesium bromide in ether[552] or by treating the chlorides with hydrogen fluoride.[553] $\Phi_3Si \cdot F$ melts at 64° and boils at 101-2°. Φ_3SiCl can be made from $Si\Phi_4$ and PCl_5 at 200°; it distils unchanged *in vacuo.* Φ_3SiBr is similar and melts at 119°. The corresponding dihalides Ar_2SiX_2 are mostly oils, volatile in a vacuum.[525]

The aryl trihalides $Ar \cdot SiX_3$ are like the dihalides in general behaviour, but give the 'silonic' acids on hydrolysis. Phenyl silicon trichloride[554-5] boils at 199°/760 mm. For further work on these halides see references [556-8].

ORGANIC Si—Si COMPOUNDS

As we have seen, the stability of the Si—Si link is in general much less than that of C—C, and no chains of more than 5 or 6 Si atoms have been prepared. This is in part at least due to the smaller heat of linkage; but among these compounds the alkyl and aryl derivatives are by far the most stable, and they are particularly remarkable for not having the Si—Si link broken by alkali with evolution of hydrogen,[562,565] as happens with all other Si—Si compounds:

$$Si—Si + H_2O = Si—O—Si + H_2.$$

The alkyl disilanes Alk_6Si_2 can be made by treating the corresponding halides such as Si_2Cl_6 with zinc alkyls (Friedel and Ladenburg, 1869), or better with a Grignard reagent such as $CH_3Mg \cdot Br$.[559-62] In this reaction there is considerable separation of the paired silicon atoms with the formation of silicon tetra-alkyl and its halogen derivatives, and the yield of Si_2Me_6 is only small. Another method of formation is to heat the silicon tetra-alkyl with hydrogen under high pressure[501]:

$$2\ SiEt_4 + H_2 = 2\ C_2H_6 + Et_3Si—SiEt_3.$$

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[542] A. Bygdén, *Z. physikal. Chem.* 1915, **90**, 250.

[543] W. F. Gilliam, H. A. Liebhafsky, and A. F. Winslow, *J.A.C.S.* 1941, **63**, 801.

[544] A. G. Taylor and B. V. de G. Walden, ib. 1944, **66**, 842.

[545] W. F. Gilliam and R. O. Sauer, ib. 1793.

[546] H. S. Booth and P. H. Carnell, ib. 1946, **68**, 2650.

[547] H. S. Booth and H. S. Halbedel, ib. 2652.

[548] H. S. Booth and W. F. Martin, ib. 2655.

[549] H. S. Booth and J. F. Suttle, ib. 2658.

[550] H. S. Booth and D. R. Spessard, ib. 2660.

[551] H. S. Booth and A. A. Schwartz, ib. 2662.

[552] G. V. Medox and N. Z. Kotelkov, *J. Gen. Chem. Russ.* 1937, **7**, 2007.

[553] W. H. Pearlson, T. J. Brice, and J. H. Simons, *J.A.C.S.* 1945, **67**, 1769.

[554] F. S. Kipping, A. G. Murray, and J. G. Maltby, *J.C.S.* 1929, 1180.

[555] A. Ladenburg, *Ann.* 1874, **173**, 143.

[556] D. T. Hurd, *J.A.C.S.* 1945, **67**, 1813.

[557] R. H. Krieble and J. R. Elliott, ib. 1810.

[558] W. F. Gilliam, R. N. Meals, and R. O. Sauer, ib. 1946, **68**, 1161.

[559] A. Bygden, *Ber.* 1912, **45**, 707.

[560] Id., *Z. physikal. Chem.* 1915, **90**, 246.

[561] G. Martin, *Ber.* 1913, **46**, 2442.

[562] Id., ib. 3294.

The methyl compound $Me_3Si—SiMe_3$ boils at 112° and melts at 12° ($Me_3C—CMe_3$ boils at 106° and melts at 103°); $Et_3Si—SiEt_3$ boils at 255°.

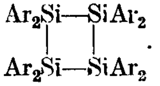
Brockway and Davidson[563] have shown by electron diffraction that $Me_3Si—SiMe_3$ has an ethane-like structure with Si—C 1·90, Si—Si 2·34 A (theory 1·94, 2·34) and the C—Si—Si angle 109°.

The compounds are stable to air and water, and are only slowly attacked by cold concentrated sulphuric acid; they react with bromine to give the bromide $R_3Si \cdot Br$.

Only a few of the aryl disilanes $Ar_3Si—SiAr_3$ are known. The hexaphenyl compound Φ_6Si_2 was made by Schlenk *et al.*,[514] and the conditions of its formation have been examined by Schumb and his collaborators[564-6]; they found that the action of sodium on a mixture of alkyl or aryl chloride and silicon hexachloride Si_2Cl_6 never gave Si_2R_6, but always SiR_4. Later[450] they found that Si_2Cl_6, Si_3Cl_8, and other similar Si—Si halides and oxyhalides, if treated with the Grignard reagent in ether, only give compounds with one silicon atom in the molecule; but that if the ether is first evaporated off, and the residue then heated with the silicon halide, fairly good yields of $R_3Si—SiR_3$ are obtained, better with chlorides than with bromides. No Si_3 compound was obtained from Si_3Cl_8. By this method $(p\text{-tol})_6\ Si_2$ (m.pt. 345°) and $(n\text{-Pr})_6Si_2$ (oil, b.pt. 114°/3 mm.) were made; both are very stable to hydrolysis by water or dilute alkali. If chlorobenzene is first converted into sodium phenyl, and this is then allowed to react with Si_2Cl_6, the main product is $Si_2\Phi_6$[566]; it seems to be the energy of the reaction of the organic halide with the sodium that disrupts the Si—Si link.

A mixed compound $\Phi_3Si—Sn\Phi_3$ has been prepared by the use of $Li \cdot Si\Phi_3$[510]; it is a colourless very viscous liquid.

A remarkable series of phenyl derivatives, whose structures are not quite certain, but must be built up with Si—Si links has been obtained by Kipping and his co-workers.[554,567-71] Some of these may contain 4-silicon ring, as in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ORGANIC COMPOUNDS OF GERMANIUM[572]

Germanium Alkyls

Mendeleef in 1871 prophesied that ekasilicon would give colourless tetra-alkyls, and that its tetra-ethyl would boil at 160° and have a density

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[563] L. O. Brockway and N. R. Davidson, *J.A.C.S.* 1941, **63**, 3287.

[564] W. C. Schumb, J. Ackerman, and C. M. Saffer, ib. 1938, **60**, 2486.

[565] W. C. Schumb and C. M. Saffer, ib. 1939, **61**, 363.

[566] Id., ib. 1941, **63**, 93.

[567] F. S. Kipping and J. E. Sands, *J.C.S.* 1921, **119**, 830.

[568] Id., ib. 848.

[569] F. S. Kipping, ib. 1923, **123**, 2590, 2598.

[570] A. R. Steele and F. S. Kipping, ib. 1928, 1431.

[571] Id., ib. 1929, 2545.

[572] See Krause and v. Grosse, 296–310.

of 0·96, these values being reached by taking the mean of those for neighbouring elements. Germanium tetra-ethyl was first made by Cl. Winkler in 1887,[573] and the more accurate investigation by Dennis and Hance[574] showed that it boiled at 163° and had a density of 0·99 at 25°. The properties of the germanium alkyls, which were worked out mainly by L. M. Dennis and C. A. Kraus, are closely intermediate between those of the silicon and the tin alkyls.

They can be made from the tetrahalides by the action of the Grignard reagent, but if all the halogen atoms are to be replaced a large excess of the reagent must be used, and it is found more convenient to use zinc alkyl[574]; this reaction is strongly catalysed by germanium tetra-ethyl. These compounds can also be made by heating germanium with alkyl or aryl halides in presence of a catalyst such as metallic copper.[576] The following are some boiling- and melting-points:

	$GeMe_4$	$GeEt_4$	$Ge(n\text{-}Pr)_4$	$Ge(CH_2 \cdot C_6H_5)_4$
B.pt. . . .	43·4°	163·5°	225°	. .
M.pt. . . .	−88°	−90°	−73°	+110°

Germanium tetramethyl has been shown to be monomeric in the vapour,[575] and $GeEt_4$ both in the vapour at 220° and in benzene by the freezing-point.[574]

The germanium tetra-alkyls are colourless pleasant-smelling liquids, stable to air and water, and insoluble in water. Germanium tetra-ethyl is oxidized only with difficulty, for example not by fuming nitric acid even on heating, unless concentrated sulphuric acid is added; the tetramethyl is oxidized more easily, nitric acid acting on it slowly even in the cold.

The germanium *aryls* are, on the whole, very like the alkyls. Germanium tetraphenyl can be made[577] by heating the tetrachloride with bromobenzene and sodium. Another method[578–9] is from germanium tetrabromide and phenyl magnesium bromide; but here under ordinary circumstances the introduction of the last phenyl groups needs a large excess of the Grignard reagent, and the main product is usually triaryl germanium bromide[581]; even with 36 moles of Grignard reagent to 1 of $GeBr_4$ only a 40 per cent. yield of the tetraphenyl is got.[580] It has, however, been found that if this reaction is carried out (using $GeCl_4$) in toluene instead of ether, over 80 per cent. of $Ge\Phi_4$ can be obtained. Another method[579,581] is to treat the Grignard reagent with zinc chloride, evaporate off the ether

[573] *J. prakt. Chem.* 1887. [2] **36**, 177.

[574] L. M. Dennis and F. E. Hance, *J.A.C.S.* 1925, **47**, 370.

[575] Id., *J. Phys. Chem.* 1926, **30**, 1055.

[576] E. G. Rochow, ib. 1947, **69**, 1729.

[577] E. A. Flood, ib. 1933, **55**, 4935.

[578] D. L. Tabern, W. K. Orndorff, and L. M. Dennis, ib. 1925, **47**, 2039.

[579] C. A. Kraus and S. L. Foster, ib. 1927, **49**, 457.

[580] G. T. Morgan and H. D. K. Drew, *J.C.S.* 1925, **127**, 1760.

[581] J. H. Simons, E. C. Wagner, and J. H. Müller, *J.A.C.S.* 1933, **55**, 3705.

without isolating the zinc phenyl compound, and add a solution of germanium tetrachloride in xylene.

Germanium tetraphenyl[583] melts at 233·4°[582]; it is very stable: it volatilizes without decomposition, and is not attacked by boiling alkalies; it is soluble in organic solvents but not in water.

Numerous other germanium tetra-aryls are known, such as the tetratolyls, which have the melting-points ortho 175°, meta 146°, para 224°.[581,584]

Hydrides

Triethyl germane $Et_3Ge{\cdot}H$ was made by Kraus and Flood[585]; they treated Et_6Ge_2 with lithium, and the salts $Li{\cdot}GeEt_3$ so formed with liquid ammonia:

$$Li{\cdot}GeEt_3 + NH_3 = Et_3Ge{\cdot}H + LiNH_2.$$

It is a colourless liquid boiling at 124·5° to give a monomeric vapour; it decolorizes bromine at once, and reacts with a solution of potassium in liquid ammonia, evolving hydrogen.[585]

Triphenyl germane $\Phi_3Ge{\cdot}H$ was made by Kraus and Foster,[579] by the action of ammonium bromide on $Na{\cdot}Ge\Phi_3$ in liquid ammonia. It is dimorphic and monotropic: the stable form melts at 47° and the unstable at 27°; the molecule is stable up to 250°. It is slowly oxidized by air.

Alkaline Compounds

These are much better known with germanium than with silicon. Germanium even forms an alkaline compound of its hydride $Na{\cdot}GeH_3$, which can be made[586] by passing germane GeH_4 into a solution of sodium in liquid ammonia. It is a white unstable easily oxidized solid, which crystallizes with 6 NH_3, and above 100° goes to sodium germanide and hydrogen.

The ethyl compound $Li{\cdot}GeEt_3$ is no doubt formed[585] when a solution of Ge_2Et_6 in liquid ethylamine (this has a smaller ammonolysing power than ammonia) is treated with lithium, since no hydrogen is evolved; but on evaporation it is reduced to the hydride $Et_3Ge{\cdot}H$. If Ge_2Et_6 is allowed to stand for 6 weeks in the cold with a solution of potassium in ethylamine a yellow solution is produced which must contain $K{\cdot}GeEt_3$, since it gives $GeEt_4$ on treatment with ethyl iodide.

The aryl germanium alkaline compounds have been isolated. If germanium tetraphenyl is treated with a solution of sodium in liquid ammonia it is converted into $Na{\cdot}Ge\Phi_3$; excess of sodium will even give $Na_2Ge\Phi_2$.[579] The mono-sodium compound $Na{\cdot}Ge\Phi_3$, which can also be got from the action of sodium on $\Phi_3Ge{-}Ge\Phi_3$, crystallizes from liquid ammonia, in

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[582] H. D. K. Drew and J. K. Landquist, *J.C.S.* 1935, 1480.

[583] D. E. Worrall, *J.A.C.S.* 1940, **62**, 3267.

[584] R. Schwarz and M. Lewinsohn, *Ber.* 1931, **64**, 2352.

[585] C. A. Kraus and E. A. Flood, *J.A.C.S.* 1932, **54**, 1635.

[586] C. A. Kraus and E. S. Carney, ib. 1934, **56**, 765.

which it is more highly ionized than the alkaline halides,[587] with 3 molecules of ammonia.

Nitrogen Compounds

The trialkyl germanium radicals Alk_3Ge and the dialkyls Alk_2Ge can replace the hydrogens in ammonia, giving for instance the imine $Et_2Ge{=}NH$ (made from the dichloride in liquid ammonia)[588] a liquid boiling at 100°/0·01 mm.; it is obviously polymerized, and the association factor in benzene by the freezing-point is 2·7.

A 'nitride' Et·GeN is formed[577] when the tri-iodide $Et \cdot GeI_3$ is treated with liquid ammonia; it is a white insoluble powder, which is easily hydrolysed by water to give ammonia and the oxide $(Et \cdot GeO)_2O$.

Diphenyl germanium dichloride reacts with ammonia to give the imine[589] $\Phi_2Ge{=}NH$, a very viscous liquid, easily soluble in organic solvents, and very easily hydrolysed by water.

Kraus and Wooster[590] find that triphenyl germanium bromide reacts with dry potassamide to give Φ_3GeNHK, which is converted by ammonium bromide into the amine $\Phi_3Ge \cdot NH_2$. This has a strong tendency to lose ammonia, and on recrystallization goes first to the secondary amine $(\Phi_3Ge)_2NH$, and then to the tertiary $(\Phi_3Ge)_3N$, which melts at 163°, sublimes *in vacuo* at 200°, and is hydrolysed by water.

$GeCl_4$ in benzene heated with AgCNO gives a liquid[591] either normal or isocyanate, colourless, of boiling-point 196°, and Trouton constant 26·8.

Oxygen Compounds

These are in general similar to the silicon compounds, but are less well known. The *monol* $Me_3Ge \cdot OH$ seems to be formed by the hydrolysis of the monobromide, but it loses water at once to form a volatile product which is probably the ether $Me_3Ge{-}O{-}GeMe_3$, and is monomeric in benzene by the freezing-point. The ethyl compound[585] is formed in the same way; boiling-point 253·9°, m.pt. below −50°; halogen acids convert it into the halides such as $Et_3Ge \cdot F$.

Triphenyl germanium hydroxide $\Phi_3Ge \cdot OH$ is formed[579-80] by the hydrolysis of the bromide; it melts sharply at 132·3°, and only begins to lose water above this temperature. It forms a sodium salt even in water. The oxide $(\Phi_3Ge)_2O$, m.pt. 184°, is monomeric by the freezing-point in benzene and is just like the ethyl analogue.[588]

Of the *diols*, as of the other derivatives of the type Alk_2GeX_2, only the diethyl series is known. The dibromide Et_2GeBr_2 (below, p. 573) is converted by alkalies into the oxide Et_2GeO, which occurs in two polymeric forms,[588] (1) a high polymer which is stable and if heated quickly melts at 175°: it is insoluble, and when distilled *in vacuo* gives (2) the trimeric

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[587] C. A. Kraus and H. S. Nutting, ib. 1932, **54**, 1622.

[588] E. A. Flood, ib. 1663.

[589] C. A. Kraus and C. L. Brown, ib. 1930, **52**, 3690.

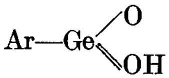
[590] C. A. Kraus and C. B. Wooster, ib. 1930, **52**, 372.

[591] A. W. Laubengayer and L. Reggel, ib. 1943, **65**, 1783.

$(Et_2GeO)_3$ (mol. weight determined cryoscopically in benzene) which melts at 18° and is soluble in organic solvents but not in water.

The aryl compound $\Phi_2Ge(OH)_2$ at once loses water to give a polymer of the oxide Φ_2GeO,[580,589] a white insoluble powder with no definite melting-point. Kraus and Brown[589] could not isolate any definite oxide, but Morgan and Drew[580] claim to have obtained a series of complicated products.

The *triols* Alk·$Ge(OH)_3$ are formed[577] by boiling the trihalide in water with silver oxide, or by the hydrolysis of the nitride Et·GeN which is formed as a white powder from ammonia and the tri-iodide Et·GeI_3. Like the diols they lose water at once, and give glassy oxides with the composition of acid anhydrides, such as $(Et{\cdot}GeO)_2O$; this does not melt when heated to 300°, and at higher temperatures sublimes *in vacuo* with some decomposition; it is obviously polymerized. In concentrated halogen acid, or if it is heated with phosphorus pentoxide in a stream of the halogen hydride, it is reconverted into the tri-halide.

The aryl compounds are very similar; they are made by hydrolysing the aryl tribromides, and appear as the 'germanonic acid'  $Ar{-}Ge\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}$ (really a polymer) or its anhydride, or mixtures of these (as with silicon); these are all amorphous substances with no definite melting-points, which are easily soluble in aqueous alkali.[592]

Halogen Compounds

The germanium alkyl halides $Alk_nGe(hal)_{4-n}$ can be made by the action of a limited amount of the Grignard reagent on the tetrahalide, or more conveniently by treating the tetra-alkyls with bromine, which splits off the alkyls (as it does with tin and lead, but only with difficulty with silicon). They cannot, however, be made from the tetra-alkyl and the tetrahalide even at 100°, though tin tetra-ethyl reacts with tin tetrachloride at the room temperature.[585] It is even possible to replace one of the four alkyls with bromine by using hydrogen bromide in the presence of aluminium bromide[593]:

$$GeMe_4 + HBr = Me_3Ge{\cdot}Br + CH_4.$$

This trimethyl bromide is an onion-smelling liquid of b.pt. 113·7° and m.pt. −25°; its vapour density is normal. The chloride $(CH_3)_3GeCl$, made with the Grignard reagent, boils at 115° and melts at −13°.[593a] The boiling-points of the ethyl compounds are[585]:

	$Et_3Ge{\cdot}H$	$Et_3Ge{\cdot}F$	$Et_3Ge{\cdot}Cl$	$Et_3Ge{\cdot}Br$	$Et_3Ge{\cdot}I$
B.pt.	124·4°	149°	176°	191°	212·3°

As with the silicon compounds the fluoride is the least easily hydrolysed; the rest are at once converted by water into the hydroxide or monol $Alk_3Ge{\cdot}OH$.

[592] W. K. Orndorff, D. L. Tabern, and L. M. Dennis, *J.A.C.S.* 1927, **49**, 2512.
[593] L. M. Dennis and W. I. Patnode, ib. 1930, **52**, 2779.
[593a] E. G. Rochow, ib. 1948, **70**, 436.

The aromatic germanium halides are made in similar ways. Φ_3GeBr is best made by boiling $Ge\Phi_4$ with bromine in ethylene dibromide (the solvent is important) for a few minutes.[592] It can also be made[587] by the action of hydrogen bromide gas on the tetra-aryl dissolved in chloroform in the cold. Simons[594] has shown from the action of hydrogen chloride on various germanium tetra-aryls that the firmness of the Ge—C linkage changes in the increasing order

$$p\text{-tolyl} < m\text{-tolyl} < \text{phenyl} < \text{benzyl}$$

The triphenyl monohalides have these melting-points[579,588]:

	$\Phi_3Ge{\cdot}F$	$\Phi_3Ge{\cdot}Cl$	$\Phi_3Ge{\cdot}Br$	$\Phi_3Ge{\cdot}I$
M.pt.	76·6°	116°	138·5°	157°

The germanium halides in general hydrolyse more easily than those of tin, but less than those of silicon. Among the different halides the fluoride is much the slowest to hydrolyse and the iodide the least stable.[579]

The *dihalides* are not easy to make, and in the alkyl series only the diethyl compounds are known. They can be made by the action of bromine on the trialkyl halide, especially the fluoride[588]: the relative rates of reaction are $Et_3GeF : Et_3GeCl : Et_3GeBr = 36 : 6 : 1$; it is not clear whether it is the dibromide or the fluorobromide that is formed, as this was hydrolysed without separation. The dialkyl dihalides can also be prepared by the action of bromine on Φ_2GeAlk_2, as the bromine removes the aryl and not the alkyl groups.[588] They can also be made by an obscure reaction by heating the mono-alkyl tri-iodide with a 40:60 lead-bismuth alloy at 150° for 2 days, the germanous compound $Alk{\cdot}Ge{\cdot}I$ being perhaps an intermediate product. The melting-points and boiling-points of the diethyl dihalides are:

	Et_2GeCl_2	Et_2GeBr_2	Et_2GeI_2
B.pt. . . .	175°	202°	252°
M.pt. . . .	−38°	. .	+10°

They are hydrolysed at once by water, and ammonolysed by NH_3 to give the imine Et_2GeNH (p. 571).

One of the monohalides derived from a dihalide was used by Schwarz and Lewinsohn[584] for the demonstration of the tetrahedral distribution of the valencies of germanium. They converted Φ_2GeBr_2 into $\Phi_2GeEtPr$, and this with bromine into the unsymmetrical $\Phi EtPrGe{\cdot}Br$, which they resolved through the bromocamphor sulphonate; as with Pope's tin compound (p. 582) only the dextro-form could be isolated, as the rest racemizes.

Among the dihalides is Φ_2GeF_2,[589] a colourless liquid which can be distilled at about 100° under 0·007 mm. pressure; it is more rapidly hydrolysed than the corresponding chloride; this chloride (m.pt. +9°) and the dibromide are rather less volatile than the difluoride.

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[594] J. K. Simons, ib. 1935, 57, 1299.

Trihalides Alk·Ge(hal)$_3$. The trichlorides can be made[595] in good yield by the action of the alkyl halides (especially the iodide) on the germanous complex halide $Cs[GeCl_3]$; thus ethyl iodide at 110° gives 60 per cent. of $Et \cdot GeCl_3$: methylene iodide at 200° gives the compound

$$Cl_3Ge—CH_2—GeCl_3, \text{ b.pt. } 110°/18 \text{ mm.},$$

which hydrolyses to the 'acid' $CH_2(GeO \cdot OH)_2$.

The tri-iodide $Et \cdot GeI_3$ can be made[577] by heating germanous iodide GeI_2 with ethyl iodide for 3 days at 110°; it is a liquid (m.pt. −2°) which is yellow when cold, but darkens on heating and is deep red by 250°; it distils without change in dry air at 281°, and does not break up even at 300° (where $H \cdot GeI_3$ goes to HI+germanous iodide). The trihalides hydrolyse to the triols, which are reconverted into them by hydrogen halide in presence of phosphorus pentoxide. The ethyl trihalides have these boiling- and melting-points:

	$Et \cdot GeF_3$	$Et \cdot GeCl_3$	$Et \cdot GeBr_3$	$Et \cdot GeI_3$
B.pt. . .	112°	144°	200°	281°
M.pt. . .	−16°	Below −33°	..	+2°

The phenyl compound $\Phi \cdot GeCl_3$ can be made from germanium tetraphenyl and tetrachloride $Ge\Phi_4+GeCl_4$ at 250°,[584] or like the alkyl analogues from the germanochloride $Cs[GeCl_3]$.[595] On reduction by sodium in xylene it is converted into the so-called hexa-germanium hexaphenyl (below).

Digermane (Ge—Ge) Derivatives

Alkyl and aryl compounds are known with 2, 3, and probably 4 and 6 germanium atoms united to one another.

Hexa-ethyl digermane $Et_3Ge—GeEt_3$ was made by Kraus and Flood[585] by treating triethyl germanium bromide with sodium for 12 hours at 210° in the absence of a solvent. It is a colourless pleasant-smelling liquid, b.pt. 265°, m.pt. below −60°, monomeric in benzene solution. It is stable in air, and can be distilled without oxidation. It readily forms the bromide Et_3GeBr with bromine; it is decomposed by lithium in ethylamine solution, presumably forming first $Et_3Ge \cdot Li$, which reacts with the amine to give $Et_3Ge \cdot H$.

Hexaphenyl digermane $\Phi_3Ge—Ge\Phi_3$[579-80,587] can be made from the bromide Φ_3GeBr and sodium in boiling xylene, or by heating germanium tetrachloride with excess of phenyl magnesium bromide for 60 hours.[596] It crystallizes from benzene in large colourless crystals with 3 molecules of benzene (like its tin and lead analogues); it loses this benzene in air, and then melts at 340°. It gives no sign of dissociation into Φ_3Ge radicals either by the freezing-point in dilute benzene solution,[579] or by its magnetic

[595] A. Tchakarian and M. Lewinsohn, *C.R.* 1935, **201**, 835.

[596] H. Bauer and K. Burschkies, *Ber.* 1934, **67**, 1041.

[597] P. W. Selwood, *J.A.C.S.* 1939, **61**, 3168.

properties,[597] or by its chemical reactions. Morgan and Drew[580] give the following melting-points of the Φ_6A_2 compounds of the subgroup, and ascribe the low melting-points at both ends of the series to dissociation.

	$C_2\Phi_6$	$Si_2\Phi_6$	$Ge_2\Phi_6$	$Sn_2\Phi_6$	$Pb_2\Phi_6$
M.pt.	146°	354°	340°	237°	155°

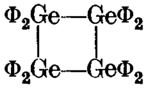
Hexaphenyl digermane is not easily oxidized; it is insoluble in boiling aqueous soda. The Ge—Ge link is broken by sodium, giving $\Phi_3Ge \cdot Na$, and by bromine, giving $\Phi_3Ge \cdot Br$. The *p*-tolyl compound $(p\text{-tol})_6Ge_2$, colourless crystals melting at 226°, is similar[596]; the hexabenzyl compound melts at 183°.

Octaphenyl trigermane $\Phi_3Ge—Ge\Phi_2—Ge\Phi_3$ is made by the reaction[598]

$$2\,\Phi_3Ge \cdot Na + \Phi_2GeCl_2 = 2\,NaCl + \Phi_3Ge—Ge\Phi_2—Ge\Phi_3$$

m.pt. 247°, monomeric in benzene by the freezing-point. It is stable to air and moisture; it decolorizes bromine with the formation of $\Phi_3Ge \cdot Br$ and Φ_2GeBr_2.

$Ge_4\Phi_8$. If diphenyl germanium dichloride is treated in xylene with sodium a solid of the composition $(Ge\Phi_2)_n$ is formed, which melts at 294°.[598] The boiling-points in benzene solution give $n = 4$ within half a per cent. It is decomposed by sodium in liquid ammonia to give $Na_2Ge\Phi_2$. The suggested ring structure



seems probable.

Schwarz and Lewinsohn[584] found that when phenyl germanium trichloride $\Phi \cdot GeCl_3$ is boiled in xylene with sodium, a colourless product is formed which has the composition $Ge\Phi$; it is soluble in benzene with the molecular weight (by the f.pt.) of $(Ge\Phi)_6$.

Later work showed that the yield is better with potassium than with sodium, but depends on the atmosphere in which the reaction is carried out; in oxygen the product is $\Phi \cdot GeO \cdot OH$: in nitrogen or argon no reaction occurs at all: in carbon dioxide it goes well: so that the gas present must catalyse the reaction in some way. The product (the composition and molecular weight in benzene are confirmed) is a white amorphous solid; its benzene solution is bright yellow. It is not readily oxidized; it is scarcely affected by boiling for 6 hours in benzene in a stream of oxygen, but in boiling xylene it gives an oxidation product containing from 3 to 4 oxygen atoms per 6 Ge, with a molecular weight in solution of 2,900 (which is that required for the compound $[(\Phi \cdot Ge)_6O_3]_3$). The original $Ge_6\Phi_6$ will also add on 8 Br or 8 I per Ge_6.

This remarkable polymer may have two structures:[599] a ring structure (I) with a resonance of the aromatic type, and an open-chain form (II). Schwarz and Schmeisser suggest that the yellow colour and the power of

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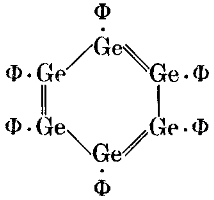
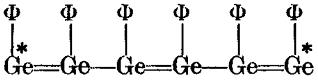
[598] C. A. Kraus and C. L. Brown, ib. 1930, **52**, 4031.

[599] R. Schwarz and M. Schmeisser, *Ber.* 1936, **69**, 579.

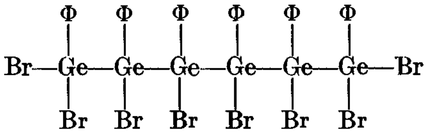
taking up 8 halogen atoms (which would give formula III from II, and possibly from I also) support the open-chain structure (II).



(I)



(II)



(III)

The colourless solid form can, however, scarcely be a diradical of trivalent germanium, and some reason is needed for the polymerization factor being 6 rather than 2 or 4. The solid may well have the ring structure and dissociate in solution into a diradical as hexaphenyl ethane does into a monoradical, and the stability of the aromatic resonance may determine the 6-fold polymerization.

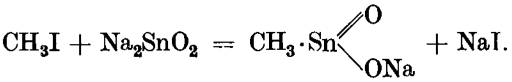
ORGANIC COMPOUNDS OF TIN[600]*

The chief methods of making compounds with carbon attached to tin are:

1. By the action of alkyl halides on metallic tin or a tin-sodium alloy; this will also give the mono- and di-halides R_3SnX and R_2SnX_2.
2. By the addition of alkyl halides to stannous halide[601]

$$SnI_2 + Alk{\cdot}I = Alk{\cdot}SnI_3.$$

3. From the alkyl halide and sodium stannite[602]:



$$CH_3I + Na_2SnO_2 = CH_3{\cdot}Sn\begin{matrix}\diagup\!\!\!\diagup O \\ \diagdown ONa\end{matrix} + NaI.$$

4. By adding aluminium carbide Al_4C_3 to an aqueous solution of stannous or stannic chloride the dichloride $(CH_3)_2SnCl_2$ is obtained; the authors say that the smell of the product (presumably a trace of Me_3SnCl, as the dichloride has no such powerful smell) enables one to detect by this reaction 0·1 mg. of tin.[603]

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* The stannous alkyls and aryls are discussed later among the A″ Compounds, p. 619.

[600] Krause and v. Grosse, pp. 311–71.

[601] P. Pfeiffer and I. Heller, *Ber.* 1904, **37**, 4619.

[602] P. Pfeiffer and R. Lehnardt, ib. 1903, **36**, 1057.

[603] S. Hilpert, M. Ditmar, and G. Grüttner, ib. 1913, **46**, 3738.

5. By the action of zinc on the diazonium stannichlorides $(Ar\cdot N_2)_2[SnCl_6]$; this of course is only available with the aryl compounds.

There are also many other methods of preparation, a sign of the great stability of the stannic alkyl and aryl compounds.

Stannic Tetra-alkyls and Tetra-aryls

The alkyl compounds can be made by any of the above methods, or by distilling the stannous alkyls

$$2\,SnAlk_2 = SnAlk_4 + Sn,$$

or better from the dihalides Alk_2SnX_2 and zinc alkyls, or from the Grignard reagent and tin tetrahalides, but in both of these last reactions excess of alkylating agent must be used, or only the trialkyl halide Alk_3SnX is formed (as with germanium). Some of this monohalide is always formed, but it can be separated from the tetra-alkyl by dissolving it in ether and passing in ammonia, which precipitates the ammine of the monohalide $Alk_3SnX, 2\,NH_3$.[604-5]

The tin tetra-alkyls are colourless liquids, insoluble in water, soluble in organic solvents, with a slight and not unpleasant smell. If the alkyl is primary they are stable to air and water, like all such compounds of Group IV elements; they mostly distil unchanged and can be distilled in steam. They neither polymerize nor co-ordinate, nor do the mixed tetra-alkyls show any tendency to disproportionate; in this, too, they are like the other tetra-alkyls of Group IV. The following are some boiling-points:

	$SnMe_4$	$SnMe_3Et$	$SnMeEt_3$	$SnEt_4$	$SnPr_4$
B.pt.	78·0°	108·2°	162°	175°	223°

For the decomposition of tin tetramethyl at 440–490° see reference [606]. The alkyl groups can be removed by the action of halogens, or even of halogen hydrides: for example:

$$SnAlk_4 + I_2 = SnAlk_3I + Alk\cdot I$$
$$SnAlk_4 + HCl = SnAlk_3Cl + Alk\cdot H.$$

With tin (as with lead) it is particularly easy to remove two alkyl groups at once; chlorine and bromine will do this, and cannot easily be made to stop at one. Iodine removes the lightest alkyl by preference.

The stannic aryl compounds are made by the same methods as the alkyls, especially by the action of the Grignard reagent on the tetrachloride; incompletely arylated products are easily removed through their much greater solubility. Melting-points are: tetraphenyl tin 225°; *o*-tolyl 214°; *m*-tolyl 128°; *p*-tolyl 278°. X-ray examination of the crystals[607] shows

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[604] A. Werner, *Z. anorg. Chem.* 1898, **17**, 97.

[605] E. Krause and K. Weinberg, *Ber.* 1930, **63**, 381.

[606] C. E. Waring and W. S. Horton, *J.A.C.S.* 1945, **67**, 540.

[607] G. Giacomello, *Gaz.* 1938, **68**, 422.

that in $Sn\Phi_4$ the Sn—C distance is 2·07 A (theory 2·17). Numerous substituted (amino-, chloro-, etc.) tetraphenyls are known.[608-9]

Some tin tetra-aryls are peculiarly difficult to make, perhaps for steric reasons; thus it has not been found possible to prepare tetra-α-naphthyl tin, and even with tetra-cyclohexyl tin, though the compound can be made, its preparation with the Grignard reagent gives much hexa-cyclohexyl distannane. Tin tetrabenzyl (m.pt. 42°) is quite normal in every way, which is rather unusual for a benzyl compound.

Mixed alkyl-aryl tins can be prepared, for example, by the action of mercury diaryls on hexa-alkyl distannane[610]:

$$Et_3Sn—SnEt_3 + HgAr_2 = 2\ Et_3SnAr + Hg.$$

Their melting-points are lower and their solubilities greater than one would expect. Thus while $Sn\Phi_4$ melts at 225°, $SnMe\Phi_3$ and $SnEt\Phi_3$ melt at 60° and 56°, while $SnMe_2\Phi_2$ and $SnEt_2\Phi_2$ are liquids; the solubilities in organic solvents correspond. They have small dipole moments, for example, $\Phi \cdot SnEt_3$ 0·5 D.[611] The mixed alkyl-aryl compounds are very reactive, and lose hydrocarbon radicals with halogens and halogen hydrides, the alkyl groups being more difficult to remove than the aryls, and the benzyl coming in between.[612-13] Among the aryl groups Kotscheschkov *et al.*[614] find by examining the reaction

$$SnAr_2Ar'_2 + 2\ HCl = SnAr_2Cl_2 + 2\ Ar'H$$

that the firmness of attachment of carbon to tin falls off in the order:

cyclohexyl > phenyl > α-naphthyl > ortho-anisyl > α-thienyl.

Alkyl and Aryl Tin Hydrides

In the alkyl series all three types, with 1, 2, and 3 hydrogen atoms, are known. They are colourless liquids, with the boiling-points[501a] CH_3SnH_3 0° C., $(CH_3)_2SnH_2$ 35°, $(CH_3)_3Sn \cdot H$ 59°: Trouton constants 21·0, 22·1, 21·8. They are relatively stable.

Trimethyl tin hydride $Me_3Sn \cdot H$ is very slightly soluble in water, and with hydrogen chloride gives Me_3SnCl and hydrogen. Sodium in liquid ammonia converts it into the unstable yellow salt $Na \cdot SnMe_3$.[615]

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[608] P. R. Austin, *J.A.C.S.* 1932, **54**, 3726.

[609] E. Krause and K. Weinberg, *Ber.* 1929, **62**, 2235.

[610] K. A. Kotscheschkov, A. N. Nesmejanov, and V. P. Pusyreva, ib. 1936, **69**, 1639.

[611] L. Malatesta and R. Pizzotti, *Gaz.* 1943, **73**, 344, 349.

[612] R. H. Bullard, *J.A.C.S.* 1929, **51**, 3065.

[613] R. H. Bullard and F. R. Holden, ib. 1931, **53**, 3150.

[614] T. S. Bobaschinskaja and K. A. Kotscheschkov, *J. Gen. Chem. Russ.* 1938, **8**, 1850.

[615] C. A. Kraus and W. Sessions, *J.A.C.S.* 1925, **47**, 2361.

Triphenyl tin hydride $\Phi_3Sn \cdot H$ is made[616] by the action of ammonium bromide in liquid ammonia on $\Phi_3Sn \cdot Na$. It is colourless and boils at 173°/6 mm. It must be made in an indifferent atmosphere, as it is soon oxidized by air to hexaphenyl distannane. Sodium expels the hydrogen and re-forms $\Phi_3Sn \cdot Na$.

Diphenyl stannane Φ_2SnH_2 is made[616] like the monohydride, from Φ_2SnNa_2 and ammonium bromide. It is very unstable, and rapidly breaks down into stannous diphenyl $Sn\Phi_2$ and hydrogen.

Alkaline Compounds

The alkaline compounds of the tin alkyls and aryls are perhaps better known than those of any other IV B elements. They can be made by the action of the alkali metal either on the halide $R_3Sn \cdot Cl$ in liquid ammonia (as these are not ammonolysed) or on the distannane R_3Sn—SnR_3. Trimethyl tin sodium has been made by both of these methods[615]; it separates from ammonia in yellow crystals; it decomposes if it is warmed, and is very reactive. It has been shown[617] that if the hydride $Me_3Sn \cdot H$ is treated with sodium in liquid ammonia two simultaneous reactions occur:

$$\text{(I)}\quad 2\,Me_3Sn \cdot H + 2\,Na = 2\,Me_3Sn \cdot Na + H_2$$

$$\text{(II)}\quad 2\,Me_3Sn \cdot H + Na + NH_3 = Me_3Sn \cdot Na + Me_3SnNH_2 + H_2$$

the proportions of the two depending on the conditions of the reaction; sodamide reacts similarly on the hexamethyl distannane

$$Me_3Sn\text{—}SnMe_3 + NaNH_2 = Me_3Sn \cdot NH_2 + Na \cdot SnMe_3.$$

Conductivity measurements in liquid ammonia at −33° show[618] that $\Phi_3Sn \cdot Na$ is a good conductor in this solution; its dissociation constant in liquid ammonia (which is of the same order as those of the corresponding carbon and germanium compounds) is given below, along with those of sodium bromate as a normal binary salt, and the corresponding trimethyl compound $Na \cdot SnMe_3$,[619] which as we should expect is much less highly dissociated:

	$NaBrO_3$	$Na \cdot Sn\Phi_3$	$Na \cdot SnMe_3$
$K \times 10^3$	3·5	14·0	0·36

Compounds with two atoms of alkali metal in the molecule, such as Na_2SnMe_2 (as with germanium) and $Na \cdot SnMe_2$—$SnMe_2 \cdot Na$, can also be made.[620]

The triphenyl sodium derivative $\Phi_3Sn \cdot Na$[618] is an amorphous yellow powder, and the conducting solution in liquid ammonia is also yellow. It is very reactive; it is slowly oxidized by air to the tetraphenyl, the

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[616] R. F. Chambers and P. Scherer, ib. 1926, 48, 1054.

[617] C. A. Kraus and A. M. Neal, ib. 1930, 52, 695.

[618] C. A. Kraus and W. H. Kahler, ib. 1933, 55, 3537.

[619] C. A. Kraus and E. G. Johnson, ib. 3542.

[620] C. A. Kraus and W. N. Greer, ib. 1925, 47, 2568.

hydroxide, and the distannane Φ_6Sn_2. It can also exchange its sodium atom for an organic radical, giving, for example, with chloracetic acid $\Phi_3Sn \cdot CH_2 \cdot COOH$, m.pt. 122°.

Oxygen Derivatives

These are known in all three classes, $R_3Sn \cdot OH$, $R_2Sn(OH)_2$, and $R \cdot Sn(OH)_3$ or their derivatives.

The monols $Alk_3Sn \cdot OH$ (unlike the silicols) have no resemblance to alcohols; they are crystalline substances and behave like the alkalies, though they are much less strongly basic. In benzene solution Et_3SnOH has a moment of 1·91, and Φ_3SnOH of 1·98 D.[611] They dissolve very slightly in water, but readily in organic solvents, especially in those that contain oxygen, such as alcohols and ethers; they lose water only very slowly near their boiling-points, and then do not (like the silicon aryls and the germanium compounds) give ether-like oxides $R_3Sn—O—SnR_3$, but disproportionate[621] according to the equation

$$2\ Alk_3Sn \cdot OH\ =\ Alk_2SnO + SnAlk_4 + H_2O.$$

Trimethyl stannol $Me_3Sn \cdot OH$ is slightly soluble in water, with an alkaline reaction; the dissociation constant according to Bredig[622] is $1 \cdot 7 \times 10^{-5}$. $Et_3Sn \cdot OH$ (b.pt. 272°, m.pt. 44°) was made by Cahours in 1860; its dissociation constant is about 10^{-5}.[623] The isobutyl compound (Cahours 1879) boils at 311–14°. The alkylates $Alk_3Sn—O—Alk$, which are made from the halide with sodium alkylate, are volatile liquids hydrolysed at once by water: b.pts.[624] $Me_3Sn \cdot O \cdot Et$ 65°; $Et_3Sn \cdot O \cdot Et$ 191°; $Me_3Sn \cdot O \cdot \Phi$[625] 223°.

These tin monols also form a series of salts, such as the sulphates $(Alk_3Sn)_2SO_4$, and nitrates, carbonates, and oxalates; the formates and acetates are volatile, the latter boiling at 230°, and so are presumably covalent; in the same way the cyanide sublimes. These salts were chiefly examined by Cahours.[626]

The aryl oxy-compounds are all much less known with tin than the alkyl, but they are very like them in behaviour. The monol $\Phi_3Sn \cdot OH$ (m.pt. 119°) loses water only at a rather high temperature, when it gives (unlike the trialkyl hydroxide) the oxide $\Phi_3Sn—O—Sn\Phi_3$.[627]

The *diols* $Alk_2Sn(OH)_2$ all lose water at once except those of the tertiary alkyls. Thus di-tertiary-butyl tin dihydroxide $(Me_3C)_2Sn(OH)_2$ and the di-tertiary-amyl compound can be isolated, the latter melting at 200°[605]; they are feebly basic to litmus, and are soluble in the ordinary organic

[621] C. A. Kraus and R. H. Bullard, *J.A.C.S.* 1929, **51**, 3605.

[622] G. Bredig, *Z. phys. Chem.* 1894, **13**, 303.

[623] F. Hein and H. Meininger, *Z. anorg. Chem.* 1925, **145**, 95.

[624] A. Ladenburg, *Ber.* 1870, **3**, 358.

[625] C. A. Kraus and A. M. Neal, *J.A.C.S.* 1929, **51**, 2405.

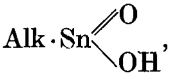
[626] A. Cahours, *Ann.* 1860, **114**, 366.

[627] See further, A. Schmitz-Dumont, *Z. anorg.* 1941, **248**, 289.

solvents. All the other diols lose water as soon as they are formed to give the (polymerized) oxides Alk_2SnO, which can also be got by the action of air on the stannous dialkyls. If stannous hydroxide $Sn(OH)_2$ is heated for 6–8 hours under aqueous alcohol with potassium hydroxide and ethyl iodide, and the alcohol distilled off and carbon dioxide passed in, the oxide Et_2SnO is precipitated.[628] These oxides are all white amorphous powders which decompose before melting, and are obviously highly polymerized, like their silicon and germanium analogues.

Like the monols the diols give a series of salts such as a sulphate $Alk_2Sn[SO_4]$, carbonate, etc., which are mostly soluble in water or alcohol. The sulphide Me_2SnS is presumably covalent, since it melts at 148°, and is insoluble in water but soluble in organic solvents.[629]

The aromatic diols go at once to oxides R_2SnO which polymerize; they are practically insoluble powders, which do not melt below a very high temperature, and usually decompose first.

The dehydration products of the *triols*, such as the stannonic acids  $Alk\cdot Sn\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}$, have long been known. The methyl compound CH_3SnO_2H can be made by treating a cold solution of potassium stannite in aqueous alcohol with methyl iodide for 23 hours.[630–1] It is a white powder, practically insoluble and infusible; it is decomposed by boiling with alkali; concentrated hydriodic acid converts it into the tri-iodide $Me\cdot SnI_3$; concentrated hydrochloric acid gives the complex acid $H_2[Me\cdot SnCl_5]$, of which salts can be made.[632–3] An insoluble stannonic sulphide

$$Me\cdot SnS—S—SnSMe$$

can also be made.[634]

The corresponding ethyl, propyl, etc., compounds are known, and are similar.

The aryl stannonic acids $Ar\cdot SnO\cdot OH$ are known in some numbers. They are made from the trihalides[635–6]; they are white amorphous powders easily soluble in both alkalies and mineral acids; they are weak acids, and are expelled from their salts by carbon dioxide. The sodium, potassium, and silver salts have been prepared. Concentrated hydrogen chloride or bromide converts them into the complex acids $H_2[ArSnX_5]$, salts of which are known.[637–8] H_2S precipitates from solutions of the acids the stannothionic acid or its anhydride $(Ar\cdot SnS)_2S$.[635–6]

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[628] P. Pfeiffer, *Ber.* 1902, **35**, 3305.

[629] K. A. Kotscheschkov, ib. 1933, **66**, 1661.

[630] G. Meyer, ib. 1883, **16**, 1442.

[631] P. Pfeiffer, ib. 1903, **36**, 1057.

[632] J. G. F. Druce, *J.C.S.* 1921, **119**, 758.

[633] Id., ib. 1922, **121**, 1859.

[634] P. Pfeiffer and R. Lehnardt, *Ber.* 1903, **36**, 3028.

[635] K. A. Kotscheschkov and A. N. Nesmejanov, ib. 1931, **64**, 628.

[636] K. A. Kotscheschkov, ib. 1929, **62**, 996.

[637] M. Lesbre and G. Glotz, *C.R.* 1934, **198**, 1426.

[638] M. Lesbre, *Bull. Soc. Chim.* 1935, [5] **2**, 1180.

Halogen Derivatives

All three series of these, R_3SnX, R_2SnX_2, and $R\cdot SnX_3$, are known.

The mono- and difluorides[639] (the trifluorides are unknown) show peculiar differences from the other halides, like those between the tetrahalides themselves[640] (SnF_4, b.pt. 705°; $SnCl_4$ 114°). The fluorides of both kinds are crystalline solids without smell, usually melting under pressures greater than an atmosphere at 200–300°, and subliming below their melting-points. The lower members are soluble in water with a slight acid reaction, and are almost insoluble in benzene or ether. The following are some boiling- and melting-points of monohalides:

		Alk_3SnF	Alk_3SnCl	Alk_3SnBr	Alk_3SnI
Alk = Me	B.pt.	..	..	165°	170°
	M.pt.	Decp. 375°	Liquid	+27°	+3·4°
Et	B.pt.	..	210°	97°/13 mm.	117°/13 mm.
	M.pt.	302°	+15·5°	−13·5°	−34·5°
n-Pr	B.pt.	..	123°/13 mm.	224°	261°
	M.pt.	275°	−23·5°	−49°	−53°
iso-Bu	B.pt.	..	142°/13 mm.	148°/13 mm.	285°
	M.pt.	244°	+15°	−26·5°	..
tert. Bu	B.pt.	..	132°/12 mm.	137°/12 mm.	148°/13 mm.
	M.pt.	Decp. 260°	+4°	..	+21°

The fluorides can be made[639] by dissolving the monol in aqueous hydrofluoric acid, or by precipitating a solution of another halide with potassium fluoride, this reaction being reversible. They can be recrystallized from alcohol as colourless crystals. Their properties show that they are ionized, while the other monohalides are covalent, at any rate in the absence of ionizing solvents. The monochlorides, bromides, and iodides can be made by the action of halogens on the tetra-alkyls or the hexa-alkyl distannanes $Alk_3Sn—SnAlk_3$, or by treating the alkyl halides with metallic tin or tin-sodium alloy. Mixed compounds with different alkyls can be prepared; these include the methyl ethyl propyl tin halide MeEtPrSnX which was resolved through the bromo-camphor sulphonate by Pope and Peachey in 1900[641]; in this the cation must be hydrated as in $[R_1R_2R_3Sn\leftarrow OH_2]^+$, otherwise the tin would have only a valency sextet; the ion would then be planar and incapable of showing optical activity.

Skinner and Sutton[642] give these values from electron diffraction of the Sn—X distances (Sn—C is in all 2·18±0·02, and the angle X—Sn—X 109±1°):

	Me_3SnX	Me_2SnX_2	$MeSnX_3$	SnX_4	*Theory*
X = Cl	2·37	2·34	2·32	2·30	2·39
X = Br	2·49	2·48	2·45	2·44	2·54
X = I	2·72	2·69	2·68	2·64	2·73

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[639] E. Krause, *Ber.* 1918, **51**, 1447.

[640] O. Ruff and W. Plato, ib. 1904, **37**, 673.

[641] W. J. Pope and S. J. Peachey, *Proc. C.S.* 1900, **16**, 42, 116.

These halides form ammines with 2 NH_3.[604] The monochlorides, monobromides, and mono-iodides have a very penetrating and repulsive smell, with a violent action on the eyes and breathing organs; this is not found in the monofluorides or in any of the triaryl monohalides, probably because they are not volatile enough; nor does it occur in the dihalides when they are pure.[643]

The aryl tin halides are also known in all three types. The following are the boiling- and melting-points of the phenyl compounds:

	Φ_3SnF	Φ_3SnCl	Φ_3SnBr	Φ_3SnI
B.pt. . .	..	249°/14 mm.	249°/14 mm.	253°/14 mm.
M.pt. . .	347°, decp.	106°	120·5°	121·5°
	Φ_2SnF_2	Φ_2SnCl_2	Φ_2SnBr_2	Φ_2SnI_2
B.pt. . .	..	335°	..	..
M.pt. . .	Over 360°	42°	38°	..
	$\Phi\cdot SnF_3$	$\Phi\cdot SnCl_3$	$\Phi\cdot SnBr_3$	$\Phi\cdot SnI_3$
B.pt. . .	Compound not	300°, decp.	182°/29 mm.	Decps.
M.pt. . .	known	Under −20°	Liquid	Liquid

There is in both the mono- and the dihalides the same sharp distinction as in the alkyls between the fluorides—non-volatile, high-melting, insoluble in practically all solvents—and the liquid or low-melting compounds of the other halogens, easily soluble in organic solvents. These fluorides can be made[609,644-5] by treating a hot dilute solution of the chloride in alcohol with potassium fluoride. The monofluoride Φ_3SnF is so insoluble that triphenyl tin chloride will precipitate the fluorine ion quantitatively.

The dipole moment of Φ_3SnCl in benzene at 25° has been found to be 3·28 D,[646] and that of Φ_3SnBr 3·15.[611]

Dihalides. The dialkyl dihalides can be made in the usual ways, for example by the action of tin on the alkyl iodide,[647] by treating the dialkyl oxides Alk_2SnO with hydrogen halide, or by heating the tetra-alkyl with the tetrahalide for 2 hours at 200-300°, a reaction in which much heat is said to be evolved.[648]

The fluorides are again peculiar. They can be made by precipitating an alcoholic solution of one of the other dihalides with an exact equivalent of potassium fluoride, and recrystallizing from methyl alcohol. They are solids which usually decompose at high temperatures without melting, and are fairly soluble in water and alcohol, but very slightly in benzene. With excess of potassium fluoride they form complex salts, such as $K_2[Et_2SnF_4]$.

[642] H. A. Skinner and L. E. Sutton, *Trans. Far. Soc.* 1944, **40**, 164.

[643] See W. A. Collier, *Z. Hyg. u. Infekt.-krankheiten*, 1929, **110**, 169.

[644] E. Krause and R. Becker, *Ber.* 1920, **53**, 173.

[645] E. Krause and R. Pohland, ib. 1924, **57**, 540.

[646] P. F. Oesper and C. P. Smyth, *J.A.C.S.* 1942, **64**, 173.

[647] T. Karantassis and C. Vassiliades, *C.R.* 1937, **205**, 460.

[648] K. A. Kotscheschkov, *J. Gen. Chem. Russ.* 1935, **5**, 211.

These are some of the solubilities of the difluorides, in g./100 g. solvent at about 30°[639]:

	MeOH	EtOH	H_2O	*Benzene*
Me_2SnF_2	0·33	0·081	4·66	..
Et_2SnF_2	2·64	0·45	2·03	0·047
Pr_2SnF_2	1·91	0·93	0·22	..

These are some melting- and boiling-points of dihalides:

		Alk_2SnF_2	Alk_2SnCl_2	Alk_2SnBr_2	Alk_2SnI_2
Alk = Me	B.pt.	..	189°	209°	228°
	M.pt.	*ca.* 360°	90°	74°	30°
= Et	B.pt.	..	220°	232°	245°
	M.pt.	288° decp.	84°	63°	44°
n-Pr	B.pt.	..	..	..	271°
	M.pt.	204°	80°	48°	Liquid
iso-Bu	B.pt.	..	135°/15 mm.	144°/15 mm.	292°
	M.pt.	..	+9°	+2°	Liquid
tert. Bu	B.pt.	..	117°/14 mm.	128°/14 mm.	186°/12 mm.
	M.pt.	Decp. 254°	42°	..	−14·5°

The dichlorides, dibromides, and di-iodides are (like the mono-compounds) quite different from the fluorides. They are liquids or low-melting solids, volatile, soluble in organic solvents but almost insoluble in water. Unlike the monohalides they have no smell when pure. They form hydrates and ammines with 2 NH_3,[604] and similar complexes with amines, aniline, quinoline, etc.[649] The aryl difluorides are similar in preparation and behaviour.

The diaryl dichlorides, bromides, and iodides are very similar to one another and to their alkyl analogues. They are formed directly by the action of chlorine or bromine on the tetra-aryls, or on the monohalides, or by heating the monohalide with stannous halide: or from the diazonium stannichlorides by reduction with zinc, or with copper or tin powder.[650]

$$(ArN_2)_2SnCl_6 + Zn = Ar_2SnCl_2 + N_2 + ZnCl_2.$$

Their melting-points are lower and their solubilities greater than those of the monohalides.

Trihalides. No trifluorides (either alkyl or aryl) are known. The alkyl trichlorides $Alk \cdot SnCl_3$ can be made by the action of hydrogen chloride gas or of phosphorus pentachloride on the stannonic acid $Alk \cdot SnO \cdot OH$, or by the action of alkyl iodides on the complex stannous salt $K[SnCl_3],H_2O$: in this way $Et \cdot SnI_3$, b.pt. 181-4°/19 mm., has been made.[651] The alkyl trihalides are volatile and have low melting-points; examples are[605] $Me \cdot SnCl_3$, m.pt. 46°; $Me \cdot SnBr_3$, b.pt. 211°, m.pt. 55°; $MeSnI_3$, m.pt. 86·5°.

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[649] P. Pfeiffer, *Z. anorg. Chem.* 1924, **133**, 91.

[650] A. N. Nesmejanov, K. A. Kotscheschkov, and W. A. Klimova, *Ber.* 1935, **68**, 1877.

[651] A. Tchakirian, M. Lesbre, and M. Levinsohn, *C.R.* 1936, **202**, 138.

They all dissolve easily in organic solvents, and most of them also in water with partial hydrolysis.

Aryl trihalides $Ar \cdot SnX_3$ are known with all the halogens except fluorine.[635-6] They are very like the alkyl compounds. They are colourless liquids or low-melting solids which fume in the air and are easily soluble in organic solvents. Boiling water or cold dilute alkaline solution converts them into the aryl-stannonic acids $Ar \cdot SnO \cdot OH$. Halogen hydrides form the complex penta-halogen stannonic acid $H_2[Ar \cdot SnX_5]$.

Sn—Sn Compounds: Distannanes

The hexa-alkyl distannanes $Alk_3Sn—SnAlk_3$ are formed to some extent by the action of tin-sodium alloy on alkyl iodides,[654] but they are better prepared by the action of sodium on the tin trialkyl halides under pressure in ether, or in boiling xylene, or best of all in liquid ammonia[652]; this last method gives a yield of some 90 per cent.; the product is then purified by distillation under reduced pressure in an indifferent gas.

They are colourless liquids or low-melting solids, with a peculiar penetrating and very unpleasant smell, quite different from that of the trialkyl monohalides; they are miscible with organic solvents, but less with the alcohols. The following are the boiling- and melting-points of some $R_3Sn—SnR_3$ compounds:

R =	Me	Et	*n*-Propyl	*iso*-Butyl	R_6 = Et_4Pr_2
B.pt. . .	182°	161°/23 m.	144°/15 m.	179°/3·5 m.	165·8°/15 mm.
M.pt. . .	23°	. .	. .	43°	. .

They distil unchanged, and are almost as stable to heat as the tetra-alkyls; but unlike these, and also unlike the hexa-aryl distannanes, they are oxidized by air (only slowly if they are quite pure) to the oxides $Alk_3Sn—O—SnAlk_3$. They take up halogens to form the monohalides Alk_3SnX, and can remove halogens for this reaction from other compounds; thus mercuric chloride or bromide is reduced to the metal (so is silver nitrate), and ethyl iodide is converted into butane, though methyl iodide adds on to $Et_3Sn—SnEt_3$ to form $Et_3SnI + Et_3SnMe$.[653]

Molecular Weights of Alkyl Distannanes

In 1869 Ladenburg found the vapour density of Et_6Sn_2 at 225° to agree with the Sn_2 formula. The results obtained in solution are conflicting. Rügheimer[655] found from the boiling-point of a 2 per cent. solution of this ethyl compound in ether that it was about 50 per cent. dissociated to Et_3Sn. Grüttner[653] found for 1·3 per cent. solutions in benzene by the freezing-point that there was very little dissociation. Kraus[615] using the

[652] C. A. Kraus and R. H. Bullard, *J.A.C.S.* 1926, **48**, 2132.

[653] G. Grüttner, *Ber.* 1917, **50**, 1808.

[654] A. Ladenburg, *Ann. Spl.* 1869, **8**, 69.

[655] L. Rügheimer, *Ann.* 1909, **364**, 51.

same method with Me_6Sn_2 in benzene found that at low concentrations it was practically completely dissociated to Me_3Sn. Similar difficulties arise with the lead compounds (p. 595).

Hexa-cyclohexyl distannane,[656] which is made similarly, forms fine shining crystals, which though colourless look very like the golden-yellow lead compound; it decomposes without melting at 300°. It is remarkable that when stannic chloride is treated with cyclohexyl magnesium bromide this distannane is formed along with the normal SnR_4. Like the hexaphenyl compound Φ_6Sn_2 the cyclohexyl distannane is extremely stable, but it is said to dissociate in dilute benzene solution to the free SnR_3 radical.

Aryl-distannanes, $Ar_3Sn—SnAr_3$

Hexaphenyl distannane is best made by heating stannous phenyl $Sn\Phi_2$, which then goes to $\Phi_3Sn—Sn\Phi_3$ and metallic tin.[657] Compounds of this type can also be made, like those of the alkyls, by the reduction of the monohalide $Ar_3Sn \cdot$hal with sodium in boiling xylene; with aryls other than phenyl this last method must be used, as the other stannous diaryls do not decompose smoothly on heating (the same occurs with lead).[657]

Hexaphenyl distannane $\Phi_3Sn—Sn\Phi_3$ melts at 237°, and begims to separate tin at 250°; it has no smell, is quite stable to air, and can be kept indefinitely without any special precautions. It takes up bromine quantitatively in chloroform solution even at $-30°$, and reduces silver nitrate to the metal at once in alcohol at $-75°$. Hexa-*p*-tolyl distannane, m.pt. 145°, is stable up to 285°, and the hexa-*p*-xylyl compound (m.pt. 196°) up to 350°.

Molecular weights. As the solids are colourless, they must be assumed to be undissociated (and so must the colourless liquid hexa-alkyls above); this is a contrast to the lead compounds. In concentrated benzene solution at the freezing-point they are also found not to be dissociated. But in dilute solution or at higher temperatures the distannane dissociates like the lead compounds.[658] The position is obscure. Morris and Selwood[659] have examined the magnetism of these compounds. They find that Me_6Sn_2 is diamagnetic at 40° and at 90°, and so must be undissociated; the almost complete dissociation found cryoscopically by Kraus and Sessions[615] they do not explain; they say the magnetic measurements would have detected 2 per cent. dissociation (later they found the same for Pb_2Et_6 (see p. 597). Later[660] they find that hexa-*o*-tolyl distannane at 25° and 80° C. is diamagnetic, and cannot be as much as 4 per cent. dissociated. The elevation of the boiling-point of benzene by this compound they find to be always less than that required for the dimeric form, and to fall rapidly with time, showing how untrustworthy such measurements are with these compounds.

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[656] E. Krause and R. Pohland, *Ber.* 1924, **57**, 532.

[657] E. Krause and R. Becker, ib. 1920, **53**, 173.

[658] J. Boeseken and J. J. Rutgers, *Rec. Trav.* 1923, **42**, 1017.

[659] H. Morris and P. W. Selwood, *J.A.C.S.* 1941, **63**, 2509.

[660] H. Morris, W. Byerly, and P. W. Selwood, ib. 1942, **64**, 1727.

Polystannanes

Hydrocarbon compounds of tin with chains of as much as 5 tin atoms are known, nearly all in the alkyl series.

Kraus and Greer[661] from disodium dimethyl tin and dimethyl tin dibromide made the compound $Na \cdot SnMe_2—SnMe_2—SnMe_2 \cdot Na$, and then replaced the sodium by methyl with methyl iodide, thus getting

$$Me_3Sn—SnMe_2—SnMe_3,$$

a colourless liquid distilling about 100° in a high vacuum.

Kraus and Neal[625] obtained from 2 Me_3SnI and $Na \cdot SnMe_2—SnMe_2Na$ the 'butane' derivative $Me_3Sn—SnMe_2—SnMe_2—SnMe_3$, a colourless viscous liquid, monomeric in benzene solution, and oxidized by the air to a white solid.

Kraus and Greer[661] treated the disodium tristannane compound above with trimethyl stannic iodide and so got the pentane-like compound $Me_3Sn—SnMe_2—SnMe_2—SnMe_2—SnMe_3$ ($Me_{12}Sn_5$), a colourless oil, monomeric in benzene solution.

No aromatic analogue with a formula corresponding to any of these polystannane alkyl compounds has been definitely proved to exist. But Boeseken and Rutgers[658] obtained a product which very probably comes under this head. This was got as a by-product in the preparation of hexaphenyl distannane from stannous diphenyl (with separation of metallic tin); the substance decomposed at 280° without melting; the molecular weight was found to be 1,360: the formula $Sn_4\Phi_{10}$ (as butane) gives 1,245, and $Sn_5\Phi_{12}$ (as pentane) 1,518. But it obviously needs further investigation.

The great stability of all these polystannanes is very remarkable.

ORGANIC COMPOUNDS OF TETRAVALENT LEAD[662]

Lead Tetra-alkyls

It is possible to make these by direct substitution from lead tetrachloride or the complex salt $(NH_4)_2[PbCl_6]$, on treatment with zinc alkyls or the Grignard reagent.[663] But in practice they are made from the alkyl halide and either the metal or plumbous chloride $PbCl_2$ a plumbous dialkyl compound being first formed, which changes on heating into the tetra-alkyl and metallic lead. The preparation from a lead-sodium alloy and alkyl halide, first used by Cahours in 1862, is now employed technically in the United States in the production of ethyl petrol (p. 588). Otherwise the Grignard reagent is used. The change from the plumbous alkyls to the plumbic is less easy with the heavier alkyls; with these therefore the 'trialkyls' Alk_6Pb_2 are made and then converted into the trialkyl halide Alk_3PbX, and so with the Grignard reagent into Alk_3PbAlk.[664]

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[661] C. A. Kraus and W. N. Greer, ib. 1925, **47**, 2568.

[662] Krause and v. Grosse, pp. 372–429.

[663] G. Grüttner and E. Krause, *Ber.* 1916, **49**, 1415.

[664] Id., ib. 1917, **50**, 278.

The lead tetra-alkyls $PbAlk_4$ are colourless substances which can be distilled up to 145° in a vacuum; the higher members are volatile in steam. Those with primary alkyls are stable also to air; when the alkyls are secondary they are much more easily oxidized; tetra-alkyls with tertiary alkyl groups are so unstable that they have not yet been obtained in the pure state. Lead tetra-ethyl has a strong poisonous action which is due to the whole molecule and not to any separated lead; it gives no symptoms of ordinary lead poisoning; the lethal dose is rather large, but it is a cumulative poison.

Lead tetramethyl $PbMe_4$ boils at 110° and melts at $-27{\cdot}5°$. It was used by Aston[665] for the isotopic analysis of lead from different geological sources. Electron diffraction[666] gives the Pb—C distance in the vapour as 2·29 A, making the Pb radius 1·52 A ('theory' 1·46). On heating to a high temperature lead tetramethyl and tetra-ethyl decompose with the production of methyl and ethyl radicals (Paneth, 1929; IV. 530). It has been shown by Leermakers[667] that the decomposition of lead tetra-ethyl vapour at 275° is almost entirely homogeneous, and is practically complete in 12 hours.

The best known of the lead alkyls is the tetra-ethyl (b. pt. 82°/13 mm.) on account of its use as an 'Antiknock' in ethyl petrol.[668-9] It was discovered in 1922[670] that the presence of a small amount of it in petrol was able to prevent 'knocking' in an engine, which made it possible to use a higher compression in the cylinders, and hence get a higher thermodynamic efficiency. The chemical mechanism of this 'knocking' is not yet clear, but the explosions which cause it are certainly of a different kind from those on which the working of the engine depends. About 1–3 c.c. of lead tetra-ethyl are used per gallon of petrol; this involved the consumption of 20,000 tons of lead tetra-ethyl in 1936. To remove deposits of lead in the cylinders ethylene dibromide (which can be partially but not wholly replaced by the dichloride) must be added. The lead ethyl is made by the action of ethyl chloride on an alloy of lead with 10 per cent. of sodium, diethyl-aniline or pyridine being used as a catalyst.

Many mixed lead aryl-alkyls are known; they have small dipole moments, for example $\Phi PbEt_3$ 0·86, Φ_3PbEt 0·81 D.[611] They show no tendency to disproportionate even after standing for years. If, however, mixtures of lead tetra-alkyls are heated in decaline at 80° in the presence of aluminium chloride,[671-2] a random rearrangement of the alkyl groups occurs; the same happens with trialkyl lead monochlorides or monobromides even in the absence of the aluminium chloride. A rearrange-

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[665] F. W. Aston, *Proc. R. S.* 1933, **140**, 535.

[666] L. O. Brockway and H. O. Jenkins, *J.A.C.S.* 1936, **58**, 2036.

[667] J. A. Leermakers, ib. 1933, **55**, 4508.

[668] Krause and v. Grosse, p. 392.

[669] *Brit. Chem. Abstracts*, 1940, B 114.

[670] T. Midgley and T. A. Boyd, *J. Ind. Eng. Chem.* 1922, **589**, 894.

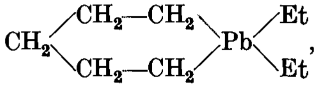
[671] G. Calingaert, H. A. Beatty, and H. Soroos, *J.A.C.S.* 1940, **62**, 1099.

[672] G. Calingaert, H. Soroos, and H. Shapiro, ib. 1104.

ment of alkyls in the presence of aluminium chloride occurs[673] with the alkyls of mercury at 25°, of silicon at 180°, and of tin at 60°; but at 60° there is no rearrangement with zinc.

The relative firmness of attachment of various hydrocarbon radicals to lead has been examined by Krause and Schlöttig.[674] They concluded that aliphatic groups adhere more firmly than aromatic, and cyclohexyl groups the most firmly of all; also while it is the lightest alkyl group that comes off first, it is the heaviest aryl that does so. In general they find the order or increasing firmness of linkage to be: α-naphthyl < *p*-xylyl < *p*-tolyl < phenyl < methyl < ethyl < propyl < *iso*-butyl < *iso*-amyl < cyclohexyl. With the aromatic groups there is evidence that steric repulsion plays a considerable part in promoting instability.

Compounds are also known in which the lead forms part of a heterocyclic ring, as in the penta-methylene derivative



which is a colourless liquid, b.pt. 111°/13·5 mm. slowly oxidized by air.[675]

The *lead tetra-aryls*, which are all colourless, are on the whole more stable than the alkyls, but fewer of them are known because there are difficulties (apparently steric) in the formation of the tetra-aryl compounds with the larger aryl groups.

Pfeiffer's method of preparation from plumbous chloride $PbCl_2$ and the Grignard reagent is believed to go through three stages[676]: (1) the formation of the plumbous aryl $PbAr_2$; (2) the conversion of this into the hexa-aryl diplumbane Ar_6Pb_2 and lead; (3) the conversion of this again into the tetra-aryl $PbAr_4$ and more lead. But it is remarkable that the third reaction should occur in the ethereal solution; if it does, some substance present, perhaps the finely divided lead, must have a strong catalytic influence. The diplumbane is often found to occur as a by-product.

Lead tetraphenyl forms snow-white crystals melting at 225° and boiling at 240°/15-20 mm. According to Giacomello[677] the crystal structure shows the Pb—C distance (theory 2·23) to be 2·39 A (in $PbMe_4$ it was found by electron diffraction to be 2·29: p. 588). Its solubilities (g./100 g. solvent) at 30° are MeOH 0·052; EtOH 0·11; benzene 1·69; chloroform 1·88. It is quite stable; above 270° it is converted into lead and diphenyl, and at 150-200° under 60 atmospheres pressure of hydrogen into lead and benzene. Glacial acetic acid gives benzene and lead tetracetate.[678] A variety of other tetra-aryls, as well as mixed tetra-alkyl-aryls, are known.[679] Those

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[673] G. Calingaert, H. Soroos, and V. Hnidza, ib. 1107.

[674] E. Krause and O. Schlöttig, *Ber.* 1925, **58**, 429.

[675] G. Grüttner and E. Krause, ib. 1916, **49**, 2666.

[676] For further details see W. C. Setzer, R. W. Leeper, and H. Gilman, *J.A.C.S.* 1939, **61**, 1609.

[677] G. Giacomello, *Gaz.* 1938, **68**, 422.

[678] L. W. Jones and L. Werner, *J.A.C.S.* 1918, **40**, 1257.

[679] Krause and v. Grosse, pp. 411-16.

with several different aryls have lower melting-points and are more soluble and more reactive than the others.

Alkaline Compounds

Foster *et al.*[680] have shown that triphenyl lead sodium $\Phi_3Pb \cdot Na$ crystallizes from its pale yellow saturated solution in liquid ammonia in cream-coloured crystals (this is the lightest in colour of the $\Phi_3A \cdot Na$ compounds, $\Phi_3C \cdot Na$ being bright red). It is stable at room temperature; unlike all the other compounds of this type it does not give a precipitate of the hydride (here $\Phi_3Pb \cdot H$) when treated with ammonium bromide in ammonia; the Pb—H link is obviously too weak to be formed; but the solution forms lead triphenyl ethyl Φ_3PbEt when it is treated with ethyl iodide, and so clearly contains the ion $[\Phi_3Pb]^+$, no doubt as the ammonium salt $(NH_4)[\Phi_3Pb]$.

Oxygen Derivatives

Not very much is known of any of these except the mono-hydroxides. These are made by treating the monohalides with potassium hydroxide or silver oxide.[681] The trialkyl hydroxides $Alk_3Pb \cdot OH$ are liquids or low-melting solids with a very unpleasant smell, fairly soluble in organic solvents and slightly soluble in water with a rather weak alkaline reaction. The moment of Et_3PbOH in benzene is about 2·4 D.[611] They are even less like alcohols than their stannic analogues, and like them form a series of salts[682-3] such as a very insoluble sulphate $[Et_3Pb]SO_4$ and carbonate, and a soluble nitrate, phosphate $Et_3PbH_2PO_4$ and formate.

Of the aromatic monols, triphenyl lead hydroxide $\Phi_3Pb \cdot OH$ is made[684] from the bromide with potassium hydroxide. It is soluble in benzene and less so in alcohol, from which it separates in colourless crystals looking exactly like its tin analogue.

The dialkyl dihydroxides $Alk_2Pb(OH)_2$ are practically unknown, though a few of their salts have been prepared,[685] such as the nitrate $Et_2Pb(NO_3)_2$, which can be made by the action of nitric acid on lead tetraethyl, or on Pb_2Et_6 in chloroform[686]; it is soluble in water and highly ionized in the solution. An unstable sulphide is also known.[663]

The *aromatic diols* appear as the oxides Ar_2PbO[687]; the di-hydroxy-form is as unknown as it is with the corresponding compounds of carbon and tin (and with the silicon dialkyls though not the diaryls). Diphenyl lead oxide Φ_2PbO is an insoluble and infusible white powder, obtained by treating the nitrate with alkali. Unlike the monol $\Phi_3Pb \cdot OH$, the diol forms salts with acids, which can also be obtained by treating the plumbous

[680] L. S. Foster, W. M. Dix, and I. J. Gruntfest, *J.A.C.S.* 1939, **61**, 1685.

[681] E. Krause and E. Pohland, *Ber.* 1922, **55**, 1283.

[682] J. Klippel, *J. prakt. Chem.* 1860, [1] **81**, 287.

[683] P. Pfeiffer, P. Truskier, and P. Disselkamp, *Ber.* 1916, **49**, 2446.

[684] G. Grüttner, *Ber.* 1918, **51**, 1298. [685] J. Tafel, *Ber.* 1911, **44**, 324.

[686] C. D. Hurd and P. R. Austin, *J.A.C.S.* 1931, **53**, 1543.

[687] A. Polis, *Ber.* 1887, **20**, 720.

diaryl with mineral acids; an example is the nitrate $\Phi_2Pb(NO_3)_2$, soluble in water and alcohol, and crystallizing with 4 molecules of pyridine from pyridine solution; if it is treated with more nitric acid it is nitrated, 94 per cent. in the meta position[688-9]; there is also a phosphate, chromate, formate, and acetate.[690] According to Koton[691] organic acids will react with lead tetraphenyl to give the salts Φ_2PbX_2; in this way a propionate (m.pt. 171°), lactate, butyrate, and benzoate can be prepared; the yields get worse as the chain lengthens, and stearic acid will not react at all. The sulphide Φ_2PbS is a white precipitate, decomposing at 90°.[690]

The plumbonic acids $Alk \cdot PbO \cdot OH$ derived from the tri-hydroxides have been made[692-3] by the action of ethyl iodide on sodium plumbite, which is made by saturating 6-normal sodium hydroxide solution with hydrated lead monoxide; it is curious that the potassium salt does not seem to react with ethyl iodide. The plumbonic acids, like the stannonic, are amorphous infusible substances, insoluble in neutral solvents, but dissolving both in acids to form compounds $Alk \cdot PbX_3$, and in alkalies to form alkaline salts.

The aryl lead triols or aryl plumbonic acids $Ar \cdot PbO \cdot OH$ do not seem to be known.

Halogen Derivatives

Those of the lead alkyls are known in all three types, R_3PbX, R_2PbX_2, and $R \cdot PbX_3$; but of the aryls only the first two have been made. Of the *alkyl* derivatives the fluorides[694] (of which only the mono-series is known), especially those with the lighter alkyls, show the same exceptional behaviour as the fluorides of tin. The following are some melting-points of these compounds; the fluorides do not melt, but have fairly sharp temperatures of decomposition. Trimethyl lead chloride Me_3PbCl sublimes at 190°, and the iodide Me_3PbI can also be sublimed.

Melting-points

	$Alk_3Pb \cdot F$	$Alk_3Pb \cdot Cl$	$Alk_3Pb \cdot Br$	$Alk_3Pb \cdot I$
Alk = CH_3	decp. 305°	..	133°	..
C_2H_5	decp. 240°	172° w. decp.	103°	..
Pr	decp. 235°	135° w. decp.	81°	..
iso-Bu	decp. 230°	122° w. decp.	107° w. decp.	..
cy. hexyl	decp. 198°	236° w. decp.	210° w. decp.	97·7°

These are the solubilities (g./100 g. solvent) of some of the monofluorides at 30°:

	H_2O	MeOH	EtOH	*Benzene*
Me_3PbF	5·51	8·24	6·89	0·028
Et_3PbF	1·30	7·24	6·11	0·185
n-Pr_3PbF	0·17	2·00	1·21	0·055
iso-Bu_3PbF	0·12	1·76	1·09	0·042
cy. hex_3PbF	0·096	0·66	0·39	0·11

The fluorides obviously behave as salts, with very high melting-points and (at least in the lower members) a much greater solubility in water than in benzene. They are colourless crystalline substances, and are the most stable of the alkyl-lead halides. They cannot be precipitated like the stannic compounds from solutions of the other halides with potassium fluoride, but must be made from the trialkyl-hydroxides with dilute hydrofluoric acid. Only the methyl and ethyl compounds have the frightful smell of the other monohalides, but this may be merely a question of their volatility; the dust of all these fluorides is extremely poisonous.

The other monohalides have (like their stannic analogues) an intense and repulsive smell, and a violent action on the eyes and the mucous membrane. They can be made by the action on lead tetra-alkyls of hydrogen chloride (Cahours 1862), or of chlorine at −75° (to prevent the replacement from going too far). Even with gaseous hydrogen chloride lead tetra-ethyl in toluene at 90° gives a mixture of lead chloride $PbCl_2$ and the dichloride Et_2PbCl_2[695]; the diplumbane Alk_6Pb_2 (from lead chloride $PbCl_2$ and the Grignard reagent) can also be treated with chlorine at −75°.

The monochlorides are less soluble than the bromides or iodides. The bromides are made in the same way as the chlorides; the alkyl bromides are colourless, but the cyclohexyl compound is straw coloured, and tribenzyl lead bromide is deep orange.

The iodides can be made in the same way, and the reaction mixture need not be cooled below 0°; but they are very unstable, and easily go to lead iodide PbI_2 and the hydrocarbon, especially in the light. They are mostly pale yellow.

The following dipole moments have been determined in benzene at 25°[611,696]: Me_3PbCl 4·47; Et_3PbCl 4·39; Et_3PbBr 4·46; Φ_3PbCl 4·32 D.

The *aryl monohalides* are difficult to make from the tetra-aryls, because the halogens convert these straight into the dihalides: even in ether at −75° bromine mainly gives the dibromide, though at this temperature lead tetra-alkyl would only give the monobromide; the reason may be partly that the monobromide is much more soluble than the tetra-aryl and so is more open to attack, or it may be due to the carbon atom attached to the lead being tertiary, or it may be for steric reasons.[697] But in pyridine solution, where the activity of the bromine is diminished by solvation, Grüttner[684] obtained a good yield of triphenyl lead monobromide; a similar effect of the solvent in weakening the effect of a halogen

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[688] F. Challenger and E. Rothstein, *J.C.S.* 1934, 1258.

[689] K. A. Kotscheschkov and G. M. Borodina, *C.R. Acad. Sci. U.S.S.R.* 1937, 569.

[690] A. Polis, *Ber.* 1887, **20**, 3332.

[691] M. M. Koton, *J. Gen. Chem. Russ.* 1941, **11**, 376.

[692] M. Lesbre, *C.R.* 1935, **200**, 559.

[693] Id., ib. 1940. **210**, 535.

[694] E. Krause and E. Pohland, *Ber.* 1922, **55**, 1282.

[695] A. J. Jakubovitsch and I. Petrov, *J. prakt. Chem.* 1935, [ii] **144**, 67.

[696] G. L. Lewis, P. F. Oesper, and C. P. Smyth, *J.A.C.S.* 1940, **62**, 3243.

[697] E. Krause and M. Schmitz, *Ber.* 1919, **52**, 2152.

through co-ordination occurs with iodine and hexaphenyl distannane Φ_6Pb_2, which in aqueous alcohol or pyridine[698] give the mono-iodide, but in benzene only the di-iodide Φ_2PbI_2 and plumbous iodide PbI_2.

The monohalides Ar_3PbX can also be made by heating the tetra-aryl with the dihalide, but this reaction is reversible[699]:

$$Ar_4Pb + Ar_2PbX_2 \rightleftharpoons 2\ Ar_3PbX.$$

The triaryl monohalides, except the fluorides which are much less soluble, dissolve easily and crystallize well. The others are commonly prepared from the bromides, which are made from the tetra-aryl and bromine in pyridine. The reduction of the mono-halides by sodium, and the properties of the sodium compounds $Ar_3Pb \cdot Na$ have been examined by Foster *et al.*[680] (see p. 590). The reduction occurs in liquid ammonia. They point out that $\Phi_3Pb \cdot$hal and $\Phi_3Sn \cdot$hal are stable in liquid ammonia, while $\Phi_3Ge \cdot$hal and $\Phi_3Si \cdot$hal are wholly and $\Phi_3C \cdot$hal partly ammonolysed.

Triphenyl lead fluoride Φ_3PbF,[700] unlike the alkyl compound, can be made by precipitating a solution of the bromide with potassium fluoride. Colourless needles: solubilities:

Solvent	*Water*	MeOH	EtOH	*Benzene*
At 30°	0·031	0·36	0·15	0·080
At 50°	0·10	1·45	0·24	0·092

Triphenyl lead chloride Φ_3PbCl, made from the oxide, or by heating lead tetraphenyl with ammonium chloride for 12 hours at 175°,[674] forms colourless crystals from alcohol, m.pt. 206°; its solubility is like that of the bromide, but rather greater.

The bromide Φ_3PbBr melts at 166°, and above this temperature slowly separates lead bromide $PbBr_2$; it is insoluble in water, slightly soluble in cold and largely in hot alcohol and benzene. It is much more stable than its alkyl analogues, and can be heated for a long time to 100° without decomposition. It attacks the mucous membrane less violently than the chloride only because it is less volatile.

The iodide Φ_3PbI is obtained from the bromide with potassium iodide.[684] It sinters at 142°, and then decomposes completely with separation of PbI_2. It is remarkably less soluble than the bromide, and much less stable even than the trialkyl iodides.

The dipole moments of these phenyl compounds have been measured in benzene solution at 25°[696]; they are Φ_3PbCl 4·21; Φ_3PbBr 4·21; Φ_3PbI 3·73 D.

Dihalides. The tendency of the tetra-alkyls and tetra-aryls to split off two hydrocarbon groups at once when treated with halogens is very characteristic of lead, and is found also to a smaller extent with tin. It

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[698] E. Krause and G. G. Reissaus, ib. 1922, **55**, 897.

[699] P. R. Austin, *J.A.C.S.* 1932, **54**, 3287.

[700] E. Krause and E. Pohland, *Ber.* 1922, **55**, 1287.

may be a sign of the stability of the 'shared quartet' in $[R_2Pb]^{++}$ as in the mercuric compounds and in $[R_2Tl]^{+}$.

The difluorides are unknown in the alkyl series; the other dihalides are less stable than the monohalides, the chlorides being most stable and the iodides least.

The dichlorides can be made like the monochlorides by the action of chlorine on the tetra-alkyls, if the temperature is allowed to rise as soon as the colour of the chlorine is visible, and more chlorine is passed in. Dimethyl lead dichloride Me_2PbCl_2 sinters at 155°; its solubility at 28° is about 0·22 in water and 0·21 in ethyl alcohol. It is the stablest of the dialkyl lead halides, and can be left for days in water without any lead chloride being formed. Diethyl lead dichloride Et_2PbCl_2, which can be made from lead tetraethyl and hydrogen chloride at 90°,[701] has a dipole moment of 4·70 D in benzene at 25°[696]; it decomposes at a little over 200°.

The *dibromides* are made in the same way, but are very unstable; dimethyl lead dibromide splits off $PbBr_2$ in contact with any solvent at 50°, and can only be kept for a few days[672]; the ethyl compound is even less stable. These dibromides are much less soluble than the dichlorides.

The *di-iodides*[672,685] are pale yellow crystalline substances, so unstable that they can hardly be got free from lead iodide, and they decompose very soon after preparation.

In the aromatic series the difluoride Φ_2PbF_2 has recently been prepared by Gilman *et al.*[676] by treating the iodide Φ_2PbI_2 with potassium fluoride. It resembles the other fluorides; it is insoluble in the ordinary organic solvents, and does not melt below 300°. The dichloride Φ_2PbCl_2, from lead tetraphenyl and chlorine, is very insoluble (just the opposite to the tin analogue), and on heating decomposes without melting. It forms a solvate with 4 molecules of pyridine, which loses its pyridine in the air.[683] The bromide Φ_2PbBr_2 is similar, and forms compounds with 4 py. and 4 NH_3.[683] The iodide Φ_2PbI_2 (from lead tetraphenyl and iodine in chloroform)[687] is yellow, soluble in organic solvents, and melts at 102°. Corresponding derivatives of other aryls are known.

The diaryl dihalides, like their alkyl analogues, form numerous salts; these have already been described as diol derivatives (p. 590).

The alkyl *trihalides* have recently been obtained by Lesbre[692,702] from the plumbonic acids (which are themselves made from the plumbite with alkyl iodide) by treatment with dilute hydrochloric acid. These trihalides $Alk \cdot PbX_3$ are yellow extremely unstable substances. With pyridinium and quinolinium halides they give complex salts of the type $(BH)_2[Alk \cdot PbX_5]$. Both the trihalides and these complex salts are much less stable with lead than they are with tin. It must be remembered that the change to the divalent form is very much more favoured by lead than by tin.

No trihalides of the aromatic series have yet been obtained.

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[701] H. Gilman and J. D. Robinson, *J.A.C.S.* 1930, **52**, 1975.

[702] M. Lesbre, *C.R.* 1938, **206**, 1481.

Diplumbane Derivatives and Trivalent Lead Radicals

The evidence for the dissociation of the diplumbanes $R_3Pb—PbR_3$ into the trivalent lead radicals R_3Pb is by no means clear, but there seems little doubt that this dissociation goes much further with lead than it does with tin. The two kinds of lead compounds must be treated together, and the symbol Pb_2R_6 must be taken to refer to the equilibrium

$$R_3Pb—PbR_3 \rightleftharpoons 2\ R_3Pb.$$

The compounds (where R = alkyl or aryl) can be made by treating the lead-sodium alloy with alkyl or aryl iodide (Löwig, 1853; Klippel, 1860), the reaction being moderated by keeping the temperature low. It has been shown[703] that methyl magnesium iodide and lead chloride give at $-5°$ a 60 per cent. yield of hexamethyl diplumbane, though from triphenyl lead iodide and sodium in liquid ammonia only a 7 per cent. yield of the hexaphenyl compound is obtained.

With the Grignard reagent there are two stages; in the first, the product is the dark coloured plumbous compound, but this rapidly changes further:

$$2\ Alk{\cdot}MgBr + PbCl_2 = PbAlk_2 + MgCl_2 + MgBr_2. \qquad (I)$$

$$3\ PbAlk_2 = Alk_3Pb—PbAlk_3 + Pb. \qquad (II)$$

A further change is possible:

$$2\ Alk_3Pb—PbAlk_3 = 3\ PbAlk_4 + Pb. \qquad (III)$$

This last change occurs more readily the smaller the alkyl; hexamethyl diplumbane changes easily in the course of its preparation; the hexaethyl needs long boiling in ether; diplumbanes with heavier alkyls go over only on distillation, though they sometimes do so with explosion.

The diplumbanes can also be made by the reduction of the monol Ar_3PbOH or its halide, either electrolytically[704] or in the case of the halide with aluminium.[705]

Hexamethyl diplumbane $Me_3Pb—PbMe_3$[703] melts at 38° C. Skinner and Sutton[706] found by electron diffraction the distances Pb—Pb $2{\cdot}88 \pm 0{\cdot}05$, and Pb—C $2{\cdot}25 \pm 0{\cdot}06$ (this gives the radius of the lead as $1{\cdot}44 \pm 0{\cdot}03$ or $1{\cdot}48 \pm 0{\cdot}06$, mean 1·46, the value adopted in the table (xxix): shorter than the value of 1·52 A found from the electron diffraction (p. 588) of lead tetramethyl).

Hexa-ethyl diplumbane[704,707] is a heavy yellow oil boiling at 100°/2 mm., which is bimolecular (Pb_2) in concentrated benzene solution, and monomolecular (Et_3Pb) in dilute; it is easily oxidized by air, and is converted by hydrogen chloride into triethyl lead chloride, and ethane; even in sealed vessels it decomposes in a few days. It melts at 36°.[703]

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[703] G. Calingaert and H. Soroos, *J. Org. Chem.* 1938, **2**, 535.

[704] T. Midgley, C. A. Hochwalt, and G. Calingaert, *J.A.C.S.* 1923, **45**, 1821.

[705] F. Hein and A. Klein, *Ber.* 1938, **71**, 2381.

[706] H. A. Skinner and L. E. Sutton, *Trans. Far. Soc.* 1940, **36**, 1209.

[707] H. Gilman and J. C. Bailie, *J.A.C.S.* 1939, **61**, 731.

The cyclohexyl compound $Pb_2(C_6H_{11})_6$ was made directly from the Grignard reagent and lead chloride[708]; the liquid first goes dark and then after 4 hours' boiling of the ether it becomes yellow, with the separation of finely divided lead; the diplumbane is then extracted with benzene. It forms bright yellow crystals which are permanent in the dark, but turn brown rapidly in the light, and blacken on heating to 195°. It is dissociated to the radical $Pb(C_6H_{11})_3$ in benzene solution even when this is fairly concentrated, and this, as well as its bright colour, indicates greater dissociation than occurs with the aryl compounds; further, unlike both the alkyl and the aryl di-plumbanes it is converted smoothly by both iodine and bromine into the monohalide without the formation of any dihalide.

Hexa-aryl Diplumbanes[697-8]

These can be made like their alkyl analogues from lead chloride and the Grignard reagent, but the diplumbane formed may change further into lead tetra-aryl and metallic lead. Whether it does so depends on the size of the aryl group (there is a similar effect with the alkyls, p. 595). With phenyl the change goes on boiling the ethereal solution; with the hexa-*p*-tolyl compound much less easily; and with the hexa-*o*-tolyl and hexa-*p*-xylyl compounds (both of which have a CH_3 group ortho to the Pb—C) not at all.

This question has been further examined by Gilman and Bailie,[707] by observing the readiness with which the reaction

$$2\ R_3Pb{-}PbR_3 \longrightarrow 3\ PbR_4 + Pb$$

occurs; the relative stabilities of the diplumbanes follow the usual course,[709] decreasing in the order mesityl, cyclohexyl > α-naphthyl > *o* and *p* alkoxyphenyl > *p*-tolyl > *m*-tolyl, phenyl > ethyl, methyl. Later[710] they make use of the reactions

$$\text{(I)}\quad 2\ Ar_6Pb_2 + 12\ Bu{\cdot}Li = 3\ Bu_4Pb + 12\ Ar{\cdot}Li + Pb$$

and

$$\text{(II)}\quad Ar_4Pb + 4\ Bu{\cdot}Li = Bu_4Pb + 4\ Ar{\cdot}Li$$

and find the order of increasing rate of change towards the right-hand side (i.e. of replacement of the aryl group on the lead by butyl) is

$$Pb\Phi_4 < Pb_2\Phi_6 < Pb(p\text{-tol})_4 < Pb_2(p\text{-tol})_6.$$

It is evident that the results depend partly but not wholly on the space-filling properties of the aryl groups.

Hexaphenyl diplumbane is made in this way from lead chloride and phenyl magnesium bromide and extracted after evaporation of the ether with benzene; it then separates as $Pb_2\Phi_6$, C_6H_6; from alcohol it separates without solvent. The solvated crystals are very pale yellow; the pure crystals are definitely yellow, and the solutions again pale yellow; they

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[708] E. Krause, *Ber.* 1921, **54**, 2060.

[709] H. Gilman, *Organic Chemistry*, New York, 1938, chap. iv.

[710] H. Gilman and F. W. Moore, *J.A.C.S.* 1940, **62**, 3206.

get darker on warming (presumably through increased dissociation), and lose this colour again on cooling. Hexa-*p*-tolyl and hexa-*o*-xylyl diplumbane are similar; they decompose on heating at 193° and 225° respectively.[711]

The solubilities of hexaphenyl and hexa-*p*-tolyl diplumbane at 30° are as follows:

Solvent	EtOH	$CHCl_3$	*Benzene*	*Pyridine*
$Pb_2\Phi_6$	0·08	26·5	20·9	9·3
$Pb_2(p\text{-tol})_6$	0·001	11·8	5·08	2·5

The hexa-aryl diplumbanes react with potassium permanganate, the Pb—Pb link being broken and not the Pb—C; the product is the monol $Ar_3Pb \cdot OH$.[712]

The statements about the degree of dissociation of these compounds into the trivalent lead triaryl (or trialkyls) are sometimes discordant with one another or even with themselves. The dipole moment of hexaphenyl diplumbane has been found[696] to be zero. If it is undissociated this is to be expected: if it were the radical, its moment should depend on whether the three covalencies of the 1, $\underline{6}$ valency septet are planar or tetrahedral; the latter is perhaps more likely, but even then the dipole measurements would not detect a small amount of dissociation.

Measurements by the boiling- and freezing-points in solution are said to give the following results. Hexa-ethyl diplumbane[704] is found to be undissociated in concentrated benzene solution, but dissociated in dilute; the cyclohexyl compound $Pb_2(C_6H_{11})_6$[708] is highly dissociated, even in fairly concentrated benzene solution. Jensen and Clausen-Kaas[713] confirm Krause's result that in 0·5 per cent. benzene solution it is about 30 per cent. dissociated, but they find by very careful measurements that in this solvent it is diamagnetic. How this can be they cannot explain. Of the aryl diplumbanes the hexaphenyl is said[698,711] to show by the freezing-point little dissociation in concentrated and almost complete in dilute solution; Foster *et al.*[680] found 18 per cent. dissociation in a 3 per cent. solution, and Krause[590] 47 per cent. in a 0·5 per cent. Similar results are got with hexa-*p*-tolyl and hexa-*o*-xylyl diplumbane.[711] The former is said to be shown by the freezing-point to be wholly dissociated in benzene solution at 0·1 per cent. and not at all at 1 per cent.: the latter to be almost wholly Pb_2 in 0·5 per cent. solution, but completely dissociated in 0·1 per cent. There must be something wrong about these figures. Even where the dissociation is small, it is proportional to the square root of the dilution, and at this rate, if it were even 10 per cent. in a 0·5 per cent. solution it would still only be 22 per cent. in a 0·1 solution.

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[711] E. Krause and M. Schmitz, *Ber.* 1919, **52**, 2165.

[712] P. R. Austin, *J.A.C.S.* 1931, **53**, 3514.

[713] K. A. Jensen and N. Clausen-Kaas, *Z. anorg. Chem.* 1943, **250**, 277.

The magnetic measurements of Selwood *et al.*[714-16] raise further difficulties, and seem to indicate that the dissociation of these substances is always very small. They find[714] that the magnetic moments of hexaphenyl diplumbane both solid and in benzene solution show that the maximum dissociation possible is 0·01 per cent. in the solid and 1·4 per cent. in a 0·7 to 1·2 per cent. solution in benzene at 30–80°. With cyclohexyl diplumbane they find[715] that the substance is diamagnetic at 10° and 90°; as little as 10·per cent. dissociation would have been detected; the 47 per cent. dissociation found by Krause they cannot explain. Later, however,[716] they find on measuring the molecular weight of $Pb_2\Phi_6$ in benzene by the boiling-point that the elevation found is always less than that required for the diplumbane formula, and falls rapidly with time. They conclude that boiling-point measurements are of no value for the study of free radicals, but of course the real conclusion is that each·case must be examined on its merits; the measurements of Krause referred to were not at the boiling-point but at the freezing-point.

Until the whole question has been re-examined experimentally all we can say is that the qualitative indications, especially the colour, point to a sensible dissociation of these diplumbanes, especially those of the aryl series, but that the quantitative results obtained so far are of doubtful value.

NITRIDES

Silicon, germanium, and tin (but apparently not lead) form nitrides, all of the type M_3N_4. They are all covalent, and probably giant molecules. Chemically they are very stable.

Silicon nitride, Si_3N_4, is made directly by heating silicon in nitrogen to 1300–80°[717]; its heat of formation at 25° is 163·0 k.cals.[718] Little is said of its properties.

Germanium nitride, Ge_3N_4, is the ultimate residue when the product of the action of ammonia on germanium tetrachloride is heated above 300°[719,720]; it can also be made by heating germanium or its dioxide in ammonia to 700°.[721] It is a light brown or white powder; it begins to evolve nitrogen at 450°, but is not completely decomposed below 1,400°.[719] Chemically it is remarkably stable[721]; it is not affected by water or dilute alkali at 100°: concentrated nitric or sulphuric acid act on it only slowly at their boiling-points; chlorine does not act on it below 600°, or oxygen below 800°. It has the crystal structure of phenacite Be_2SiO_4, each germanium atom being surrounded tetrahedrally by four nitrogens, and every three tetrahedra having one nitrogen in common.[722]

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[714] R. Preckel and P. W. Selwood, *J.A.C.S.* 1940, **62**, 2765.

[715] H. Morris and P. W. Selwood, ib. 1941, **63**, 2509.

[716] H. Morris, W. Byerly, and P. W. Selwood, ib. 1942, **64**, 1727.

[717] A. G. Nasini and A. Cavallini, *Congr. Internat. Quim.* 1938, **9**, iii. 280.

[718] S. Satoh, *Inst. Phys.-Chem. Res. Tokyo*, 1938, **34**, 144.

[719] R. Schwarz and P. W. Schenk, *Ber.* 1930, **63**, 296.

[720] J. S. Thomas and W. Pugh, *J.C.S.* 1931, 60.

Tin nitride, Sn_3N_4, is similar.[723] When the product of the action of liquid ammonia on tin tetrachloride is heated to 270°, a brown powder of the composition NSnCl remains. At 360° this further decomposes into tin nitride and tin tetrachloride

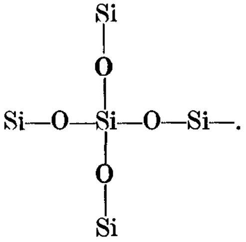
$$4\ NSnCl = Sn_3N_4 + SnCl_4.$$

But already at this temperature the nitride is beginning to break up into its elements; hence it is not surprising if lead nitride does not exist.

DIOXIDES[724]

	CO_2	SiO_2	GeO_2	SnO_2	PbO_2
B.pt. . .	−78·5° subl.	2,590°	1,200°	1,900° subl.	..
M.pt. . .	−56·5°	1,710°	1,116°	1,900°	..

Silicon Dioxide. The sudden change from gaseous carbon dioxide to the relatively infusible silica is no doubt due to the instability of multiple links with silicon, leading to the formation of singly linked giant molecules, with the groupings



Silica occurs in three different forms

$$\text{Quartz} \xrightleftharpoons{870^\circ} \text{Tridymite} \xrightleftharpoons{1470^\circ} \text{Cristobalite} \xrightleftharpoons{1710^\circ} \text{Liquid.}$$

The changes are all slow (as is shown by these forms occurring as minerals), and the liquid commonly solidifies to a glass, with the same structure as germanium dioxide glass.[725-6] Each crystalline form has a low- and a high-temperature modification, but these differ only slightly in structure. The three main forms (and also the glass) are made up of SiO_4 tetrahedra, each oxygen atom being common to two; the differences between the three are not unlike those between the diamond, zinc blende, and wurtzite lattices.[727] Chemically silica is very stable; it is scarcely affected by hydrogen at any temperature, nor by chlorine or bromine, though it is of course by fluorine.

[721] W. C. Johnson, *J.A.C.S.* **52**, 5160.

[722] R. Juza and H. Hahn, *Naturwiss.* 1939, **27**, 32.

[723] R. Schwarz and A. Jeanmaire, *Ber.* 1932, **65**, 1443.

[724] Wells, *S.I.C.* 463.

[725] B. E. Warren, *Phys. Rev.* 1934, ii. **45**, 292.

[726] B. E. Warren, H. Krutter, and O. Morningstar, *J. Amer. Ceram. Soc.* 1936, **19**, 202.

[727] See W. Nieuwkamp, *Z. Krist.* 1937, **96**, 454.

The only metals that will reduce it alone are the alkali and alkaline earth metals, and imperfectly aluminium; other metals reduce it in presence of carbon, forming silicides.

Germanium dioxide occurs in two forms, one (*a*) with a quartz[728-9] and the other (*b*) with a rutile lattice.[730] The ordinary form *a* is metastable below the transition point of 1033°, and can be converted into *b* by heating with water in a bomb to 350°[731]; the melting-points are (*a*) 1,116°, (*b*) (metastable) 1,086°.[732] The *b* form is insoluble in water; the *a* preceptibly soluble (sol^y 0·41/20°: the solution may be colloidal[733]). This greater solubility makes germanium dioxide more reactive than silica, and it is readily soluble in alkali.

Tin dioxide SnO_2 is trimorphic, the ordinary form (cassiterite, the chief ore of tin) having a rutile lattice. It is insoluble in water, and scarcely attacked at all by acids or alkalies except when they are concentrated and hot; it dissolves in fused alkalies to give stannates, or in presence of sulphur thiostannates.

Lead dioxide, PbO_2, can be made by oxidizing the ordinary oxide PbO by fusion with alkaline chlorate and nitrate, or by anodic oxidation of plumbous solutions. Only one form is known, which is dark brown or black; it has a rutile lattice. Its existence is sharply limited by the ease with which it loses oxygen to give Pb_3O_4; the dissociation tension of oxygen is 68 mm. at 287° C. and 1 atmosphere at 752°.[734] This is a sign of the stability of the divalent state of lead ('inert pair'). Lead dioxide is practically insoluble in water, and only slightly soluble in concentrated nitric or sulphuric acid; with hydrochloric acid it evolves chlorine.

HYDROXIDES $A(OH)_4$ AND THEIR METALLIC SALTS

Silicic Acid, $Si(OH)_4$. This has a strong tendency, like its germanium and tin analogues, to form colloidal solutions, and so it is difficult to say exactly what forms of the acid exist. When first precipitated from a solution of an alkaline silicate it probably has the simple (Si_1) formula, but then it slowly condenses by forming Si—O—Si links, to complex and ultimately to colloidal forms. It is, however, clear that it is a very weak acid (K_1 about 10^{-10}) and that it has no basic properties whatever.

The simplest *silicates* are of the types of Na_2SiO_3 (meta) and Na_4SiO_4 (ortho). Only the alkaline silicates are soluble in water; the ammonium salts cannot be prepared. The natural silicates are of course of enormous practical importance, the chief being felspar, of the type $K_2O,Al_2O_3, 6\,SiO_2$. So are many artificial silicates, including glass, which is usually derived

[728] V. M. Goldschmidt, *Naturwiss.* 1926, **14**, 296.

[729] W. H. Zachariasen, *Z. Krist.* 1928, **67**, 226.

[730] J. H. Müller and H. R. Blank, *J.A.C.S.* 1924, **46**, 2358.

[731] A. W. Laubengayer and D. S. Morton, ib. 1932, **54**, 2303.

[732] R. Schwarz and E. Haschke, *Z. anorg. Chem.* 1943, **252**, 170.

[733] R. Schwarz and E. Huf, ib. 1931, **203**, 188.

[734] J. Krustinsons, *Z. Elektrochem.* 1937, **43**, 65.

from Na_2O, CaO, 6 SiO_2, in which the sodium can be replaced by potassium, the calcium by lead, and the silicon by boron or aluminium. 'Lindemann glass', which is used for the windows of discharge tubes, has the sodium and calcium entirely replaced by lithium and beryllium, so as to have the minimum stopping power for swift particles.

Pure clay or kaolin (china clay), which is formed by weathering of felspars, is Al_2O_3, 2 SiO_2, 2 H_2O. Cement is made by burning a mixture of clay and limestone, and usually contains about 2 parts of 'basic' oxides (Ca, Mg) to 1 of 'acidic' oxides (Al, Si, and sometimes Fe). Thus it starts with the composition (mainly) Ca_2SiO_4; on adding water this changes to hydrated lime and $CaSiO_3$. In ordinary cement the lime forms the carbonate with the carbon dioxide of the air; hydraulic cements contain more silica, which combines with the lime to form more metasilicate $CaSiO_3$. In any case the whole passes into an interlacing mass of crystals.

The structures of the natural silicates have been worked out in great detail by X-ray analysis, largely by the Braggs.[735-6] The most important point about them is that in all the silicon is surrounded tetrahedrally by 4 oxygen atoms.

Orthosilicic acid forms a series of volatile esters such as $Si(O \cdot CH_3)_4$, b.pt. 121°; $Si(O \cdot C_2H_5)_4$ 165·5°; $Si(O \cdot C_3H_7)_4$ 191°; they are readily hydrolysed[739,740]; the alkyloxy-groups can be replaced successively by alkyls on treatment with zinc alkyl and sodium (Ladenburg, 1872) or with the Grignard reagent[737-8]: or by chlorine on treatment with silicon tetrachloride or acetyl chloride.[743] If the ester is heated with benzene and aluminium chloride the benzene is alkylated, with the production of aluminium silicate.[744] Several chlorosilicates such as $Me\text{-}O\text{-}SiCl_3$ (b.pt. 79°) are also known.[741-2]

Germanium hydroxide, $Ge(OH)_4$, resembles silicic acid, but is more soluble in water; its dissociation constant is probably about 2×10^{-9},[745-6] greater than that of silicic acid, but not much greater. It shows no signs of forming cations such as $[Ge(OH)_3]^+$, but is so far basic that it can form covalent derivatives with acids in presence of water; if germanium dioxide is distilled with concentrated hydrochloric acid, the germanium comes over, no doubt as the tetrachloride, the hydrolysis of which is reversible and incomplete. It often separates from its salts as a colloid, and it cannot be isolated in the pure state.

Germanic hydroxide forms a series of germanates, which are usually isomorphous with the silicates; thus Na_2GeO_3 forms a continuous series of

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[735] See Pauling, *Chem. Bond.* ed. 2, 386 ff. [736] See Wells, *S.I.C.* 465-87.

[737] H. W. Post and C. H. Hofrichter, *J. Org. Chem.* 1939, **4**, 363.

[738] Id., ib. 1940, **5**, 443.

[739] D. F. Peppard, W. G. Brown, and W. C. Johnson, *J.A.C.S.* 1946, **68**, 73.

[740] Id., ib. 77. [741] Id., ib. 70. [742] Id., ib. 76.

[743] H. W. Post and H. M. Norton, *J. Org. Chem.* 1942, **7**, 528.

[744] H. L. Kane and A. Lowy, ib. 1936, **58**, 2605.

[745] W. Pugh, *J.C.S.* 1929, 1994.

[746] C. E. Gulezian and J. H. Müller, *J.A.C.S.* 1932, **54**, 3142, 3151.

solid solutions with Na_2SiO_3[747] and the pairs M''_2GeO_4 and M''_2SiO_4, where $M'' =$ Be and Zn, are shown by X-ray analysis to be fully isomorphous.[748] The germanates of the alkalies are easily soluble in water (the lithium salt the least), but the other salts are mostly insoluble; thus Na_2GeO_3 (m.pt. 1,078° C.) gives a heptahydrate whose sol^y is 25·9/25°, while Mg_2GeO_4 has the sol^y 0·0016/26°. The ions, like the hydroxide itself, readily become colloidal; if 0·1 g. each of lime and germanium dioxide are dissolved separately in 100 c.c. of water and mixed, the whole forms a solid gel.[749]

Germanic acid forms esters; $Ge(O\cdot C_2H_5)_4$, b.pt. 185°, m.pt. −81°, was made by Dennis *et al.*[750] by boiling the tetrachloride with sodium ethylate in alcohol.

Stannic hydroxide, $Sn(OH)_4$, has the usual tendency to form colloids, and no definite crystalline acid can be separated.[751-2] The salts seem to exist in two definite isomeric forms of the composition M'_2SnO_3, $x\ H_2O$, known as normal and meta stannates; this was discovered by Berzelius, who invented the word isomerism to describe the phenomenon. The usual form of the stannates is of the type of K_2SnO_3, $3\ H_2O$; salts with more water than this lose the excess *in vacuo*, but retain the $3\ H_2O$[753]; if these are driven off (for example, from the potassium salt by heating to 140°) the salt is fundamentally changed; thus the sodium salt is then no longer soluble in water. This suggests that the $3\ H_2O$ form part of an ion $[Sn(OH)_6]^{--}$[754]; this is confirmed by the fact that the stannate $K_2[Sn(OH)_6]$ is isomorphous with the plumbate $K_2[Pb(OH)_6]$ and the platinate $K_2[Pt(OH)_6]$,[755] and still more by the observation of Wyckoff[756] that the lattice of $K_2[Sn(OH)_6]$ is similar to that of the chloroplatinate $K_2[PtCl_6]$, with six groups arranged octahedrally round the central atom, though somewhat distorted as we should expect from the interaction (association) of the hydroxyl groups.[757]

Stannic hydroxide is more definitely amphoteric in character than the germanium compound. It not only forms stannates with alkalies, but also dissolves in hydrochloric acid to give stannic chloride, which is only partly hydrolysed in water, and of which the unhydrolysed part is ionized to give Sn^{4+} cations. Colloid formation makes an exact determination of the dissociation constants of the hydroxide impossible, but it seems clear[758] that it is stronger as an acid than as a base.

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[747] R. Schwarz and M. Lewinsohn, *Ber.* 1930, **63**, 783.

[748] W. Schutz, *Z. physikal. Chem.* 1936, B **31**, 292.

[749] J. H. Muller and C. E. Gulezian, *J.A.C.S.* 1929, **51**, 2029.

[750] D. L. Tabern, W. R. Orndorff, and L. M. Dennis, ib. 1925, **47**, 2039.

[751] R. Willstätter, H. Kraut, and W. Fremery, *Ber.* 1924, **57**, 63, 1491.

[752] P. A. Thiessen and O. Koerner, *Z. anorg. Chem.* 1931, **195**, 83.

[753] I. Bellucci and N. Parravano, ib. 1905, **45**, 149.

[754] H. Zocher, *Z. anorg. Chem.* 1920, **112**, 1.

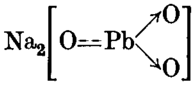
[755] See further, F. Reiff and S. M. Toussaint, ib. 1939, **241**, 372.

[756] R. W. G. Wyckoff, *Am. J. Sci.* 1928, [v] **15**, 297.

[757] This has been disputed by C. O. Björling, *Arkiv. Chem. Min. Geol.* 1942, **15**, B, No. 2.

Plumbic hydroxide, $Pb(OH)_4$. This again gives a series of salts, the plumbates, of various types, such as Ca_2PbO_4 and Na_2PbO_3. They can be made by the action of fused alkalies or alkaline earths on lead dioxide, or by the anodic oxidation of plumbite solutions. The acid is very weak, and the salts are decomposed by water or carbon dioxide.

The plumbates are sometimes coloured; thus while $CaPbO_3$ is white, Ag_2PbO_3 and $CuPbO_3$ are black, and $ZnPbO_3$ is reddish-brown; they often crystallize with 3 H_2O and then usually decompose on dehydration. The trihydrates as we have seen are isomorphous with the stannates and platinates, and must form similar ions $[Pb(OH)_6]^{--}$.[759] A curious difference between plumbic acid and its analogues is that it loses its water much more easily, and then separates as PbO_2 instead of in a colloidal hydrated form. The same is true of some of the plumbates; thus $Na_2[Pb(OH)_6]$ loses all its water at 110° without any essential change; the product



rehydrates at once to $Na_2[Pb(OH)_6]$.[760]

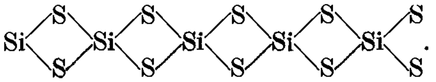
It is to be noticed that the tetravalent state of lead is much more stable in the plumbates than in the dioxide; while lead dioxide loses oxygen below 200° sodium plumbate does not do so below 750°. Indeed it is possible to make a plumbate by atmospheric oxidation of a plumbite; if lead monoxide (litharge, PbO) is heated with lime in air, it is converted into the plumbate Ca_2PbO_4. This salt has a dissociation tension of 1 atmosphere at 1,090° (that of lead dioxide is 1 atmosphere at 752°), and equal to that of the oxygen in air at about 1000°; so that it could be used in place of barium oxide to remove oxygen from air.

Red lead Pb_3O_4, which can be made by heating litharge in air, behaves in many ways like a mixture of the monoxide and the dioxide, but it has a much lower dissociation tension of oxygen than the dioxide (about 150 mm. at 550°), and may very likely be plumbous plumbate $Pb_2[PbO_4]$. For its crystal structure see references [761-3].

DISULPHIDES

Silicon disulphide, SiS_2, is made by heating the elements together, and is purified by sublimation. It forms colourless needles, stable in dry air but hydrolysed by water to silica and hydrogen sulphide.

The crystal structure is shown[764-5] to consist of infinite chains of SiS_4 tetrahedra with opposite edges in common:



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[758] See G. E. Collins and J. K. Wood, *J.C.S.* 1922, **121**, 441, 2760.

[759] I. Bellucci and N. Parravano, *Z. anorg. Chem.* 1906, **50**, 101, 107.

[760] A. Simon, ib. 1929, **177**, 109.

Silicon disulphide is said to form thiosilicates with alkaline sulphides, but little is known of them.

Germanium disulphide GeS_2 can be made by the action of hydrogen sulphide on a strongly acid solution of germanium dioxide (Winkler) or by acidifying a thiogermanate solution; and also by heating germanium dioxide with sulphur or hydrogen sulphide above 800°[766-8]; it is purified by sublimation. It forms white or (if large) amber coloured crystals, melting about 800° to a dark liquid; its sol^{y} in water is 0·455/20°, but the solution slowly evolves hydrogen sulphide and in the end is wholly hydrolysed.

X-ray analysis[769] shows that in the crystal, as in silica, every germanium atom has 4 tetrahedrally arranged S atoms, and every S atom 2 Ge atoms; the S—Ge—S angle is about 103°, and the Ge—S distance 2·19 A (theory 2·26).

Germanium disulphide readily dissolves in alkaline sulphide solutions, obviously forming thiogermanates, but these cannot be isolated from water. In presence of alcohol a complicated salt

$$M_6Ge_2S_7,\ 9\ H_2O\ (M = Na,\ K)$$

separates out; it is hygroscopic and rapidly hydrolysed. The only simple thiogermanates known are minerals, such as argyrodite $4\ Ag_2S,\ GeS_2$[771] (which can also be made synthetically[770]), and one or two others. A selenide $GeSe_2$ can also be made.[772]

Tin disulphide or *stannic sulphide* SnS_2 can be made from the elements, or by precipitating stannic solutions with hydrogen sulphide. It forms golden crystals ('mosaic gold' used as a bronze powder for covering wood, etc.). It readily dissolves in alkaline sulphides to give thiostannates. It has a cadmium iodide layer lattice,[773] in which each Sn has 6 nearest S neighbours.

The thiostannates are readily made by dissolving the disulphide in alkaline sulphide solutions and precipitating with alcohol.[774-6] They are mainly of two types, as in Na_2SnS_3, aq. and Na_4SnS_4, aq.; they are usually highly hydrated. They are hydrolysed by excess of water and are decomposed by acids.

[761] M. Straumanis, *Z. physikal. Chem.* 1942, B **52**, 127.

[762] A. Byström and A. Westgren, *Arkiv. Kemi, Min. Geol.* 1943, **16**, B. No. 14.

[763] S. T. Gross, *J.A.C.S.* 1943, **65**, 1107.

[764] E. Zintl and K. Loosen, *Z. physikal. Chem.* 1935, **174**, 301.

[765] W. Büssem, H. Fisher, and E. Gruner, *Naturwiss.* 1935, **23**, 740.

[766] W. Pugh, *J.C.S.* 1930, 2370.

[767] L. M. Dennis and J. Papish, *J.A.C.S.* 1921, **43**, 2136.

[768] Id., *Z. anorg. Chem.* 1928, **174**, 114.

[769] W. H. Zachariasen, *J. Chem. Phys.* 1936, **4**, 618.

[770] R. Schwarz and H. Giese, *Ber.* 1930, **63**, 778.

[771] S. L. Penfield, *Z. Krist.* 1894, **23**, 240.

[772] B. N. Ivanova-Emin, *J. Gen. Chem. Russ.* 1940, **10**, 1813.

[773] Wells, *S.I.C.* 389; and compare pp. 101, 145, 276.

[774] E. E. Jelley, *J.C.S.* 1933, 1580.

[775] G. Spacu and A. Pop, *Bull. Acad. Sci. Roumaine*, 1939, **21**, 52.

[776] Id., *Bull. Soc. Stiinte Cluj*, 1939, **9**, 307.

Esters of thiostannic acid $Sn(S \cdot R)_4$ have been made from stannic chloride and the sodium salts of the mercaptans.[777-8] They are volatile at very low pressures; examples are $Sn(S \cdot CH_3)_4$ b.pt. 81°/0·001 mm., m.pt. 31°, and $Sn(S \cdot C_2H_5)_4$, b.pt. 105°/0·001 mm.

Lead disulphide PbS_2 does not seem to exist.

TETRAHALIDES[778a]

All four tetrahalides are known of all the elements of the series except lead, where the relative instability of the tetravalent state makes it impossible to isolate any except the tetrachloride. Also many mixed halides as SiF_3Br are known, and hydride-halides such as $SiHCl_3$.

In general they are (with the exception of the obviously salt-like tin tetrafluoride) volatile covalent compounds, as the following boiling-points and melting-points show:

		Carbon	*Silicon*	*Germanium*	*Tin*	*Lead*
AF_4	B.pt.	−128°	−95·7° sbl.	−36·4° sbl.	705° sbl.	. .
	M.pt.	−185°	−90·2°	−15°	. .	. .
ACl_4	B.pt.	+76·4°	+57·0°	86·5°	114·1°	*ca.* 150° extrap.
	M.pt.	−22·9°	−70·4°	−49·5°	−36·2°	−15°
ABr_4	B.pt.	Decp.	154·6°	186·5°	203·3°	. .
	M.pt.	+93·7°	+5·2°	+26·1°	+33·0°	. .
AI_4	B.pt.	Decp.	290°	*ca.* 348°	346°	. .
	M.pt.	171·0°	123·8°	144°	144·5°	. .

There are some interesting points of comparison. (1) The ease of hydrolysis. The high resistance of the tetrahalides of carbon to hydrolysis (they are unaffected by cold water, and the tetrafluoride and tetrachloride even by hot alkali) has already been ascribed to their being covalently saturated. The others, which can act as acceptors, readily replace the halogen by hydroxyl, but less completely as the atomic number of the central atom rises. The effect of water on the tetrachlorides is: carbon, nothing; silicon, complete hydrolysis; germanium, hydrolysis not quite complete; tin, ionization and some hydrolysis; lead, hydrolysis, and some conversion into plumbous chloride $PbCl_2$ and chlorine. (2) Effect of atomic size on stability. It is remarkable that carbon tetrabromide and tetraiodide decompose below their boiling-points, which $SiBr_4$, SiI_4, and $GeBr_4$ do not, although the affinity of silicon and germanium for the halogens is probably little greater than that of carbon, and the boiling-points of their tetrahalides are no doubt higher. This may be partly due to the crowding of the larger halogens round the little carbon atom; but this effect cannot be very large since the A—X distance has been shown to be the same in

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[777] H. J. Backer and J. Kramer, *Rec. Trav.* 1933, **52**, 916.

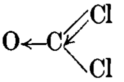
[778] Id., ib. 1934, **53**, 1101.

[778a] For a general discussion of the forces between tetrahalide molecules see J. H. Hildebrand, *J. Chem. Phys.* 1947, **15**, 727.

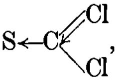
methylene chloride as in carbon tetrachloride,[779] and very little larger (angle 112°) in methylene bromide than in carbon tetrabromide[780] (109·5°). The AX_4 molecules are tetrahedral, with valency angles of 109·5°, so that the distance *d* between 2 halogen atoms is 1·633 times A—X, which may itself be taken to be the sum of the link radii of the central atom r_A and the halogen r_X. If we imagine the molecule to be formed of spheres with the link radii, the peripheries of the halogen atoms are separated by a distance $d—2r_X$, which we may call *E*. The relation between the size of *E* and the mutual repulsion of the X atoms is still obscure, but in stable molecules *E* is seldom less than 1 A.U. The values of *E* (using the normal link-radii) are for CCl_4 0·90, for CBr_4 0·84, and for CI_4 0·76 A, while for the other tetrahalides they are never less than 1·42 (SiI_4), and rise to 2·5 ($PbCl_4$); so the crowding must cause instability. (3) The measurement of the actual A—X distances in these halides by electron diffraction has led to interesting results. With the chlorides, for example, Brockway and Wall[781] have found:

A—Cl	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$
Obs.	1·76	2·02	2·10	2·29 A.
Calc.	1·76	2·16	2·21	2·39
Diff.	±0	—0·14	—0·11	—0·10
Diff. %	±0	—7·0	—5·0	—4·2

Similar though rather smaller differences are found with the other halogens. The shortening of the link with the last three elements but not with carbon they explained by assuming resonance with a doubly linked form containing the group $\mathrm{A}\underline{\leftarrow}\mathrm{Cl}$, as is assumed by organic chemists to explain the reactions of chlorobenzene. This must shorten the distance, and would not be possible with carbon, since the octet of the carbon in CCl_4 cannot expand. This view was strongly supported by the discovery of Brockway, Beach, and Pauling[782] that the C—Cl link is actually shortened when this back-co-ordination does not contravene the covalency maximum, as in phosgene (C—Cl calc. 1·76, obs. 1·68) and in thiophosgene (C—Cl obs. 1·70), where we can have the resonance forms



and



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which still retain the octet.

(4) A further point is that the boiling-point of silicon tetrachloride is lower than that of carbon tetrachloride.* This is found in the Si—Cl

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* The differences between the melting-points of the carbon and the silicon tetrahalides are curious and not explained. These are (for $CX_4—SiX_4$) AF_4—94·8°, ACl_4+48·5°, ABr_4+88·5°, AI_4+47·2°.

[779] L. E. Sutton and L. O. Brockway, *J.A.C.S.* 1935, **57**, 473.

[780] H. A. Levy and L. O. Brockway, *J.A.C.S.* 1937, **59**, 1662.

[781] L. O. Brockway and F. T. Wall, ib. 1934, **56**, 2373.

[782] L. O. Brockway, J. Y. Beach, and L. Pauling, ib. 1935, **57**, 2704.

compounds generally, but not in any other halides nor in the hydrides or alkyls, nor with any other elements of the subgroup, as the following table shows:

B.pts.	ACl_4	ACl_3H	ACl_2H_2	$AClH_2$	AH_4	$A(CH_3)_4$
A = C	76·4°	61·3°	40·1°	−24°	−162°	+0·5°
A = Si	57·5°	33°	+8°	−30°	−112°	+27°
Diff. (C—Si)	+18·9°	+28°	+32°	+6°	−50°	−26·5°

It would seem as if this (which implies a heat of evaporation about 0·4 k.cals., greater for the carbon compound) must be connected with the occurrence of back co-ordination in the silicon but not in the carbon compounds.

The boiling- and melting-points of the binary halides have been given above (p. 605).

SILICON HALIDES

Silicon tetrafluoride is usually made from calcium fluoride, silica, and concentrated sulphuric acid; the purest is got by heating barium fluorosilicate, $BaSiF_6$. It does not attack glass when quite dry. It is hydrolysed by water, but only partially, owing to the formation of fluorosilicic acid (below, p. 615).

Silicon tetrachloride is made from the elements or from silica, carbon, and chlorine at a white heat, or best from the action of chlorine on ferrosilicon. It reacts violently with water, but is stable by itself. The tetrabromide is similar[792]; the Si—Br distance was found by electron diffraction to be 2·16 A (theory 2·31) in $SiBr_4$, $SiHBr_3$, and SiF_2Br_2.[783] Silicon tetra-iodide is similar.

A variety of mixed tetrahalides of silicon have been made: these are some boiling- and melting-points:

	SiF_3Cl^a	$SiF_2Cl_2{}^a$	$SiFCl_3{}^b$	SiF_3Br^c	$SiF_2Br_2{}^c$	$SiFBr_2{}^c$
B.pt. .	−70·0°	−31·7°	+12·2°	−41·7°	+13·7°	83·8°
M.pt. .	−138°	−144°	. .	−70·5°	−66·9°	−82·5°

	$SiCl_3Br^d$	$SiCl_2Br_2{}^d$	$SiClBr_3{}^d$	$SiFCl_2Br^d$	$SiFClBr_2{}^d$
B.pt. . .	80°	105°	128°	35·4°	59·5°
M.pt.^{e} . .	−62°	−45·5°	−20·8°	. .	. .

a = [784], b = [785], c = [786], d = [787], e = [788].

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[783] R. Spitzer, W. J. Howell, and V. Schomaker, ib. 1942, **64**, 62.

[784] W. C. Schumb and E. L. Gamble, ib. 1932, **54**, 3943.

[785] H. S. Booth and C. F. Swinehout, ib. 4750.

[786] W. C. Schumb and H. H. Anderson, ib. 1936, **58**, 994.

[787] Id., ib. 1937, **59**, 651.

[788] H. H. Anderson, ib. 1945, **67**, 2176.

[789] H. S. Booth and W. D. Stillwell, ib. 1934, **56**, 1531.

[790] Id., ib. 1529.

[791] W. C. Schumb and F. A. Bickford, ib. 1934, **56**, 852.

SILICON HYDRIDE-HALIDES

The easiest to make is silicochloroform $SiHCl_3$, which is prepared from silicon and hydrogen chloride gas at 380°. These compounds on the whole resemble the halides, but are less stable. Some of the boiling- and melting-points are given in the table:

	$SiHF_3$[a]	$SiHF_2Cl$[a]	$SiHFCl_2$[a]	$SiHCl_3$[b]	$SiHBr_3$[c]	SiH_2Br_2[c]	$SiHI_3$ extrap.
B.pt. .	−97·5°	−50°	−18·4°	31·5°	111·8°	64°	*ca.* 185°
M.pt. .	−131·2°	−144°	−149·1°	−128·2°	−73·5°	. .	+8°

a = [789], *b* = [790], *c* = [791].

GERMANIUM HALIDES

Germanium tetrafluoride is best made[793] by heating barium fluorogermanate $BaGeF_6$ to 700°; it does not attack glass when dry, nor dissociate up to 1,000°. A hydrate GeF_4, 3 H_2O crystallizes out from a solution of germanium dioxide in concentrated hydrofluoric acid; on heating this melts and hydrolyses.

Germanium tetrachloride can be made from the elements at 100-180°.[795-6] It is a colourless liquid; electron diffraction[797] gives the Ge—Cl distance as 2·10 A (theory 2·21). Its hydrolysis by water is reversible, and the whole of the germanium can be removed from a solution in concentrated hydrochloric acid by distillation. The *tetrabromide* is similar[795,798-9]; electron diffraction[800] gives Ge—Br as 2·32 (theory 2·36). It is colourless liquid with a conductivity less than 8×10^{-5}, which is hydrolysed by water.

Germanium tetraiodide is similar[801]; it is a red liquid freezing at 144° to red crystals isomorphous with SnI_4 (Jaeger); the colour fades to orange at −10° and pale yellow at −185°. It dissociates above its melting-point and is hydrolysed by water.

Mixed halides have been made with these boiling- and melting-points[802]:

	GeF_3Cl	GeF_2Cl_2	$GeFCl_3$
B.pt. . .	−20·3°	−2·8°	+37·5°
M.pt. . .	−66·2°	−51·8°	−49·8°

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[792] W. C. Schumb and R. C. Young, *J.A.C.S.* 1930, **52**, 1464.

[793] L. M. Dennis and A. W. Laubengayer, *Z. physikal. Chem.* 1927, **130**, 523.

[794] Cl. Winkler, *J. prakt. Chem.* 1887, [2] **36**, 194.

[795] L. M. Dennis and F. E. Hance, *J.A.C.S.* 1922, **44**, 299.

[796] A. W. Laubengayer and D. L. Tabern, *J. Phys. Chem.* 1926, **30**, 1047.

[797] L. O. Brockway, *J.A.C.S.* 1935, **57**, 958.

[798] F. M. Brewer and L. M. Dennis, *J. Phys. Chem.* 1927, **31**, 1101.

[799] G. T. Morgan and H. D. K. Drew, *J.C.S.* 1924, **125**, 1264.

[800] M. Rouault, *C.R.* 1938, **206**, 51.

[801] L. M. Dennis and F. E. Hance, *J.A.C.S.* 1922, **44**, 2854.

[802] H. S. Booth and W. C. Morris, ib. 1936, **58**, 90.

GERMANIUM HYDRIDE-HALIDES

These are known with all the halogens except fluorine. The following are some melting- and boiling-points.

	GeH_4	GeH_3Cl	GeH_2Cl_2	$GeHCl_3$	$GeCl_4$
B.pt. . .	−90°	+28°	69·5°	75·2°	86·5°
M.pt. . .	−165°	−52°	−68°	−71°	−49·5°

	GeH_3Br	GeH_2Br_2	$GeHBr_3$	$GeBr_4$
B.pt. . .	+52°	81·5°	. .	186·5°
M.pt. . .	−32°	−15°	. .	+26·1°

Germanium chloroform $GeHCl_3$ is made (Winkler, 1887[794]; Dennis)[803] by passing hydrogen chloride over warm germanium. It begins to break up into hydrogen chloride and germanous chloride $GeCl_2$ at 140°; it is oxidized by air, slowly even at 0°, to water, $GeCl_4$ and $GeCl_2$; with water it gives germanous oxide GeO; bromine gives $GeCl_2Br_2$ and iodine $GeICl_3$.[804] GeH_2Cl_2 and GeH_3Cl are made[805] by treating germane GeH_4 with hydrogen chloride in presence of aluminium chloride; they are unstable and change slowly even in the cold mainly to GeH_4, HCl, and germanium; with water they give GeO, HCl, and hydrogen; with ammonia they form also[806-7] the solid hydride $(GeH_2)_x$ (p. 554).

The hydride-bromides and iodides[807] are similar but less stable; the iodides cannot be purified.

STANNIC HALIDES

Stannic fluoride SnF_4 cannot be made from water, but was obtained by Ruff and Plato[808] by passing hydrogen fluoride gas over stannic chloride until no more HCl came over. The residue is $SnCl_4$, SnF_4 (perhaps $SnCl_2F_2$, and a salt), which begins to evolve $SnCl_4$ at 130°, and at 220° leaves pure crystals of stannic fluoride SnF_4, which sublime under 1 atm. at 705°; it is very hygroscopic, and readily soluble in water with hydrolysis. SnF_4 is obviously a salt, the only one in this series of tetrahalides.

Stannic chloride, $SnCl_4$, is made from its elements; it is obviously covalent, but in water it ionizes and also is considerably but rather slowly hydrolysed, probably with the production of complex ions like $[SnCl_6]^{--}$.[809]

Stannic bromide, $SnBr_4$,[814] is similar; it forms a tetrahydrate. The *iodide* SnI_4 is also similar; the extrapolated b.pt. is 348°; the Trouton

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[803] L. M. Dennis, W. R. Orndorff, and D. L. Tabern, *J. Phys. Chem.* 1926, **30**, 1050.

[804] F. M. Brewer, ib. 1927, **31**, 1820.

[805] L. M. Dennis and P. R. Judy, *J.A.C.S.* 1929, **51**, 2321.

[806] L. M. Dennis and R. W. Work, ib. 1933, **55**, 4486.

[807] L. M. Dennis and L. A. Skow, ib. 1930, **52**, 2369.

[808] O. Ruff and W. Plato, *Ber.* 1904, **37**, 681.

[809] J. Guéron, *Ann. Chim.* 1935, [xi] **3**, 225.

constant is 22·1[810-12]: it is rapidly and completely hydrolysed by water. The molecules are tetrahedral both in the vapour and in the crystal, with an Sn—I distance of 2·65 A[813] (theory 2·73). For the kinetics of the reaction of tin with bromine in organic solvents see reference [813a].

Mixed stannic halides are rare. From freezing-point and melting-point diagrams Raeder[815] finds no sign of the formation of any except $SnCl_2I_2$, which has a very small temperature range, from −50° to −40°; the fluoride SnF_2Cl_2 should perhaps be added.

PLUMBIC HALIDES

Lead tetrafluoride cannot be obtained,[816] though double fluorides are known (below, p. 616). It would no doubt be a salt (like SnF_4), and tetravalent lead is much less stable as an ion than in the covalent state.

Lead tetrachloride $PbCl_4$ is made[817] by the action of concentrated sulphuric acid on the double salt $(NH_4)_2PbCl_6$. It is a yellow mobile liquid freezing to a yellow crystalline solid at about −15°. It explodes at 105°. It fumes in air, being partly hydrolysed and partly converted into plumbous chloride $PbCl_2$ and chlorine. With a little water it forms an unstable hydrate, and with cold concentrated hydrochloric acid a crystalline solid, which may be H_2PbCl_6, aq.

The tetrabromide $PbBr_4$ and tetraiodide PbI_4 are unknown; presumably (as with cupric iodide) the metallic atom oxidizes the halogen, and the compound breaks up into PbX_2+X_2.

'MULTINUCLEAR' HALIDES OF SILICON

These contain 2 or more (up to 4) silicon atoms joined together.

Silicon hexafluoride Si_2F_6 can be made[818] by warming the hexachloride Si_2Cl_6 with zinc fluoride. It is a colourless gas freezing to a white solid which melts at −19·0°, and has a vapour pressure of 760 mm. at −19·1°. It is at once hydrolysed by moist air, giving 'silico-oxalic acid' $H_2Si_2O_4$, together with some hydrogen and fluorosilicic acid H_2SiF_6.

Silicon hexachloride Si_2Cl_6 can be made by the action of chlorine on the iodide Si_2I_6, on ferrosilicon,[819] or best on calcium silicide[818]; it is also formed when a zinc arc burns in the vapour of $SiCl_4$.[820] B.pt. 147°,

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[810] G. R. Negishi, *J.A.C.S.* 1936, **58**, 2293.

[811] S. S. Todd and G. S. Parkes, ib. 2340.

[812] M. E. Dorfman and J. H. Hildebrand, ib. 1927, **49**, 729.

[813] O. Hassel and A. Sandbo, *Z. physikal. Chem.* 1938, B **41**, 75; see also Wells, *S.I.C.* 282.

[813a] A. F. Trotman-Dickenson and E. J. F. James, *J.C.S.* 1947, 736.

[814] For the kinetics of the reaction of tin with bromine and iodine see id., ib.

[815] M. G. Raeder, *Z. anorg. Chem.* 1927, **162**, 222.

[816] O. Ruff, *Z. Angew. Chem.* 1907, **20**, 1217.

[817] H. Friedrich, *Ber.* 1893, **26**, 1434.

[818] W. C. Schumb and E. L. Gamble, *J.A.C.S.* 1932, **54**, 583.

[819] G. Martin, *J.C.S.* 1914, **105**, 2836.

[820] A. Stock, A. Brandt, and H. Fischer, *Ber.* 1925, **58**, 643.

m.pt. +2·5°. Above 350° it slowly goes to silicon and its tetrachloride, and it burns to the tetrachloride in chlorine. On hydrolysis it forms 'silico-oxalic acid'.

The compound Si_3Cl_8 is also formed in small quantities when metallic silicides are treated with chlorine.[819] It boils at 210-13° with some decomposition. With water it gives a white mass of 'Silico-mesoxalic acid' which evolves hydrogen with alkali.

The compound Si_4Cl_{10}, b.pt. 150°/15 mm., was found by Besson and Fournier[821] among the products of the action of the electric discharge on a mixture of silicon tetrachloride and hydrogen; a viscous residue remaining after this had been evaporated may have been Si_5Cl_{12}.

Silicon hexabromide Si_2Br_6 can be made by the action of bromine on the hexaiodide Si_2I_6; it is similar to the hexachloride, and boils at 240°; it is very sensitive to water.

Silicon hexaiodide Si_2I_6 was made by Friedel and Ladenburg in 1880[822] by heating silicon tetraiodide with silver powder to 280°. It melts with decomposition at 250°. Water converts it into silicic acid with evolution of hydrogen, some 'silico-oxalic acid' being formed at the same time.

DERIVATIVES OF OXY-ACIDS

These are practically confined to the lead compounds, where they are limited by the tendency of the lead to become divalent. Stannic nitrate and sulphate probably exist in the solutions of stannic hydroxide in concentrated nitric and sulphuric acids, but they cannot be isolated.

A plumbic pyrophosphate PbP_2O_7 has been made from lead dioxide and phosphoric acid at 300°[823]; it is isomorphous with the pyrophosphates MP_2O_7 of other members of Group IV (Si, Sn, Ti, Zr, Hf).[824]

Lead tetracetate $Pb(O\cdot CO\cdot CH_3)_4$ can be made by saturating hot glacial acetic acid with red lead (Pb_3O_4), when the tetracetate separates out on cooling,[825] being only 1/40 as soluble in this solvent as the plumbous acetate.[826] It can also be made by oxidizing a solution of plumbous acetate in acetic acid with chlorine[827] or electrolytically[828]; similar derivatives can be made from other carboxylic acids, such as propionic, butyric, stearic, and benzoic.[827-9,837] The tetracetate melts at 175°, and at 190° breaks up to give plumbous acetate.[837] It is at once hydrolysed by water to lead dioxide. It has a strong oxidizing power; it converts glycols into aldehydes or ketones (with separation of the HOC—COH carbons)[830] and

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[821] A. Besson and L. Fournier, *C.R.* 1909, **149**, 34.

[822] C. Friedel and A. Ladenburg, *Ann.* 1880, **203**, 247.

[823] G. Peyronel, *Gaz.* 1939, **69**, 254.

[824] G. R. Levi and G. Peyronel, *Z. Krist.* 1936, **92**, 190.

[825] A. Hutchinson and W. Pollard, *J.C.S.* 1893, **63**, 1136.

[826] A. W. Davidson, W. C. Lanning, and M. M. Zeller, *J.A.C.S.* 1942, **64**, 1523.

[827] A. Colson, *C.R.* 1903, **136**, 1664.

[828] C. Schall and W. Melzer, *Z. Elektrochem.* 1922, **28**, 474.

[829] A. Colson, *C.R.* 1903, **136**, 675, 891.

[830] R. Criegee, *Ber.* 1931, **64**, 260.

converts the C—H group, if the hydrogen is at all mobile, into C—OH (for example, acetone into dihydroxyacetone).[831-2] Other organic compounds conveniently oxidized by it are acenaphthene,[833] amino-alcohols,[834] and sugars.[835]

The tetracetate behaves as a covalent compound (like boron triacetate) rather than a salt. In glacial acetic acid it has no measurable conductivity, while the diacetate is a weak electrolyte. At the same time there must be at least a minute concentration of plumbic ions in the solution, for Hevesy and Zechmeister[836] showed that interchange of radioactive and inactive lead atoms occurs between plumbous and plumbic acetates in acetic acid, which does not happen with a plumbic compound that is not ionized, such as lead tetraphenyl. This is the only good evidence we have of the existence of the plumbic ion.

COMPLEX COMPOUNDS

The covalency limits of these elements are carbon 4, silicon and germanium 6, tin and lead 8. The limitation of the covalency of carbon to 4 was pointed out by Werner; the most elaborate efforts to obtain fluorocarbonates M_2CF_6, analogues to the very stable fluorosilicates and fluorogermanates, have all failed.

The complexes of the other elements are not very numerous, very few with nitrogen, rather few with oxygen; the only considerable class is that of the complex halides. There is a very marked increase in complex-formation when we pass from germanium to tin; the further increase we might expect in lead is more than counterbalanced by the instability of the plumbic state.

NITROGEN COMPLEXES

The halides both of silicon[838-41] and germanium[842-4] so readily form amines and imines with ammonia that no true ammines ($A \leftarrow NH_3$) are known. Stannic chloride behaves in the same way, but less violently, and there is some reason to think that a true ammine $(NH_3)_2SnCl_4$ exists.[845] With pyridine, which cannot eliminate the chlorine, ammines such as

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[831] O. Dimroth and R. Schweizer, *Ber.* 1923, **56**, 1375.

[832] E. Baer, *J.A.C.S.* 1940, **62**, 1597.

[833] R. F. Brown and L. S. Yee, ib. 1945, **67**, 874.

[834] N. J. Leonard and M. A. Rebenstorf, ib. 49.

[835] R. C. Hockett, M. Conley, M. Yusem, and R. I. Mason, ib. 1946, **68**, 922.

[836] G. Hevesy and L. Zechmeister, *Z. Elektrochem.* 1920, **26**, 151.

[837] C. D. Hurd and P. R. Austin, *J.A.C.S.* 1931, **53**, 1546.

[838] F. Lengfeld, ib. 1899, **21**, 531.

[839] E. Vigouroux and C. Hugot, *C.R.* 1903, **136**, 1670.

[840] M. Blix and W. Wirbelauer, *Ber.* 1903, **36**, 4220.

[841] O. Ruff and E. Geisel, ib. 1905, **38**, 2235.

[842] L. M. Dennis and R. W. Work, *J.A.C.S.* 1933, **55**, 4486.

[843] J. S. Thomas and W. Pugh, *J.C.S.* 1931, 60.

[844] J. S. Thomas and W. W. Southwood, ib. 2083.

[845] R. Schwarz and A. Jeanmaire, *Ber.* 1932, **65**, 1443.

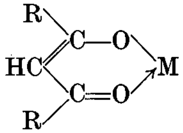
$SnCl_4$, 2 py can be made. The replacement of chlorine atoms by alkyls weakens the co-ordination tendency for nitrogen, though not so much as for oxygen or halogens.[846] Thus with pyridine Alk_4Sn adds on none, $(CH_3)_3SnCl$ one, to give $[(CH_3)_3Sn \leftarrow py]Cl$, while Alk_2SnCl_2 and $Alk \cdot SnCl_3$ (like $SnCl_4$) add on 2 py to give the 6-covalent tin.

Ammonia compounds of plumbic chloride $PbCl_4$ have been described,[847] but it is uncertain whether they are true ammines.

A small affinity for nitrogen is characteristic of all the IV B elements from silicon to lead, in contrast to those of IV A.

OXYGEN COMPLEXES

Silicon forms these practically only when the co-ordination is supported by ring formation (in chelate or 'ato' complexes). The β-diketones (like acetylacetone) form characteristic chelate complexes with the elements of this group. The formation of the ordinary chelate β-diketone ring (often written MA) uses up one valency of M, and gives it a covalency of 2.



A tetravalent element might thus form MA_4 if it could have a covalency of 8. If it is limited to 6, then since this is reached in MA_3, where one valency is still unsatisfied, it could either form the salt $[MA_3]X$, or it might take on only 2 chelate rings, forming the divalent radical MA_2'' in $A_2M\begin{smallmatrix}X\\X\end{smallmatrix}$ or the ionized $[A_2M]X_2$. The Group IV elements form compounds of all these types,[848] which are distributed thus:

$[SiA_3]X$	$[TiA_3]X$
$[GeA_3]X$	$[ZrA_3]X$
GeA_2X_2	ZrA_4
SnA_2X_2	HfA_4
	ThA_4

Silicon. Dilthey[849,850] showed that various β-diketones (acetylacetone, methyl-acetyl acetone, dibenzoyl methane, etc.) react in chloroform with silicon tetrachloride, and a solid salt is formed of the composition $[A_3Si]Cl, HCl$, convertible into less soluble and more easily purifiable salts of complex halide acids such as $HFeCl_4$, $HAuCl_4$, H_2PtCl_6, and $HZnCl_3$; these salts are mostly insoluble in benzene, easily soluble in chloroform, and quickly hydrolysed by water.

[846] P. Pfeiffer and O. Halperin, *Z. anorg. Chem.* 1913, **87**, 335.

[847] J. M. Matthews, *J.A.C.S.* 1898, **20**, 815.

[848] G. T. Morgan and H. D. K. Drew, *J.C.S.* 1924, **125**, 1261.

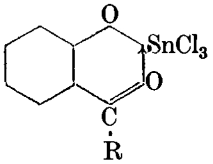
[849] W. Dilthey, *Ber.* 1903, **36**, 923.

[850] Id., *Ann.* 1906, **344**, 304.

Germanium. When its tetrachloride reacts with β-diketones in chloroform, the product[848] is different; it is the dichelate A_2GeCl_2. These substances form monomeric solutions in benzene and chloroform, and are no doubt covalent $A_2Ge\begin{smallmatrix}\diagup Cl\\ \diagdown Cl\end{smallmatrix}$. If, however, the tetrachloride reacts in chloroform with the cupric diketone derivative, the product which separates is the cuprochloride of a base of the siliconium type $[A_3Ge]CuCl_2$.

Tin. The usual break in properties between germanium and tin is very marked in their oxygen complexes, which with tin are numerous and not confined to the ring structures. The ordinary hydrated stannates $M_2[Sn(OH)_6]$ are examples of this, and the corresponding ethoxy-compounds such as $K_2[Sn(O \cdot C_2H_5)_6]$ have been obtained.[851] Stannic chloride will combine with alcohols[852] and ethers to form, for example, $SnCl_4$, 2 EtOH and $SnCl_4$, 2 Et_2O. In fact stannic chloride (and to a less extent the bromide and still less the iodide) forms crystalline compounds of the type $(RO)_2SnCl_4$ with practically all organic compounds containing oxygen (RO), especially those with the C=O group (aldehydes, ketones, acids, esters, amides),[853-4a] in which it is obvious that the tin is 6-covalent. This tendency is much weakened (as usual) if the halogen atoms are replaced by alkyls; $Alk \cdot SnCl_3$ will only form a limited number of these addition products, and the di- and tri-alkyl halides form none at all.

Among the chelate tin derivatives those of the B-diketones seem to be unknown. But both *o*-acetyl phenol[853] and methyl salicylate[855] form complexes of the same rather unusual type, in which the tin is 5-covalent;



it will not react further to give a dichelate complex.

Among the very few *plumbic* complexes of this kind that have been obtained (largely owing to the instability of tetravalent lead) are the derivatives of plumbic acid $M_2[Pb(OH)_6]$ and $M_2[PbO_3]$, including the sulphato-compounds such as $K_2[Pb(SO_4)_3]$. It will be noticed that none of the nitrogen or oxygen complexes of tin or lead exceed the co-ordination number of 6.

COMPLEX HALIDES

Silicon. Silicon tetrafluoride is only partially hydrolysed by water, the hydrogen fluoride so formed combining with more tetrafluoride to give the

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[851] H. Meerwein and T. Bersin, *Ann.* 1929, **476**, 113.

[852] P. A. Thiessen and O. Koerner, *Z. anorg. Chem.* 1931, **195**, 88.

[853] P. Pfeiffer, *Ann.* 1913, **398**, 137.

[854] P. Pfeiffer and O. Halperin, *Z. anorg. Chem.* 1914, **87**, 335.

[854a] H. S. Sisler and J. C. Cory, *J.A.C.S.* 1947, **69**, 1515.

[855] P. Pfeiffer, *Ber.* 1927, **60**, 111.

very stable fluorosilicic acid H_2SiF_6. This is a strong acid, as highly ionized in water as sulphuric, and though slightly dissociated to $HF + SiF_4$, not enough to etch glass. It cannot be got in the anhydrous state, nor is it formed from anhydrous hydrogen fluoride and anhydrous silicon tetrafluoride, no doubt because as a strong acid its hydrogen ions must be solvated (hydrogen fluoride cannot solvate hydrogen ions). It can be isolated from aqueous solution as a tetrahydrate below 0° or a dihydrate above (i.e. as either $[H, 2\,H_2O]_2SiF_6$ or $[H, H_2O]_2SiF_6$). The fluorosilicates are numerous and stable, being only about 1 per cent. hydrolysed in deci-normal solution in the cold,[856-7] but completely by metallic oxides with separation of silica. Most of them are easily soluble in water (e.g. Cu″ 234; Mg 39·1; Mn″ 140), except those of Na (0·65), K (0·12), Rb (0·16), Cs and Ba (0·027): the figures in brackets are the solubilities at 17-20°. In the crystal the anions have the usual symmetrical octahedral form[858,862].

It is remarkable that no corresponding complex halides are formed by silicon chloride, bromide, or iodide.

Germanium. The fluorogermanates M_2GeF_6 are very similar to the fluorosilicates. K_2GeF_6 melts at 730° and boils without decomposition at 835°; sol^y 0·536/18°.[859] It is decomposed by hydrochloric acid, or by heating with water. The rubidium and caesium salts are similar; the last has been shown[860] to have the same type of lattice as K_2PtCl_6; the complex halides of germanium are in general isomorphous with those of silicon.[861-3] For thiogermanates of ammines and nitrogenous bases see Dennis.[864]

Unlike silicon, germanium can form a complex chloride M_2GeCl_6.[865] The caesium salt is precipitated on adding alcohol to a concentrated solution of germanium tetrachloride and caesium chloride in strong hydrochloric acid. It is rapidly hydrolysed by water, but can be recrystallized from a mixture of 12-normal hydrochloric acid and alcohol. The crystal structure is like that of $(NH_4)_2[PtCl_6]$, with Ge—Cl 2·35 A (theory 2·21).

The complex halides of *tin* are much more stable again; they are known with all 4 halogens, and are all of the 6-covalent type. A large number of fluorostannates $M_2[SnF_6]$ and $M''[SnF_6]$ have been made (Marignac, 1859).[866] By treatment with potassium carbonate one of the 6 fluorine atoms can be replaced by hydroxyl giving $K_2[SnF_5(OH)]$, from which other salts can be got, as well as a kind of anhydride-salt $K_4[F_5Sn—O—SnF_5]$.[867]

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[856] P. Kubelka and V. Pristoupil, *Z. anorg. Chem.* 1931, **197**, 391.

[857] J. G. Ryss and N. F. Bakina, *C.R. Acad. Sci. U.R.S.S.* 1936, **2**, 21.

[858] J. A. A. Ketelaar, *Z. Krist.* 1935, **92**, 155.

[859] J. H. Muller, *J.A.C.S.* 1921, **43**, 1087.

[860] R. W. G. Wykoff and J. H. Muller, *Am. J. Sci.* 1927, [5], **13**, 346.

[861] J. L. Hoard and W. B. Vincent, *J.A.C.S.* 1939, **61**, 2849.

[862] Id., ib. 1940, **62**, 3126.

[863] W. B. Vincent and J. L. Hoard, ib. 1942, **64**, 1233.

[864] L. M. Dennis and B. J. Staneslow, ib. 1933, **55**, 4392.

[865] A. W. Laubengayer, O. B. Billings, and A. E. Newkirk, ib. 1940, **62**, 546.

[866] See further, A. Skrabal and J. Gruber, *Mon.* 1917, **38**, 19.

[867] S. H. C. Briggs, *Z. anorg. Chem.* 1913, **82**, 441.

With chlorine the free acid H_2SnCl_6, 6 H_2O, m.pt. 20°, can be got by saturating a concentrated aqueous solution of stannic chloride with gaseous hydrogen chloride. This gives a series of salts, the alkaline all soluble (caesium least); $(NH_4)_2SnCl_6$ is known as pink salt, and is used as a mordant; it has a neutral reaction and is not decomposed by boiling water. The structures of the alkaline[868] and amine[869] salts have been determined, and show the usual octahedral distribution of the 6 Cl atoms. Mono-alkyl chloride $Alk \cdot SnCl_3$ give similar salts, including an acid $H_2[Alk \cdot SnX_5]$ aq. ($X = Cl, Br, I$).[870-2]

Similar bromides $M_2[SnBr_6]$ have been prepared[873-4] but they are less stable, and are readily hydrolysed by water, though not by alcohol. The crystal lattices of the alkaline salts are of the K_2PtCl_6 type, with the Sn—Br distance 2·60 A (theory 2·54).[875-6]

The iodides $M_2[SnI_6]$ can be made[877] from a solution of the tetraiodide in 2-normal hydriodic acid; they are black, and decompose with water or alcohol, and even slowly in the presence only of chloroform or carbon tetrachloride. Their crystal structure is like that of the bromides.[878]

Complex plumbic halides are formed with fluorine and chlorine, the plumbic atom being more stable in the covalent state. The fluoro-compounds apparently have rather complicated formulae. A salt of the composition $K_3H[PbF_8]$ was obtained by Brauner[877] (see also refs.[879-80]) by the action of hydrogen fluoride on lead plumbate $K_2[PbO_3]$ or lead tetracetate. It is very soluble in water, and hydrolysed by it; it is stable alone when cold, and at a red heat evolves a small amount of free fluorine. Whether it really has (as is quite possible) an 8-covalent Pb atom is uncertain as we do not know the crystal structure.

Chloroplumbates, all of the type M_2PbCl_6, are well known, and can be made by saturating a solution of plumbous chloride in hydrochloric acid with chlorine and adding ammonium chloride.[881] $(NH_4)_2PbCl_6$ (yellow crystals stable up to 225°) and the similar K salt are isomorphous with the chloroplatinates. They are all hydrolysed by water even in the cold, precipitating lead dioxide.

[868] R. G. Dickinson, *J.A.C.S.* 1922, **44**, 276.

[869] R. B. Corey and R. W. G. Wyckoff, *Z. Krist.* 1934, **89**, 469.

[870] J. G. F. Druce, *J.C.S.* 1921, **119**, 758.

[871] Id., ib. 1922, **121**, 1859.

[872] M. Lesbre and G. Glotz, *C.R.* 1934, **198**, 1426.

[873] K. Seubert, *Ber.* 1887, **20**, 793.

[874] G. I. Gosteanu, ib. 1927, **60**, 1312.

[875] J. A. A. Ketelaar, A. A. Rietdijk, and C. H. van Staveren, *Rec. Trav.* 1937, **56**, 907.

[876] G. Markstein and H. Nowotny, *Z. Krist.* 1938, **100**, 265.

[877] B. Brauner, *J.C.S.* 1894, **65**, 393.

[878] W. Werker, *Rec. Trav.* 1939, **58**, 257.

[879] See also O. Ruff, *Z. Angew. Chem.* 1907, **20**, 1217.

[880] F. C. Mathers, *J.A.C.S.* 1920, **42**, 1309.

[881] H. Friedrich, *Ber.* 1893, **26**, 1434.

COMPOUNDS OF DIVALENT IV B ELEMENTS

The divalency of carbon has already been discussed, and shown to involve a triple link; this would be very unstable with the later elements of the series, whose divalency must arise in a different way. It is almost negligible with silicon, but increases with the atomic number until it becomes the most stable form for the ion in lead.

This divalency is commonly referred to the 'inertness' of the first pair of valency electrons. But while this is true of simple divalent cations like the stannous Sn^{++}(—(18) 2), in the covalent state the divalent atom of Group IV has not too many electrons but too few; in covalent Cl—Sn—Cl, for example, the tin has only a sextet (2, $\underline{4}$) of valency electrons. Now there are practically no simple cations with silicon or germanium, and so there is no reason to assume that with these elements the first electron pair can be inert. The instability of the valency sextet is overcome by co-ordination with the Si or Ge atom as acceptor, as will be shown.

Divalent Silicon

The only compound of divalent silicon for which there is any good evidence is the *monoxide* SiO. This certainly exists in the vapour, as is shown not only by the spectrum, but also by the fact that if silica[882] or a silicate[883] is heated with silicon *in vacuo* at 1,450°, practically the whole of the silicon sublimes as an oxide, the condensate having the composition SiO (the b.pts. of silicon and silica are 2,360° and 2,590° C. respectively). With rapid cooling this forms a very light brown powder, which gives no X-ray pattern, and may be amorphous SiO; it is pyrophoric, burning to silica in air, and is oxidized by water at 400° and by carbon dioxide at 500°. Slow cooling gives a hard black glass, also of the composition SiO, the X-ray pattern of which indicates that it is a mixture of silicon and silica.[884] It is thus clear that the monoxide SiO can exist in the vapour, but on condensation changes almost if not quite at once into $Si+SiO_2$.

Divalent Germanium

The compounds of divalent germanium are very unstable, but they certainly exist; an oxide, a sulphide, and all four halides are well established.

Germanous oxide GeO is made by the action of water on germanous chloride $GeCl_2$ (Winkler, 1886), by reducing the solution of the dioxide with hypophosphorous acid,[885] or by the action of water or ammonia on germanium chloroform $GeHCl_3$.[886] It is a black powder which sublimes at 710° in nitrogen; the ultra-violet absorption spectrum of the vapour shows[887] that the Ge—O distance is $1{\cdot}65 \pm 0{\cdot}06$ A (theory for Ge=O 1·67).

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[882] W. Biltz and P. Ehrlich, *Naturwiss.* 1938, **26**, 188.

[883] E. Zintl, W. Bräuning, H. L. Grube, W. Krings, and W. Morawietz, *Z. anorg. Chem.* 1940, **245**, 1.

[884] H. N. Baumann, *Trans. Electrochem. Soc.* 1941, **80**, 75.

[885] L. M. Dennis and R. E. Hulse, *J.A.C.S.* 1930, **52**, 3553.

[886] F. M. Brower and L. M. Dennis, *J. Phys. Chem.* 1927, **31**, 1537.

[887] R. W. Shaw, *Phys. Rev.* 1937, ii. **51**, 12.

It is readily oxidized by heating in air or treatment with nitric acid, permanganate, or hydrogen peroxide. It is almost insoluble in water; but if it is formed in water, as by the hydrolysis of germanous chloride, it appears in a yellow hydrated form which is definitely acidic; it forms salts (germanites), and though weaker than acetic acid it is stronger than stannous hydroxide and much stronger than plumbous.[888]

The *sulphide* GeS is similar. It can be made by reducing the disulphide GeS_2 with hydrogen or with ammonia at 800°.[889] It melts at 625° and sublimes at 430°. It dissolves in hot alkalies.

Germanous fluoride GeF_2 is a white powder, made by the action of germanium on the tetrafluoride at 100–300°[890]; above this temperature it is reconverted into the tetrafluoride and germanium. It dissolves readily in water to give a strongly reducing solution.

Germanous chloride $GeCl_2$[891-2] can be made from the element and the tetrachloride, and also (reversibly) by heating germanium chloroform:

$$GeHCl_3 \longrightarrow GeCl_2 + HCl.$$

It is a pale yellow solid which will sublime; at 450° it is completely reconverted into germanium and the tetrachloride.[893] As with the other dihalides the only solvent which will dissolve it without decomposition is the tetrahalide. It hydrolysed by water and readily oxidized by air.

Germanous bromide (colourless, m.pt. 122°) is similar.[894]

The iodide GeI_2[893,895] is again similar; it is pale yellow. Powell and Brewer[896] have shown by X-ray analysis that it has a cadmium iodide lattice with the Ge—I distance 2·94 A. This certainly suggests that in the crystal the molecule may be ionized; the covalent Ge—I link was found to have a length of 2·57 (theory 2·55) in the tetraiodide[897]; 2·94 for $[Ge^{++}] \cdot [I^-]$ would give (since $[I^-]$ radius = 2·20) the Ge^{++} radius as 0·74; for the (smaller imaginary) Ge^{4+} Goldschmidt gives 0·44.

Complex chlorides, all of the type of $Cs[GeCl_3]$, have been prepared; they are hygroscopic and hydrolysed by water.[898] A corresponding iodide $Cs[GeI_3]$ was made[899] by adding CsI to a solution of germanous hydroxide in hydriodic acid, and gave with ammonium iodide a colourless $NH_4[GeI_3]$.

The behaviour of these germanous compounds supports the view that germanium cannot have an inert pair. A covalent molecule B—Ge—B

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[888] A. Hantzsch, *Z. anorg. Chem.* 1902, **30**, 313.

[889] W. C. Johnson and A. C. Wheatley, ib. 1934, **216**, 273.

[890] L. M. Dennis and A. W. Laubengayer, *Z. physikal. Chem.* 1927, **130**, 530.

[891] L. M. Dennis, W. R. Orndorff, and D. L. Tabern, *J. Phys. Chem.* 1926, **30**, 1050.

[892] L. M. Dennis and H. L. Hunter, *J.A.C.S.* 1929, **51**, 1151.

[893] F. M. Brewer, *J. Phys. Chem.* 1927, **31**, 1817.

[894] F. M. Brewer and L. M. Dennis, ib. 1530.

[895] L. M. Dennis and P. R. Judy, *J.A.C.S.* 1929, **51**, 2326.

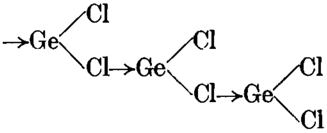
[896] H. M. Powell and F. M. Brewer, *J.C.S.* 1938, 197.

[897] F. M. Jaeger, P. Terpstra, and H. G. K. Westerbrink, *Proc. K. Acad. Sci. Amst.* 1925, **28**, 747.

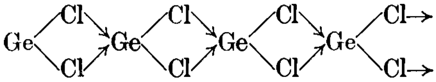
[898] A. Tschakirian, *C.R.* 1931, **192**, 233.

[899] T. Karantassis and L. Capatos, ib. 1935, **201**, 74.

would have a valency sextet 2, $\underline{4}$, which for stability must be increased to an octet. When B can act as a donor (like oxygen and the halogens) this can happen by co-ordination of the type



which can go on indefinitely; this is why the germanous halides, unlike the germanic, are relatively non-volatile. (The alternative form found with palladous



chloride, is excluded because it involves the decet 2, $\underline{8}$, possible only with an inert pair.)

So, too, in the complex germanous halides; the structure $M[GeCl_3]$ gives the germanium the octet 2, $\underline{6}$; in a salt $M_2[GeCl_4]$ it would have the decet 2, $\underline{8}$, involving an inert pair, and so this does not occur, although with tin, where an inert pair is possible, the corresponding salt $M_2[SnCl_4]$ is known.

STANNOUS COMPOUNDS

The stannous compounds are less stable than the stannic, but far more than the germanous, from which they are also distinguished by the existence of the simple divalent cation Sn^{++}.

Stannous Alkyls and Aryls[900]

The stannous alkyls $SnAlk_2$ are coloured somewhat unstable substances, which are readily oxidized to the stannic state, and also (like other alkyls) polymerize in ways that are not fully understood.

Tin diethyl $SnEt_2$ was made in 1852[902] from ethyl iodide and tin-sodium alloy; the dialkyls can also be made by reducing the tin dialkyl-dihalides with zinc, or from stannous chloride and the Grignard reagent.[903] They are variously described as colourless[902] or yellow or red[904] oils, insoluble in water but soluble in organic solvents (the dimethyl is said to occur also as an insoluble yellow solid[905]); it is probable that they have never been got in the pure condition. Their chief characteristic is a strong tendency to go over into the stannic state. On distillation they decompose into the stannic alkyls $SnAlk_4$ and metallic tin; they are soon converted by air into the oxides $SnAlk_2O$; alkyl halides form $Alk_3Sn(hal)$ and halogens (chlorine, bromine, and iodine) form the dihalides $Alk_2Sn(hal)_2$.

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[900] Krause and v. Grosse, pp. 353-5.

[901] K. A. Jensen and N. Clauson-Kaas, *Z. anorg. Chem.* 1943, **250**, 277.

[902] C. Löwig, *Ann.* 1852, **84**, 320.

[903] P. Pfeiffer, *Ber.* 1911, **44**, 1269.

[904] E. Krause and K. Weinberg, unpublished, quoted in Krause and v. Grosse, p. 354.

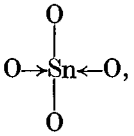
[905] C. A. Kraus and W. N. Greer, *J.A.C.S.* 1925, **47**, 2568.

The stannous *diaryls* are much easier to make and to purify; they are made from dry stannous chloride and aryl magnesium halide, which react in ether to give a bromine-red solution.[906] They are bright yellow powders giving solutions in benzene that are bright yellow if very dilute, but otherwise deep red. Tin diphenyl melts at 130°, the di-*p*-tolyl at 111·5°, the di-α-naphtyl at 200°, all giving red liquids. Tin diphenyl is diamagnetic both as a solid and in benzene solution; the freezing-points in benzene and in ethylene dibromide show that in these solvents the diaryls are monomeric at first, but polymerize on standing[906] (see, however, ref. [901]). Tin diphenyl has in benzene solution a dipole moment of about 1·10 D.[901]

Their reactions are like those of the dialkyls but less violent. When heated with excess of the Grignard reagent the diphenyl compound is converted into tin hexaphenyl $Sn_2\Phi_6$ (with the heavier aryls and with the di-cyclohexyl compound this does not occur,[907] no doubt for steric reasons). They are not acted on by water, but are so readily oxidized (especially in the light) that all work on them must be done in an inert atmosphere and in subdued light.

Stannous Oxide and its Derivatives

Stannous oxide SnO can be made by precipitating the hydrated oxide from a stannous solution with alkali, and dehydrating at 100°. When quite free from water it forms blue-black crystals or a brown powder[908]; lighter-coloured forms are shown by X-ray examination to contain hydroxide. The crystal structure has been shown[909] to have, as in plumbous oxide, each oxygen surrounded tetrahedrally by 4 metallic atoms, each of which has 4 oxygens in a square to one side of it. The distances are Sn—O 2·21, Pb—O 2·30 (theory $\mathrm{Sn^{iv}}$—O 2·00, $\mathrm{Pb^{iv}}$—O 2·06). This is obviously a giant molecule with the grouping



$$\mathrm{O}\rightarrow\overset{\overset{\mathrm{O}}{|}}{\underset{\underset{\mathrm{O}}{|}}{\mathrm{Sn}}}\leftarrow\mathrm{O},$$

where the Sn has the decet 2, $\underline{8}$. We should expect a trigonal bi-pyramid with one point empty, and the observed structure is only a slight distortion of this.

Stannous hydroxide $Sn(OH)_2$ is no doubt present in the colloidal precipitate formed by alkalies or ammonia in a stannous solution; this loses water below 100°, and no definite compound $Sn(OH)_2$ is known. The sol^{y} in water is very small, about 0·7 mg./litre at 25°. It is amphoteric, about equally strong as acid and as base. As a base it forms the stannous salts, and as an acid it dissolves in alkalies to give solutions which must

[906] E. Krause and R. Becker, *Ber.* 1920, **53**, 173.

[907] E. Krause and R. Pohland, ib. 1924, **57**, 532.

[908] M. Straumanis and K. Strenk, *Z. anorg. Chem.* 1933, **213**, 301.

[909] W. J. Moore and L. Pauling, *J.A.C.S.* 1941, **63**, 1392.

contain stannites of the type $M_2[SnO_2]$ or $M[SnO \cdot OH]$, although the salts do not appear to have been isolated.[911] Stannous solutions, both acid and alkaline, are well known strong reducing agents; the alkaline solution is used to reduce diazo-compounds to hydrazines, and its instability is shown by its decomposing spontaneously if it is left to itself into metallic tin, which separates as crystals, and the stannate. Acid stannous solutions will reduce triphenyl carbinol (though not benzyl alcohol) to the hydrocarbon,[910] and will separate silver, gold, and mercury in the metallic state from solutions of their salts.

Stannous Sulphide, SnS

This can be made from its elements, the heat of formation being 18·61 k.cals. per mole[912]; it melts at a red heat (950–1,000° C.) and boils at 1,090°.[913] Above 265° it slowly[914] changes into a mixture of stannic sulphide SnS_2 and metallic tin. Hydrogen chloride acts on it (in the dry state on warming, and in aqueous solution in the cold) to give stannous chloride and hydrogen sulphide.

No stannous sulpho-salts are known, but if the stannite solutions are warmed with sulphur stannic sulpho-salts are formed.

Stannous Halides

All four of these are known. *Stannous fluoride* (m. and b.pts. apparently unknown) can be made by dissolving the metal or stannous hydroxide in hydrofluoric acid; it forms white crystals stable in air, which dissolve in water to a clear solution, suggesting (since the hydrolysis must be at least as great with the fluoride as with the chloride) that the products of hydrolysis are soluble in water.

The melting- and boiling-points of the other stannous halides are as follows:

	$SnCl_2$	$SnBr_2$	SnI_2
M.pt. . . .	247°	215°	320°
B.pt. . . .	603°	619°	720°

The vapour density[915] indicates that the molecules are mainly $SnCl_2$, with 30 per cent. of double molecules at 639°; according to Eijkmann[916] the molecular weight by the freezing-point in urethane solution is that of $SnCl_2$. The results of electron diffraction of the vapour[917] indicate that the $SnCl_2$, $SnBr_2$, and SnI_2 molecules are not linear but triangular; this would

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[910] A. Wanscheidt and B. Moldarski, *Ber.* 1930, **63**, 1362.

[911] R. Scholder, *Z. Angew. Chem.* 1936, **49**, 255.

[912] I. A. Korschov, *J. Gen. Chem. Russ.* 1940, **10**, 2087.

[913] J. Guinchant, *C.R.* 1902, **134**, 1224.

[914] W. Spring, *Z. Physikal. Chem.* 1895, **18**, 553.

[915] H. Biltz and V. Meyer, ib. 1888, **2**, 184.

[916] J. K. Eijkmann, ib. 1889, **4**, 497.

[917] M. W. Lister and L. E. Sutton, *Trans. Far. Soc.* 1941, **37**, 406.

be expected for a molecule Cl—Sn—Cl, where the tin has a valency group of 2, 4, and the valency angle should therefore be 120°. The distances are Sn—Cl 2·42, Sn—Br 2·55, Sn—I 2·73 A (theory, using Sn = 1·40 as for Sn^{iv}, 2·39, 2·54, 2·73).

Stannous chloride is very soluble, not only in water (sol^y 270/15°), but also in organic solvents such as acetone (sol^y 55·4/18°) and even ethyl acetate (4·46/18°).[918] It is obviously covalent in the vapour, but is highly ionized in water, though according to Prytz[919] the solution contains much $SnCl_3^-$ anions, to which its reducing power is due. It forms a dihydrate with water (mono- and tetra-hydrates have also been described) which is the 'tin salt' used in dyeing as a mordant. This melts at 40·5°; if it is dissolved in a little water it gives a clear solution (like bismuth trichloride) no doubt owing to complex formation; but on dilution the basic salt Sn(OH)Cl comes down.

Stannous bromide is similar, and also forms a hydrate.

Stannous iodide SnI_2 is again similar, but is much less soluble in water (sol^y 0·99/20°), so that it can be precipitated from a stannous chloride solution with potassium iodide.

All these halides (including the fluoride) form complex salts (below).

Stannous Salts of Oxy-acids

Several of these are known, especially a nitrate and a sulphate. The former, $Sn(NO_3)_2$, 20 [?] H_2O has been described by Weber[920] as a hygroscopic salt, made by dissolving stannous oxide in nitric acid. If metallic tin is dissolved in aqueous nitric acid a mixture of stannous and stannic nitrates is formed.

Stannous sulphate $SnSO_4$ is a colourless salt, of which, according to Marignac (1857), the solubility in water is 18·8/19° and 18·1/100°: this fall of solubility with rise of temperature is not unusual with sulphates.

Stannous Complexes

These are almost confined to the halides. Stannous chloride will add on one molecule of ammonia, but the constitution of the product is unknown. A series of complex formates of the type

$$M_2[Sn(HCO_2)_4],\ 5\ H_2O\ (M = Na, K, NH_4)$$

have been made,[921] all hydrolysed by water.

Complex halides of divalent tin seem to be formed by all four halogens; the solubilities of stannous chloride and stannous iodide on addition of the corresponding halogen acid show the characteristic form of a small initial fall (common ion effect) followed by a considerable rise.

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[918] A. Naumann, *Ber.* 1910, **43**, 313.

[919] M. Prytz, *Z. anorg. Chem.* 1928, **172**, 147.

[920] R. Weber, *J. prakt. Chem.* 1882, **26**, 121.

[921] E. Elöd and F. Kolbach, *Z. anorg. Chem.* 1927, **164**, 297.

Stannous fluoride gives complex halides of the types $M[SnF_3]$ and $M_2[SnF_4]$,[922-3] though little is known about them.

Stannous chloride forms complex salts of the two corresponding types, with 0, 1, and 2 H_2O. The salt $K_2[SnCl_4]$, 2 H_2O[924] is very slightly soluble in water, and can be used to estimate potassium; in water it is slowly hydrolysed and oxidized by the air, but it is stable in aqueous hydrochloric acid. It was supposed that the $SnCl_4$ anion had been proved by X-ray measurements to be planar, but this conclusion has been found to be incorrect.

Complex bromides and iodides[925] of the same types are known, and are very similar.

PLUMBOUS COMPOUNDS

In lead, as we should expect, the effect of the inert pair is far more marked: the stability of the plumbous ion is much greater than that of the plumbic. The discharge potential Pb^{++}/Pb^{++++}, that is, the E.M.F. calculated for a platinum electrode in a solution containing equal concentrations of plumbous and plumbic ions, against a normal hydrogen electrode, is $+1{\cdot}8$ volts, whereas the corresponding value for tin is 0·2 volts. Accordingly all the true salts of lead are plumbous.

In the covalent state the plumbic compounds are the more stable. This is to be expected since, as we saw with germanium, the covalent state of the divalent atom involves a valency sextet.

Plumbous Alkyls and Aryls[926]

These are few, and quite as unstable as the corresponding stannous compounds. They are intensely coloured, and rapidly oxidized by air; on keeping they separate metallic lead, with the formation of the plumbic derivatives PbR_4 or Pb_2R_6 (or PbR_3 radicals). They show how much less stable divalent lead is in the covalent than in the ionized state.

The dialkyl lead compounds have not yet been obtained in the pure state. Tafel[927] and Renger[928] by reducing acetone electrolytically with a lead cathode got a red liquid which was decolorized by bromine with the production of lead di-isopropyl dibromide, and no doubt contained lead di-isopropyl $Pb(CHMe_2)_2$; and the transient red colour produced[929] when lead chloride is added to a Grignard reagent is presumably due to a lead dialkyl, though the ultimate product is the trialkyl or the tetra-alkyl.

The lead *diaryls* are more stable, and if lead chloride is treated with aryl magnesium halide at 0°, the reaction can be stopped at this stage. In this way (in absence of air) lead diphenyl and ditolyl have been prepared

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[922] M. E. Frémy, *Ann. Chim. Phys.* 1856, [3] **47**, 1.

[923] R. Wagner, *Ber.* 1886, **19**, 896.

[924] T. Karantassis and L. Capatos, *C.R.* 1932, **194**, 1938.

[925] T. Karantassis, *Ann. Chim.* 1927, [x] **8**, 71.

[926] Krause and v. Grosse, pp. 372–4.

[927] J. Tafel, *Ber.* 1911, **44**, 323.

[928] G. Renger, ib. 337.

[929] G. Grüttner and E. Krause, ib. 1916, **49**, 1415.

in the pure state[930]; they are dark red powders, giving blood-red solutions in benzene or ether, from which they are precipitated by alcohol. Freezing-points in benzene solution show them to be monomeric, with even less association than with the tin diaryls. But the lead very easily goes from the divalent to the tetravalent state. The solids and their solutions absorb oxygen from the air with remarkable ease, being oxidized with the loss of their colour to plumbic compounds; they add on iodine in the cold to give di-aryl-di-iodides $PbAr_2I_2$, and they reduce silver nitrate to metallic silver. In the complete absence of air and light, however, they keep their colour for weeks.

Their reactions are in general like those of the stannous di-aryls, but they are less stable: thus the reaction with excess of the Grignard reagent to give the triaryl or hexa-aryl goes so easily that it is difficult to separate the diaryl, whereas the analogous change with tin does not go at all easily except with the diphenyl compound itself.

Plumbous Oxide PbO

[The suboxide Pb_2O supposed to be left on heating lead oxalate has been shown by X-ray diagrams, magnetic susceptibility, and conductivity[931-2] to be a mixture of lead oxide PbO and metallic lead.]

Lead oxide or litharge PbO occurs in two enantiotropic forms, a red tetragonal low-temperature α-form and a yellow high-temperature orthorhombic β-form[933]; the interconversion is slow, and the forms are easily got in a metastable state: the transition temperature is variously given as 350°,[934] 490°,[935] and 585°.[936] The crystal structure of the α-form has already been described under stannous oxide (p. 620). The solubilities of the two forms in g. per litre of water at 25° are: red 0·0504, yellow 0·1065.[937]

The colour does not seem to be always sufficient to distinguish the forms; Rencker[938] finds that the α-form may have any colour from red to yellow.[939]

Plumbous hydroxide, $Pb(OH)_2$. Plumbous oxide will take up water, but no definite compound of the composition $Pb(OH)_2$ has been isolated. The hydroxide is amphoteric, but as we should expect much less acidic than stannous; the acid dissociation constant K_a is 8×10^{-12}, and the basic K_b 1×10^{-3}.[940] The aqueous solution turns red litmus blue.

Plumbous sulphide, PbS, is the mineral galena, the most important ore

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[930] E. Krause and G. G. Reissaus, *Ber.* 1922, **55**, 888.

[931] A. Baroni, *Gaz.* 1938, **68**, 387.

[932] L. L. Bircumshaw and I. Harris, *J.C.S.* 1939, 1637.

[933] For crystal structure of the orthorhombic form see A. Bystrom, *Arkiv. Kemi, Min. Geol.* 1944, **17**, B, No. 8.

[934] E. Rencker and M. Bassiere, *C.R.* 1936, **202**, 765.

[935] M. Petersen, *J.A.C.S.* 1941, **63**, 2617.

[936] M. Le Blanc and E. Eberius, *Z. physikal. Chem.* 1932, **160**, 69.

[937] A. B. Garrett, S. Vellenga, and C. M. Fontana, *J.A.C.S.* 1939, **61**, 367.

[938] E. Rencker, *Bull. Soc. Chim.* 1936, [v] **3**, 981.

[939] G. L. Clark and W. P. Tyler (*J.A.C.S.* 1939, **61**, 58) agree.

[940] H. Töpelmann, *J. prakt. Chem.* 1929, [ii] **121**, 320.

of lead. In the mineral it forms large regular crystals with a grey-blue metallic glance, and a high density (7·5–7·7); it is precipitated from plumbous solutions by hydrogen sulphide as a black solid. It melts at about 1,100°; it is almost insoluble in water (about 1 mg. per litre) and does not dissolve in acids unless they are either very concentrated (hydrochloric) or oxidize it (nitric). On heating in air it is oxidized to lead oxide and lead sulphate.

A selenide PbSe and a telluride PbTe are known.

Plumbous Halides

These are all definite salts, though the chloride shows signs of auto-complex formation in solution.[941] Their melting- and boiling-points and their solubilities (as usual in g. salt to 100 g. water) are as follows:

	PbF_2	$PbCl_2$	$PbBr_2$	PbI_2
M.pt.	818°	298°	373°	412°
B.pt.	1,285°	954°	916°	..
Sol^y^ 25°	0·135	1·08	0·97	0·076
Sol^y^ 100°	..	3·34	4·75	0·436

Lead fluoride is readily hydrolysed by steam, and even by moist air, to hydrogen fluoride and a basic fluoride.

Lead chloride is hydrolysed by water above 110°, forming the basic salt Pb(OH)Cl.

Lead bromide is similar; it forms a tri-hydrate $PbBr_2$, 3 H_2O.

Lead iodide is relatively insoluble in water, and separates from the hot (colourless) solution on cooling in the familiar golden spangles; the yellow colour of the crystals darkens to red on heating but fades again on cooling, and the colour in liquid air is very pale.

Of the other salts there is little to say beyond the solubilities in water. Easily soluble salts are (the solubilities in the usual units are given in brackets) the nitrite, nitrate (59·6/25°; 134/100°), chlorate (255/25°), bromate (134/20°), perchlorate (439·6/25°), dithionate and acetate (55·2/25°). Slightly soluble salts are the carbonate (*circa* 0·2 mg./25°), oxalate (0·15 mg./18°), azide, cyanide, thiocyanate, sulphite, sulphate (4·5 mg./25°), thiosulphate, chromate (0·01 mg./18°), and iodate (2·3 mg./25°).

The very insoluble carbonate (cerussite, isomorphous with aragonite) has a dissociation pressure of 1 atmosphere of carbon dioxide at 300°. The basic carbonate $Pb(OH)_2$, 2 $PbCO_3$ is white lead, a pigment of very high covering power. Lead chromate is the well-known pigment chrome yellow.

Plumbous Complexes

These seem to be rather more numerous than the complexes of divalent tin.

Various ammines have been described, and in particular the diammine ion seems to have considerable stability. The temperatures at which the

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[941] C. L. v. Ende, *Z. anorg. Chem.* 1901, **26**, 162.

following ammine salts have a dissociation tension of ammonia of 100 mm. are[942-3] $PbCl_2, 2\,NH_3$ +30°; $PbBr_2, 2\,NH_3$ 42·5°; $PbI_2, 2\,NH_3$ 33°; $PbSO_4, 2\,NH_3$ 36·8°; $Pb(NO_3)_3, NH_3$ 121°.

Of the possible or certain oxygen complexes we have examples of several kinds. Double acetates $K[Pb(O\cdot CO\cdot CH_3)_3]$ and $K_2[Pb(O\cdot CO\cdot CH_3)_4]$ have been obtained,[944] and double sulphites, sulphates, and thiosulphates have also been described; but with none of these salts is there any evidence of complexity. The position is different with the nitrates. It was shown by Noyes[945] that the addition of potassium nitrate (and in a less degree that of ammonium nitrate) increases the solubility of lead nitrate in water, and at the same time diminishes the concentration of lead cations in the solution; but he found that sodium nitrate has the opposite effect on both properties. Glasstone and Saunders[946] examined the complete systems $Pb(NO_3)_2$—KNO_3—H_2O and $Pb(NO_3)_2$—$NaNO_3$—H_2O; no double salts separated, but the opposite effect of the two alkaline nitrates on the solubility of the lead salt was confirmed. This is good evidence for the formation in solution in presence of potassium nitrate of a complex nitrato-ion (a very rare occurrence); the fact that the complex could not be isolated may be only due to its high solubility. The very remarkable behaviour with sodium nitrate is presumably due to the abstraction of water from the system by the highly hydrated sodium ion; it must be remembered that the solubilities of these nitrates are very high: the saturated solution in contact with solid lead nitrate and sodium nitrate at 50° contains only 38·9 per cent. of water.

Cox, Shorter, and Wardlaw[947] have got X-ray evidence of complex formation in the oxalate-compound $K_2[Pb(C_2O_4)_2]$, the neutral bis-benzoylacetonate PbA_2, and the thiourea compound $Pb(SC(NH_2)_2)_2Cl_2$. It is very remarkable that they find the valencies of the lead in all these compounds to lie in a plane; since the lead in all of them has the valency group 2, $\underline{8}$, this is an exception to the general rule that the steric positions with a valency decet are always derived from a trigonal bipyramid (see Introduction, p. xx).

Complex Halides. No double fluorides seem to have been prepared, perhaps because of the low solubility of the binary fluoride PbF_2; but the other halides all form double salts, and all show the characteristic solubility curves in presence of hydrogen or alkali halides, with an initial fall and a subsequent rise.[948] Double plumbous chlorides of various types have been described, such as $MPbCl_3$, M_2PbCl_4 and M_4PbCl_6. The complex bromides and iodides are similar.[949,950]

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[942] W. Biltz, *Z. anorg. Chem.* 1922, **124**, 230.

[943] W. Krings, ib. 1929, **181**, 309.

[944] A. Lehrmann and E. Leifer, *J.A.C.S.* 1938, **60**, 142.

[945] M. Le. Blanc and A. A. Noyes, *Z. physikal. Chem.* 1889, **6**, 386.

[946] S. Glasstone and H. N. Saunders, *J.C.S.* 1923, **123**, 2134.

[947] E. G. Cox, A. J. Shorter, and W. Wardlaw, *Nature*, 1937, **139**, 71.

[948] For the iodides see O. E. Lanford and S. J. Kiehl, *J.A.C.S.* 1941, **63**, 667.

[949] L. Roger, *C.R.* 1938, **206**, 1181.

[950] Id., ib., 1940, **211**, 388.

The crystal structures of a curious series of complex bromides

$$MPb_2Br_5 \ (M = K, Rb, NH_4)$$

have been examined by Powell and Tasker.[951] They find the structure to consist of chains of (ionized) MBr molecules separated by (covalent) $PbBr_2$ molecules, the Br—Pb—Br angle being 85·5° and the Pb--Br distance 2·89±0·05 A (theory for Pb^{iv}—Br 2·60, for $[Pb]^{++}(Br)^{-}$ 3·28). We should expect the undistorted Br—Pb—Br angle (with Pb 2, $\underline{4}$) to be 120°.

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[951] H. M. Powell and H. S. Tasker, *J.C.S.* 1937, 119.

SUBGROUP IV A

Ti—Zr—(Ce, Pr, Tb)—Hf—Th

THIS is the first series of elements we have met which from a chemical point of view shows a definitely transitional character. The elements of Group III A are transitional in their isolated atoms, but in their compounds all three valency electrons are always used as such.

A transitional element in the wider sense is one in which the second outermost electron group contains more than 8 and less than 18 electrons. Such elements differ from the typical and B elements in that this excess over 8 can be used for forming positive electrovalencies or covalencies, but when it is not so used remains in the penultimate group. Hence the valency can vary by single units from 2 (perhaps sometimes 1) up to the group valency, which here of course is 4. We may compare in various valencies the structure of a transitional element such as zirconium (40 = 2.8.18.(8+2)2) with that of a B element like tin (50 = 2.8.18.18.4):

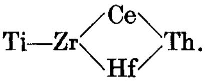
Valency 4		Zr^{4+}	$-\overset{\vert}{\underset{\vert}{\mathrm{Zr}}}-$	Sn^{4+}	$-\overset{\vert}{\underset{\vert}{\mathrm{Sn}}}-$
2. 8. 18.	+	(8)	(8) $\underline{8}$	(18)	(18) $\underline{8}$
Valency 3		Zr^{3+}	$-\overset{\vert}{\mathrm{Zr}}-$	Sn^{3+}	$-\overset{\vert}{\mathrm{Sn}}-$
2. 8. 18.	+	(8+1)	(8+1) $\underline{6}$	(18) 1	(18) 1, $\underline{6}$
Valency 2		Zr^{2+}	—Zr—	Sn^{2+}	—Sn—
2. 8. 18.	+	(8+2)	(8+2) $\underline{4}$	(18) 2	(18) 2, $\underline{4}$

The practical outcome is that with the transitional elements valencies of 4, 3, and 2 are all possible, but presumably increasingly unstable, while with the non-transitional (in Gp. IV) 2 is only possible when there can be an inert pair of electrons, and 3 is not possible at all except in free radicals. Further, experiment shows in all groups that whereas with the B elements the stability of the 'inert pair' valency (Gp. val. −2) increases with the atomic number, in the transitional (A) series the reverse occurs, each lower valency becoming increasingly unstable as we descend the series.

In the structures of the isolated atoms the second transitional period (Y 39 to Pd 46) differs markedly from the first (Sc 21 to Ni 28) and third (La 57 to Pt 78). In the first period all the elements except chromium have 2 electrons in the outermost group, as in Ti −(8+2) 2; Cr alone has 1, −(8+5) 1 instead of −(8+4) 2. In the second period there are 2 in yttrium −(8+1) 2 and in zirconium −(8+2) 2, but all the rest have only one, except palladium which has none —(18). In the third period we return to the state of the first, and the number is always 2. This difference between the series has no perceptible effect on the chemistry (no more than the peculiar structure of chromium), and the only sign we have of it is its reflection in the great stability in the univalent state of silver as compared with either copper or gold.

Tetravalent Compounds

Among these we have to include those of tetravalent cerium* (and also of tetravalent praseodymium and terbium, so far as these are known). The properties of these elements indicate that they do not form a linear series, but rather a branched chain



This follows from their structures. The normal change in descending a sub-group is that at each step the valency groups increase their principal quantum numbers by 1: this happens with Ti→Zr, Zr→Hf and Hf→Th; but Ce and Hf both have their valency electrons in the fifth and sixth quantum groups, the difference between them being that the fourth quantum group contains 18 electrons in Ce and 32 in Hf. The effect of this is shown in the following table, which gives the radii of the atoms and of the ions with the group valency for these A elements and their neighbours.

Quantum Group	*I*	*II*	*III*	*IV*	*V*	*VI*	*VII*
22 Ti	2	8	(8+2)	2	. .	. .	. .
40 Zr	2	8	18	(8+2)	2	. .	. .
58 Ce	2	8	18	18	(8+2)	2	. .
72 Hf	2	8	18	32	(8+2)	2	. .
90 Th	2	8	18	32	18	(8+2)	2

	Gp. III	*Gp. IV*	*Gp. V*	*Gp. VI*
	21 Sc	22 Ti	23 V	24 Cr
Rad. of atom	1·44	1·36	1·23	1·25
ion	0·78	0·64	. .	. .
	39 Y	40 Zr	41 Nb	42 Mo
Rad. of atom	1·62	1·48	1·34	1·36
ion	0·93	0·87	. .	. .
	57 La	58 Ce	. .	. .
Rad. of atom	1·69	1·65	. .	. .
ion	1·22	1·18	. .	. .
	71 Lu	72 Hf	73 Ta	74 W
Rad. of atom	1·56	1·48	1·34	1·37
ion	0·99	0·87	. .	. .
	. .	90 Th	. .	92 U
Rad. of atom	. .	1·65	. .	1·49
ion	. .	1·10	. .	. .

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* The compounds of quadrivalent cerium have already been discussed (III. 451).

In Group III A the contraction caused by this increase of the fourth quantum group (the 'lanthanide contraction') more than compensates for the increase of size in going from the second to the third period, and lutecium actually has a smaller ion than yttrium. In Groups IV (Zr, Hf), V (Nb, Ta), and VI (Mo, W) the effects balance within the limits (0·01 A) of experimental error of the X-ray measurements. The chemical resemblance of hafnium to zirconium is closer than that of niobium to tantalum or molybdenum to tungsten (though both pairs are very similar), and we may suppose that the resemblance in size is closer also. In what follows, up to the special section on hafnium, it may be assumed that what is said of zirconium is meant to apply to hafnium as well.

The essential changes in properties along the series are those to be expected from the dimensions. The tendency to covalency formation and the acidity fall off markedly from titanium to thorium. Titanium hydroxide is weakly acidic and weakly basic. It can form alkaline titanates, such as K_2TiO_3, 4 H_2O, though these are very highly hydrolysed in water. Its salts with acids, such as the chloride and nitrate, are completely hydrolysed by water. Zirconium hydroxide is less acidic and more basic. This is still more true of the ceric salts, and when we reach thorium the acidic properties have completely disappeared, and the basic are reasonably strong. Thorium hydroxide is no more soluble in alkaline hydroxides than it is in water, and the salts, though they are considerably hydrolysed in water, as we should expect with a quadrivalent base, can be recrystallized unchanged from water unless the acid is very weak. Thorium is the most definitely salt-forming of all the quadrivalent metals: the tetra-chloride at its melting-point has a conductivity (814°) of 0·61, which is that of a fused salt, while titanium tetrachloride is a non-conductor.

Lower Valencies

These are always markedly less stable than the tetravalency. The titanous (Ti''') compounds are numerous and well known. The Ti^{+++} ion has a stronger tendency to go over into the quadrivalent state than the stannous ion: it is a stronger reducing agent, and in presence of platinum can even decompose water with evolution of hydrogen. Its halides, and a series of salts, simple and complex, are known. The divalent titanium compounds are still less stable. They are confined to such compounds as the oxide sulphide and halides: they are all solid (like the germanous compounds), and are very readily oxidized by air.

Zirconium was long supposed to give no compounds of lower valency than 4; but Ruff in 1923 showed that the tetrachloride can be reduced to give a tri- and a dichloride, and one or two other compounds with these valencies have since been prepared. They are much less stable than the corresponding titanium compounds.

Cerium of course does not come into the series at all: in the cerous state, which is much more stable than the ceric, the extra electron has not gone into the penultimate electronic group, but into the one before.

With hafnium little is known of the tri- or divalent compounds, although they might afford a first-order method of separation from zirconium.

Thorium is not known to occur with any valency except 4.

It is thus evident that in these elements (unlike the B subgroup) as the atomic number increases, the lower valencies become increasingly unstable.

Metals

The elements of this subgroup are very infusible; their melting-points are as follows (cerium is added to show how it differs from the subgroup proper):

	Ti	Zr	[Ce]	Hf	Th
M.pt.	1725°	1857°	[635°]	2227°	1730°

As a result of this infusibility, and of their strong tendency to combine at high temperatures with carbon, oxygen, and especially nitrogen, it was long before they were obtained in the pure state.

Titanium can be made by reducing the tetrachloride with sodium[952] or sodium hydride.[953] More recent work shows[954-6] that the metal is dimorphic, with a hexagonal low-temperature α-form, going over at about 880° to the cubic body-centred β-form; the change is very slow. Titanium can be obtained in the pure and coherent state by the method of van Arkel and de Boer[957]; the crude powdered metal, mixed with a little iodine, is heated in an evacuated vessel which has above the solid a fine tungsten wire heated to a higher temperature. The whole is heated to a temperature at which the metal forms the tetraiodide (for titanium to 50–250°; for zirconium to 600°) which volatilizes; the tungsten wire (m.pt. of tungsten is over 3,000°) is heated electrically so as to dissociate the tetraiodide (to 1,100° for titanium, to 1,800° for zirconium). The metal is deposited on the wire in a coherent form, and as this deposit grows the current is increased so as to keep up the temperature; a rod of the metal is thus formed, in which the thin tungsten core can be neglected. The pure titanium so made[956] has a density of 4·51, and a conductivity at 25° of $2{\cdot}4 \times 10^4$/ohm, cm.; it melts at 1,725±10° C.

Titanium is ductile only when it is quite free from oxygen.[956] It is used in steel: as little as 1 part in 1,000 greatly increases the strength. It is also used to remove the last traces of oxygen and nitrogen from incandescent lamps.

Titanium combines with oxygen at a red heat, with fluorine at 150°, with chlorine at 300°, and with nitrogen at 800°. It is attacked by acids only on heating; nitric acid converts it (like tin) into the dioxide, giving 'metatitanic acid'.

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[952] M. A. Hunter, *J.A.C.S.* 1910, **32**, 33.

[953] M. Billy, *C.R.* 1914, **158**, 578.

[954] J. H. de Boer, W. G. Burgers, and J. D. Fast, *Proc. K. Akad. Amst.* 1936, **39**, 515.

[955] F. M. Jaeger, E. Rosenbohm, and R. Fonteyne, *Rec. Trav.* 1936, **55**, 615.

[956] J. D. Fast, *Z. anorg. Chem.* 1939, **241**, 42.

[957] See J. H. de Boer, *Ind. Eng. Chem.* 1927, **19**, 1256.

Zirconium is also difficult to obtain in the pure and coherent state, but this can be done by van Arkel and de Boer's method; it can then be drawn or rolled like copper. Zirconium, like titanium, is dimorphic, the transition point being 865°[958]; but the metal can absorb homogeneously up to 10 atoms per cent. of oxygen or nitrogen, which raises the transition point, even up to 1,550°.[959] For the mechanism of the transition see Burgers and van Amstel.[960]

Chemically zirconium is very inert (especially in the compact form) at all but high temperatures, and is only attacked by hydrofluoric acid or aqua regia among acids. When strongly heated it combines with carbon, nitrogen, oxygen, and the halogens.

Little is known of the independent properties of *hafnium*; but the metal was obtained in the same way as zirconium by the decomposition of the iodide, and could then be drawn into wire.[961] The atomic volume was determined from the Debye-Scherrer diagrams, the results at the ordinary temperature being

$$\text{Zr : dens. } 6{\cdot}53 \ \pm 0{\cdot}01\text{; at. vol. } 13{\cdot}97 \ \pm 0{\cdot}02$$
$$\text{Hf : dens. } 13{\cdot}08 \ \pm 0{\cdot}01\text{; at. vol. } 13{\cdot}66 \ \pm 0{\cdot}02.$$

This is a difference of 2·2 per cent. in atomic volume, and hence in the atomic radius of 0·7 per cent. (or of 0·011 A in a radius of 1·58). The melting-point, as already given, is 2,227°, nearly 400° higher than that of zirconium.[962]

Thorium. The thorium nucleus decomposes both spontaneously and under bombardment. ^{232}Th (almost the only natural isotope) is radioactive (α) with a half-life of $1{\cdot}34 \times 10^{10}$ years; it has five natural isotopes (belonging to all three series) with lives ranging from 85,000 years (ionium) to 20 days (radioactinium).

Under bombardment, especially by fast neutrons, it breaks up like uranium into two particles of more or less the same size, with an evolution of energy almost as great as that of uranium (see, for example, refs. [956,963-4]). Its decomposition is not as easy as that of uranium, and especially it differs from ^{235}U in not being affected by slow but only by fast neutrons (0·5 to 2·5 m.e.v.); but deuterons and γ-rays if they are energetic enough will also bring about the fission. The products are numerous, since the primary often change further; krypton and barium are among the more important, as they are with uranium ($36+56 = 92$), but bromine, iodine, palladium, ruthenium, and others have been identified.

Metallic thorium is relatively little known, but it differs from the other elements of the series in not (or scarcely) absorbing oxygen or nitrogen,[956]

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[958] J. H. de Boer, P. Clausing, and J. D. Fast, *Rec. Trav.* 1936, **55**, 450.

[959] J. H. de Boer and J. D. Fast, ib. 459.

[960] W. G. Burgers and J. J. A. Ploos van Amstel, *Nature*, 1938, **141**, 330.

[961] A. E. van Arkel, *Z. physikal. Chem.* 1927, **130**, 100.

[962] J. H. de Boer and J. D. Fast, *Z. anorg. Chem.* 1930, **187**, 207.

[963] A. H. W. Aten, C. J. Bakker, and F. A. Heyn, *Nature*, 1939, **143**, 679.

[964] L. Meitner, ib. 637.

and so it can be got in a coherent form by heating the powder under pressure.[965] It is grey metal, which is attacked by concentrated but not by dilute acids, and reacts with halogens on heating.

Hydrides

All these metals have a considerable power of absorbing hydrogen, up to a composition approaching MH_2 if they are cooled in hydrogen from a high temperature,[966] but no definite compounds have been isolated. The supposed volatile hydrides of thorium and of zirconium have been shown not to exist.[967]

Carbides

Carbides can be obtained of all these elements by heating the metal or its oxide with carbon to a high temperature. Those of titanium, zirconium, and hafnium are of the type MC, and those of cerium and thorium MC_2.

Titanium carbide TiC was made by Moissan[968] from the oxide and carbon in the electric furnace; it is more stable than the metal: it is not attacked by hydrogen chloride or by water at 700°, and is insoluble in boiling potash; it dissolves in nitric acid.

Zirconium carbide ZrC, made in the same way,[969-70] is hard enough to scratch quartz, and is a good conductor of electricity (a remarkable property). It melts at 3,530°C.[971] It dissolves more carbon on heating, which separates as graphite on cooling. It is less stable than titanium carbide, and is attacked by oxygen and by nitrogen at a red heat, as well as by nitric and sulphuric acids; it is soluble in fused alkali.

Hafnium carbide HfC is similar, but melts 360° higher, at 3,890° C.[971]

The structure of these AC carbides seems to be unknown, but their hardness and infusibility suggest giant molecules.

Cerium and thorium give carbides of the AC_2 type. *Cerium carbide* CeC_2[972] is easily decomposed by cold water and by dilute acids. *Thorium carbide* ThC_2[973] is similar, and is decomposed with the same ease. The products of the action of water on these two carbides[973] are remarkably similar:

Per cent.	C_2H_2	CH_4	C_2H_4	H_2
CeC_2	75	20	4	. .
ThC_2	48	29	5	17

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[965] J. W. Marden, *Trans. Electrochem. Soc.* 1934, **66**, 39.

[966] A. Sieverts, A. Gotta, and S. Halberstadt, *Z. anorg. Chem.* 1930, **187**, 155.

[967] R. Schwarz and E. Konrad, *Ber.* 1921, **54**, 2122.

[968] H. Moissan, *C.R.* 1895, **120**, 290.

[969] H. Moissan and F. Lengfeld, *Bull. Soc.* 1896, [3] **15**, 1275.

[970] E. Wedekind, *Ber.* 1902, **35**, 3929: *Chem. Ztg.* 1907, **31**, 654.

[971] C. Agte and H. Alterthum, *Z. techn. Phys.* 1930, **11**, 182.

[972] H. Moissan, *C.R.* 1897, **124**, 1233.

[973] H. Moissan and A. Etard, ib. 1896, **122**, 573: *Ann. Chim. Phys.* 1897, [7] **12**, 427.

The structures of these two carbides[974] are identical, with the carbon atoms united in pairs, so that they are presumably acetylides M″[C≡]. This involves a divalency otherwise unknown with cerium or with thorium. It has been suggested that the formation of hydrogen and reduction products of acetylene with water is due to the return of the metal from its abnormal valency (presumably stabilised by the lattice energy) to the normal. It is conceivable that the metal is quadrivalent, and the structure $M^{4+}[C{=}C]^{4-}$.

Nitrides

Titanium and zirconium (and no doubt hafnium) form very stable and infusible nitrides of the type TiN; thorium, however, gives only Th_3N_4.

Titanium nitride TiN is formed very easily when a titanium compound is reduced in nitrogen, or when the compound of the tetrachloride and ammonia is heated to a high temperature[975-6]. It forms large hard plates with a sodium chloride lattice; according to Brager,[977] if it is made below 1,400° it has excess of titanium and is blue-black: if made above 1,600° it is TiN and golden brown; but the lattice is the same with both (see further, ref. [978]).

Zirconium nitride ZrN (m.pt. 3,200°) is made by heating the dioxide ZrO_2 with carbon in nitrogen; it also has a sodium chloride lattice[979]; it is very stable and has a considerable electric conductivity.[980]

Thorium nitride Th_3N_4 is made by heating the tetrachloride or the dioxide in ammonia. It is a brown powder, decomposed by water to the dioxide and ammonia.[981-2] It can be got in the form of black crystals with a low electric conductivity.[983] The heat of formation (solid) is 308 k.cals. per g.-mol. Th_3N_4.[984]

Thorium nitride is regarded by Wells[985] as an ionic compound, and no doubt has the rare N^{---} ion only found in these nitrides (see under Nitrogen, V. 664). The nitrides of the TiN type[986] are also no doubt ionized (from their lattice); it is remarkable that such stable compounds can be formed from these unusual N^{---} ions with the titanium and zirconium ions in their unstable trivalent state; this must be due to an unusually large lattice energy. The fact that thorium forms no such ThN compound is evidence that thorium cannot become trivalent even under these exceptionally favourable circumstances.

[974] Wells, *S.I.C.* 457.
[976] O. Ruff and F. Eisner, *Ber.* 1905, **38**, 742.
[975] Id., ib. 1908, **41**, 2250.
[977] A. Brager, *Acta phys. Chem. U.R.S.S.* 1939, **11**, 617.
[978] E. A. Ostroumov, *Z. anorg. Chem.* 1936, **227**, 37.
[979] E. Friederich, *Z. Phys.* 1925, **31**, 813.
[980] P. Clausing, *Z. anorg. Chem.* 1932, **208**, 401.
[981] C. Matignon and M. Delépine, *C.R.* 1901, **132**, 36.
[982] Id., *Ann. Chim. Phys.* 1907, [8] **10**, 150.
[983] W. Düsing and M. Huniger, *Chem. Centr.* 1932, i. 208.
[984] B. Neumann, C. Kröger, and H. Haeble, *Z. anorg. Chem.* 1932, **207**, 145.
[985] Wells, *S.I.C.* 425. [986] Id., ib. 566.

Dioxides, AO_2

	TiO_2	ZrO_2	CeO_2	HfO_2	ThO_2
Melting-points	1,825°	2,677°	2,600°	2,774°	3,050°

Titanium dioxide TiO_2 is iso-trimorphic with silica, and occurs as the three minerals rutile, anatase, and brookite. It can also be made by drying the hydroxide precipitated from a titanium tetrachloride solution with alkali. For its polymorphism and crystal structures see references[987-8]. It breaks up above its melting-point into Ti_2O_3 and oxygen, the dissociation pressure being 1 atm. at 2,230° C.[989] Water, dilute acids, and fusion with potassium cyanide or nitrate have no action on it. Various oxides from Ti_2O_3 to TiO_2 seem to occur, with much mutual solubility in the solid state.

Zirconium dioxide ZrO_2 is also trimorphic, and very similar.[990] It melts at 2,677°[991]; it is not attacked by any acids except hydrofluoric, but gives zirconates on fusion with alkalies.

Hafnium dioxide HfO_2 is again similar, and melts at 2,774° C.[991]

Thorium dioxide ThO_2 is made by heating the hydroxide or the halide in air; it is probably isomorphous with TiO_2, ZrO_2, and SnO_2; it readily goes into a colloidal form. By the use of a radioactive isotope of shorter life it has been shown[992] that the solubility in water at 25° is 0·02 mg./litre.

The heat of formation of the solid dioxides in k.cals. per gram-atom of metal is[993]

TiO_2	ZrO_2	HfO_2	ThO_2
214·4	255·5	290	328

Hydroxides, $A(OH)_4$

The acidity of these compounds falls off in the order Si > Ti > Zr > Th; thus the silicates can be formed from aqueous solution; the titanates are made by fusion, and so largely hydrolysed by water that it is doubtful whether they can be recrystallized even from concentrated alkali; zirconium hydroxide is almost insoluble in aqueous alkali; thorium hydroxide is quite insoluble, and forms no salts with alkalies at all.

Titanium hydroxide $Ti(OH)_4$. No such definite compound can be isolated; X-rays are said to show that the moist oxide only contains absorbed water.[994] The only titanates that are at all soluble are those of the alkalies, and titanium can often replace silicon in silicates; minerals of the composition of titanates of polyvalent metals are known such as ilmenite, which has the composition $FeTiO_3$, but is isomorphous with haematite Fe_2O_3, and no doubt is a mixed oxide.

[987] P. Ehrlich, *Z. Elektrochem.* 1939, **45**, 362.

[988] F. Schossberger, *Z. Krist.* 1942, **104**, 358.

[989] E. Junker, *Z. anorg. Chem.* 1936, 228, 97.

[990] W. M. Cohn and S. Tolksdorf, *Z. physikal. Chem.* 1930, B **8**, 331.

[991] P. Clausing, *Z. anorg. Chem.* 1932, **204**, 33.

[992] V. Spitzin (or Spicin), *J. Russ. Phys. Chem. Ges.* 1917, **49**, 357. (*Chem. Centr.* 1923, iii. 657.)

[993] A. Sieverts, H. Gotta, and S. Halberstadt, *Z. anorg. Chem.* 1930, **187**, 155.

[994] H. B, Weiser and W. O. Milligan, *J. physikal. Chem.* 1934, **38**, 513.

Titanic esters $Ti(O \cdot R)_4$ can be made from sodium alkylate and titanium tetrachloride[995]; with alcohol the chlorine of this is only partially replaced by alkoxy-groups[996]; examples of these esters are $Ti(O \cdot CH_3)_4$, m.pt. 210°, b.pt. 243° at 52 mm.; $Ti(O \cdot C_2H_5)_4$ oil, rapidly hydrolysed by moist air.

Zirconium hydroxide $Zr(OH)_4$ is readily converted into a colloid,[997] which has an enormous absorptive power that may be mistaken for combination (e.g. in alkaline solution). When precipitated in the cold it readily dissolves in acids, but very little in alkalies. The zirconates, such as Na_2ZrO_3 and $CaZrO_3$, are mostly isomorphous with the titanates and the silicates.

Thorium hydroxide $Th(OH)_4$[998] is precipitated by alkalies from the salt solutions as a gel; it is soluble in mineral acids but not in bases (its solubility in alkaline carbonate solutions is due to the formation of complex double carbonates). Like zirconium hydroxide it adsorbs carbon dioxide strongly from the air. X-ray patterns show that it is always amorphous, and that if it is heated only the thorium dioxide lines appear.

Peroxides

The power of forming peroxide (—O—O—) compounds with hydrogen peroxide is especially marked in the oxy-acids of group valency belonging to Groups IV A, V A, and VI A; as a rule it is more marked in the even than in the odd groups, and in each group in the heaviest element; the latter relation holds in Group IV A, though thorium peroxide (like the dioxide) forms no salts with bases.

Titanium solutions are coloured yellow by hydrogen peroxide through the formation of peroxides; this can be used as a test for both reagents (Schönn 1870); the effect is visible with 0·001 per cent. titanium, and a millinormal solution can be titrated (the colour being measured photoelectrically) with an accuracy of 0·25 per cent.[999] From the solution a hydrated peroxide can be precipitated in which the ratio of TiO_2 to active oxygen is usually 1:1; its composition has been found to be TiO_3, 2 H_2O.[1001-3]

A series of peroxytitanates can be prepared[1004-7] which contain more oxygen the stronger the hydrogen peroxide used; thus we have $Na_2[TiO_5]$, 3 H_2O, and even $K_4[TiO_8]$, 6 H_2O. Mixed salts can also be made such as the fluoride $(NH_4)_3[TiO_2F_5]$[1007] formed by the oxidation of $(NH_4)_2[TiF_6]$, a

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[995] F. Birchoff and H. Adkins, *J.A.C.S.* 1924, **46**, 256.

[996] J. S. Jennings, W. Wardlaw, and W. J. R. Way, *J.C.S.* 1936, 637.

[997] See Abegg, 1909, pp. 885–90.

[998] Ib. 903-6.

[999] C. B. Allsop, *Analyst*, 1941, **66**, 371.

[1000] R. Schwarz and W. Sexauer, *Ber.* 1927, **60**, 500.

[1001] M. Billy, *C.R.* 1921, **172**, 1411.

[1002] Id., ib. 1928, **186**, 760.

[1003] M. Billy and I. San-Galli, ib. 1932, **194**, 1126.

[1004] A. Mazzucchelli, *Atti R.* 1907, [v] **16**, ii. 265, 349.

[1005] A. Mazzucchelli and E. Pantanelli, ib. 1909, [v] **18**, 608.

[1006] E. Kurowski and L. Nissenmann, *Ber.* 1911, **44**, 224.

[1007] R. Schwarz and H. Giese, *Z. anorg. Chem.* 1928, **176**, 209.

further proof of the stability of these peroxides: this compound is isomorphous with $(NH_4)_3[TiF_7]$. There is also a sulphate $K_2[TiO_2(SO_4)_2]$, 3 H_2O. These peroxytitanates are reduced to titanates by ozone,[1008] and by chromates and permanganates.[1000]

Zirconium behaves in the same way with hydrogen peroxide and also (curiously) with sodium hypochlorite.[1009-10] Here again alkaline salts can be made, such as K_4ZrO_8, 6 H_2O,[1007] as well as more complicated types such as $Na_4Zr_2O_{11}$, 9 H_2O. The peroxide group is more acidic than hydroxyl, as is shown by the fact that these salts, unlike the simple zirconates, can be recrystallized from alkaline solutions.

Hafnium gives a similar peroxide HfO_3, 2 H_2O or $Hf(OH)_3O.OH$. It is curious that this is not found to give any metallic salts.[1007]

Thorium peroxide can be made in the same way by oxidizing a thorium solution with hydrogen peroxide, sodium hypochlorite, or electrolytically.[1010] The solid appears to have the composition Th_2O_7, 4 H_2O; it is more stable than the peroxides of titanium or zirconium, but as would be expected it refuses (like thorium dioxide) to form metallic salts.

Tetrahalides

		AF_4	ACl_4	ABr_4	AI_4
A = Ti	B.pt.	284°	136·4°	230°	377·2° C.
	M.pt.	..	—23°	+38·2°	150°
A = Zr	Sbl./1 at.	(Subl.)	331°	357°	431°
	M.pt.	..	437°/25 at.	450°/15 at.	499°/6·3 at.
A = Th	B.pt.	..	922°	725°	..
	M.pt.	..	765°	..	..

Titanium tetrafluoride TiF_4 can be made from the elements, or by igniting titanium in hydrogen fluoride, or better by the (reversible) action of excess of hydrogen fluoride on the tetrachloride. It is a white solid[1011] with the vapour density of TiF_4 at 444°, forming a hydrate TiF_4, 2 H_2O with a large evolution of heat.

Titanium tetrachloride $TiCl_4$[1012-13] is made from the elements or by passing chlorine over heated titanium dioxide and carbon. Its dielectric constant is 2·73 at 24°; it is a non-conductor of electricity and its vapour density is normal.[1021] In benzene solution it acts on ethers and alkyl halides like aluminium chloride.[1014]

Titanium tetrabromide $TiBr_4$ is made[1012.1015] in the usual ways; it is soluble in organic solvents (sol^y at 20° in alcohol 360, in ether 4·8), and also

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[1008] F. Fichter and A. Goldach, *Helv. Chem. Acta*, 1930, **13**, 1200.

[1009] L. Pissarjewski, *Z. anorg. Chem.* 1900, **25**, 378.

[1010] Id., ib. 1902, **31**, 359.

[1011] O. Ruff and W. Plato, *Ber.* 1904, **37**, 673.

[1012] W. Biltz and K. Jeep, *Z. anorg. Chem.* 1927, **162**, 32.

[1013] W. Biltz, A. Sapper, and E. Wünneberg, ib. 1932, **203**, 277.

[1014] G. L. Stadnikov and L. J. Kaschanov, *Ber.* 1928, **61**, 1389.

[1015] P. A. Bond and E. C. Crone, *J.A.C.S.* 1934, **56**, 2028.

in 34 per cent. hydrobromic acid[1016]; like the other halides it is converted into oxyhalides by water.

Titanium tetraiodide TiI_4 is made from the elements at a red heat, or by the action of iodine and hydrogen on $TiCl_4$ vapour at a high temperature; the vapour density at 444° is 7 per cent. below normal. It dissolves in water, but the solution soon precipitates titanic acid. TiI_4 (b.pt. 377·2° C.) has a Trouton constant of 21·5.[1017]

Zirconium tetrafluoride ZrF_4 can be made by the action of hydrogen fluoride on the tetrachloride, or better by igniting $(NH_4)_2ZrF_6$[1018]; the mono- and trihydrates (perhaps $H_2[ZrOF_4]$ and $H_2[ZrOF_4]$, $2\,H_2O$) are known.[1019]

The crystal structure of *hafnium tetrafluoride* HfF_4[1020] is practically identical with that of the zirconium compound; the molecular volumes are[1018] ZrF_4 35·88 c.c., HfF_4 35·71 c.c., a difference of 0·49 per cent.

Zirconium tetrachloride $ZrCl_4$, made in the usual ways, is a white solid hydrolysed by water even in presence of concentrated hydrochloric acid; it can be used in the Friedel-Crafts reaction in place of aluminium chloride.[1023] The *tetrabromide* is similar. The *tetraiodide* is best made[1022] by the action of hydrogen iodide on zirconium carbide at 340°.

The *hafnium tetrahalides* so far as they are known are very similar to those of zirconium.

The *thorium tetrahalides* are all definite salts. The tetrafluoride ThF_4 can be got as the tetrahydrate by dissolving a thorium salt or the dioxide in hydrofluoric acid; unlike zirconium tetrafluoride it is insoluble in hydrofluoric acid, and the metals can be separated in this way.[1024] When heated in air it leaves the dioxide. Anhydrous ThF_4 can be made[1025] by passing hydrogen fluoride over the tetrachloride or tetrabromide at 350-400°.

Thorium tetrachloride $ThCl_4$ can be made from the elements at a red heat, or by heating the dioxide in a stream of chlorine and sulphur chloride, the $ThCl_4$ being sublimed off above 800°.[1026-7] In its purification every trace of air must be excluded, or the oxychloride is formed. It consists of colourless needles fairly stable in air; in a vacuum it begins to sublime at 750°[1028]; the vapour density is normal at 1,000°, but 24 per

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[1016] J. C. Olsen and E. P. Ryan, *J.A.C.S.* 1932, **54**, 2215.

[1017] J. M. Blocher and I. E. Campbell, ib. 1947, **69**, 2100.

[1018] G. v. Hevesy and W. Dullenkamp, *Z. anorg. Chem.* 1934, **221**, 161.

[1019] E. Chauvenet, *Ann. Chim. Phys.* 1920, [9], **13**, 59.

[1020] G. E. R. Schultze, *Z. Krist.* 1934, **89**, 477.

[1021] O. Rahlfs and W. Fischer, *Z. Elektrochem.* 1932, **38**, 592; *Z. anorg. Chem.* 1933, **211**, 351.

[1022] A. Stähler and B. Denk, *Ber.* 1905, **38**, 2611.

[1023] H. W. Heine, D. L. Cottle, and H. L. van Mater, *J.A.C.S.* 1946, **68**, 524.

[1024] M. Delafontaine, *Bull. Soc. Chim.* 1897, [3] **20**, 69.

[1025] E. Chauvenet, *C.R.* 1908, **146**, 973.

[1026] C. Matignon and F. Bourion, ib. 1904, **138**, 631.

[1027] R. J. Meyer and A. Gumpers, *Ber.* 1905, **38**, 817.

[1028] H. Moissan and Martinsen, *C.R.* 1905, **140**, 1510.

[1029] G. Krüss and L. F. Nilson, *Z. physikal. Chem.* 1887, **1**, 301.

cent. low at 1,400°.[1029] The electrical conductivity just above the melting-point[1030] is 0·61—i.e. is that of a fused salt. It dissolves in water with some evolution of heat and considerable hydrolysis; hydrates with 9, 8, and 7 H_2O have been described.[1031-2]

The *tetrabromide* is very similar[1028,1033]; it is said to form hydrates with 10, 8, and 7 H_2O.[1034-5]

Thorium tetraiodide ThI_4 is again similar, and can be made from the elements by heating, but it is readily decomposed by light or heat; it forms a decahydrate and a basic decahydrate $Th(OH)I_3$, 10 H_2O.[1031,1036]

Salts of Oxy-acids

Titanium and zirconium, mainly owing to their weak basicity, give scarcely any normal salts of oxyacids weak or strong. Thus titanium forms no simple oxalate, nitrate, or sulphate. Zirconium forms a sulphate $Zr(SO_4)_2$, but this cannot be recrystallized from water, which converts it into basic salts; in the same way the normal nitrate can only be obtained with great difficulty, and readily goes over into a basic nitrate; there is no simple oxalate.

Thorium, on the other hand, with its much stronger basicity, forms relatively stable oxy-salts. It gives a very soluble nitrate, sulphate, chlorate, bromate, etc., and a very insoluble oxalate (0·07 mg. per litre at 25°). The formate and acetate can be made, but the solutions precipitate basic salts on boiling.

The sulphate shows very singular solubility relations.[1037] It occurs with 0, 2, 4, 6, 8, and 9 H_2O. The anhydrous salt dissolves up to 25 per cent. in water at 0°, but this solution is metastable, and slowly in the cold or more rapidly on warming separates the stable 9-hydrate, or sometimes the slightly metastable 8-hydrate, the solubilities of which at 0° are 1 per cent. or less. The stable forms are the 9-hydrate from the cryohydric point to 43°, the tetrahydrate from this to about 100°, and the dihydrate above 100°. The 6- and 8-hydrates are always metastable, and slightly more soluble than the 9. With a rise of temperature the solubility of the tetrahydrate and probably that of the anhydrous salt fall; those of the 9-, 8-, and 6-hydrates rise. These changes are remarkably large: the solubilities in g. $Th(SO_4)_2$ to 100 g. water are:

Temp.	*Anh.*	*9 aq.*	*8 aq.*	*6 aq.*	*4 aq.*
0°	*circa* 33	0·74*	1·00	1·50	(> 10)
40°	..	3·0*	3·4	3·6	4·0
55°	..	6·8	..	..	1·9*

* Stable form.

[1030] W. Biltz, *Z. anorg. Chem.* 1924, **133**, 312.

[1031] A. Rosenheim, V. Samter, and I. Davidsohn, ib. 1903, **35**, 424.

[1032] C. Matignon and M. Delépine, *Ann. Chim. Phys.* 1907, [8] **10**, 130.

[1033] F. Bourion, *C.R.* 1907, **145**, 243.

[1034] J. Lesinsky and C. Gundlich, *Z. anorg. Chem.* 1897, **15**, 81.

Reverse solubility curves are common with sulphates; the peculiarity of this salt is the enormously long time—hours or even days—required to establish phase-equilibrium. Cerous sulphate behaves in the same way.[1038-9] This is probably only an extreme example of the general tendency of the rate of establishment of equilibrium between salt and solution to fall off greatly as the valencies of the ions rise. This is so with an alkaline sulphate, and still more with the phosphates of the alkaline earths. The thorium ion has the highest valency of any really stable monatomic cation, and the sulphate of any strong anion; so the phenomenon is naturally most marked with thorium sulphate, and less so, but still highly, with the sulphate of a trivalent metal such as cerium.

COMPLEXES

The tendency to complex formation as a whole falls off from titanium to thorium, as the basicity increases; but owing to the extent to which the simple salts of the lighter elements are hydrolysed by water, the number of double salts is much greater with thorium.

Nitrogen Complexes

These are few and little known. All the halides form solid compounds with ammonia, some of them stable up to fairly high temperatures, but these can often be shown to be mixtures of ammonium halides with a substitution product such as $M(NH_2)_4$; this can be determined by extracting the ammonium salt with liquid ammonia, but that has not always been done.

Titanium. TiF_4, 4 NH_3 has been made, but its constitution is uncertain; it seems to occur in two isomeric forms.[1040] The ammonia addition compounds of the tetrachloride and tetrabromide,[1041] when the ammonium salt is removed, leave the curious compounds $N{\equiv}Ti{-}Cl$ and $N{\equiv}Ti{-}Br$.[1042-4]

Zirconium. The ammonia compounds of the tetrahalides certainly contain ammonium salt, but the nature of the substitution product is unknown.[1045]

Thorium. Numerous ammines have been described, but their constitution is unknown.[1046]

[1035] A. Rosenheim and J. Schilling, *Ber.* 1900, **33**, 977.

[1036] G. N. Wyrouboff and A. Verneuil, *Ann. Chim. Phys.* 1905, [8] **6**, 441.

[1037] H. W. B. Roozeboom, *Z. physikal. Chem.* 1890, **5**, 198.

[1038] I. Koppel, *Z. anorg. Chem.* 1904, **41**, 377.

[1039] See Abegg, *Cer*, 1906, p. 202.

[1040] A. Brager, *Acta phys.-chem. U.R.S.S.* 1939, **10**, 887.

[1041] O. C. Dermer and W. C. Fernelius, *Z. anorg. Chem.* 1934, **221**, 83.

[1042] M. Blix and W. Wirbelauer, *Ber.* 1903, **36**, 4228.

[1043] O. Ruff and F. Eisner, ib. 1905, **38**, 742.

[1044] Id., ib. 1908, **41**, 2250.

[1045] A. Stähler and B. Denk, ib. 1905, **38**, 2611.

[1046] R. C. Young, *J.A.C.S.* 1935, **57**, 997.

Oxygen Complexes

These are much more numerous, and include both open-chain and ring (chelate) complexes.

Titanic chloride and bromide, like the stannic halides, readily combine with one, or more usually two molecules of oxygen compounds such as ethers, ketones, and esters, as well as inorganic oxy-compounds such as phosphorus oxychloride.[1047-8] The tendency seems to be weaker than with tin.

Zirconium halides (except the fluoride) behave in the same way, but the products are usually stable only at low temperatures; above these they react internally with elimination of hydrogen halide.[1049]

Thorium halides are similar; they form addition compounds with alcohols, aldehydes, ketones, and esters,[1031,1050] which again have a strong tendency to react with separation of the halogen; thus thorium bromide on boiling with ethyl benzoate gives ethyl bromide and thorium benzoate $Th(O \cdot CO \cdot C_6H_5)_4$. These thorium complexes frequently contain 4 molecules of the organic component, while those of titanium and zirconium only have 2, though a covalency of 8 is possible for zirconium, and is attained by it in certain chelate (and so more stable) complexes. Thorium can evidently (as often with the heavier elements) reach the high covalency more easily (compare the selenates and the tellurates).

Thorium and quadrivalent cerium form series of double nitrates, which may be complex. The chief are $M_2[Ce(NO_3)_6]$ and $M_2[Th(NO_3)_6]$, which form mixed crystals with one another[1051] (trivalent cerium, praseodymium, etc., form double nitrates, mostly of the type $M_2[Ce(NO_3)_5]$.[1052]

Chelate Oxygen Complexes

These are numerous with all the elements of Group IV A. They include derivatives of β-diketones and the like, and also 'ato' compounds formed from dibasic oxy-acids such as sulphuric and oxalic, as well as catechol and its relatives.

The structure of the β-diketone derivatives depends on the covalency maximum. Titanium forms salts of the type $[TiA_3]X$,[1053] corresponding to the siliconium salts (p. 613), in which the titanium has its maximum covalency of 6; X is usually a complex anion such as $FeCl_4^-$. The other elements, having a covalency maximum of 8, can form non-ionized (tetrachelate) compounds MA_4, of which the zirconium, cerium, and hafnium (but apparently not the thorium) compounds when formed in water contain 10 molecules of water, to which it is difficult to assign places in the

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[1047] G. Scagliarini and G. Tartarini, *Atti R.* 1926, [vi] **4**, 318.

[1048] F. Evard, *C.R.* 1933, **196**, 2007.

[1049] G. Jantsch, *J. prakt. Chem.* 1927, ii. **115**, 7.

[1050] A. Rosenheim and R. Levy, *Ber.* 1904, **31**, 3662.

[1051] V. Cuttica and A. Tocchi, *Gaz.* 1924, **54**, 628.

[1052] C. Brasseliten, *C.R.* 1940, **211**, 30.

[1053] W. Dilthey, *Ann.* 1906, **344**, 300.

structure, and which are easily removed (e.g. by recrystallization from alcohol) and when removed cannot be replaced.

Zirconium acetylacetonate can be made[1054] by the action of alkali or ammonia on a zirconium salt and acetylacetone in water, and then has 10 H_2O; it crystallizes from alcohol as the anhydrous $Zr(C_5H_7O_2)_4$, which is volatile at a rather high temperature, and cannot be made to take up water again. The formation of these compounds takes place in stages. Zirconium tetrachloride forms an addition compound with acetylacetone at $-10°$, which goes at 0° to $ZrCl_2A_2$, and this on boiling with benzene changes into $ZrClA_3$,[1049] which reacts with more acetylacetone in presence of ammonia to give ZrA_4. In the same way[1055] benzoyl acetone reacts with the tetrachloride in water to give the zirconyl compound $O{=}ZrA_2$ (6-covalent), which in benzene solution is highly (2·83 times) associated (perhaps forming a Zr_3O_3 ring). In benzene the two substances give $ZrClA_3$, which has a normal molecular weight in benzene, which seems to show that it has the unusual covalency of 7.

Hafnium forms a similar compound HfA_4, 10 H_2O.[1056]

Cerium is described[1057] as forming $Ce(C_5H_7O_2)_4$, 11 H_2O; this is within experimental error of 10 H_2O, which seems more probable in view of the composition of the other two compounds.

Thorium acetylacetonate,[1054,1058-9] which is always anhydrous, is made in the same way; it can be purified by sublimation at 160° under 0·1 mm. pressure.[1060] It is to some extent polymerized in solution, and forms addition compounds with ammonia of the composition $(ThA_4)_2$, NH_3 (as do the rare earth compounds MA_3). These combinations presumably involve a co-ordination of the metallic atoms with the oxygen or the nitrogen, and so a rise in their covalency, which would mean for thorium an increase to more than 8.

An interesting type of compound formed by zirconium is the 'basic zirconyl benzoate' $Zr_4O_5(O{\cdot}CO{\cdot}C_6H_5)_6$.[1061] This should evidently be written $(ZrO)_4O(O{\cdot}CO{\cdot}C_6H_5)_6$, and is the analogue of the 'basic' beryllium acetate $Be_4O(O{\cdot}CO{\cdot}CH_3)_6$ (II. 213), in which the 4 beryllium atoms are replaced by 4 divalent $O{=}Zr$ groups, the covalency of the Zr being 6, while that of the beryllium is 4.

Ato-Complexes

These, being derived from simple salts of dibasic oxy-acids, are much the most frequent with thorium.

[1054] W. Biltz and J. A. Clinch, *Z. anorg. Chem.* 1904, **40**, 218.

[1055] G. T. Morgan and A. R. Bowen, *J.C.S.* 1924, **125**, 1252.

[1056] G. v. Hevesy and M. Lögstrup, *Ber.* 1926, **59**, 1890.

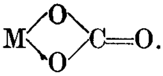
[1057] A. Job and P. Goissedet, *C.R.* 1913, **157**, 50.

[1058] G. Urbain, *Bull. Soc.* 1896, [3] 15, **338**, 347.

[1059] W. Biltz, *Ann.* 1903, **331**, 334.

[1060] R. C. Young, C. Goodman, and J. Kovitz, *J.A.C.S.* 1939, **61**, 876.

[1061] S. Tanatar and E. Kurowski, *Chem. Centr.* 1908, i. 1523.

Carbonato-complexes . Titanium and zirconium, being very weakly basic, do not form simple or complex salts of so weak an acid as carbonic; the same is true of quadrivalent cerium, though here a complex carbonate of the composition $Na_6[Ce(CO_3)_5], 12 H_2O$ has been described[1062]; it has been little examined.

Thorium behaves like cerium. It forms no normal but only a basic carbonate, but this dissolves in excess of sodium carbonate solution, and a number of complex salts have been obtained, which are of two types: (1) such as $(NH_4)_2[Th(CO_3)_3]$, 6 H_2O (6-covalent), and (2) (similar to the ceric salt) $M_6[Th(CO_3)_5]$aq. (Na, 12 H_2O: K, 10 H_2O: Tl′ anhydrous) (Cleve, 1874, and see ref. [1031]).

While the hydroxides of silicon, titanium, and zirconium are soluble in alkalies with increasing difficulty, and that of thorium not at all, alkaline carbonate solutions will dissolve thorium hydroxide but none of the others; this is due to the formation by thorium alone of a carbonato-complex.

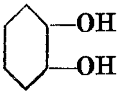
The abnormal stability of the ceri- and thori-carbonates seems to show that the carbonato groups must be attached to the central atom through both oxygen atoms, and if so the Ce and Th atoms in these penta-carbonato anions must be 10-covalent. There is no certain proof that such a covalency ever occurs, though there is no theoretical reason against it. The crystal structure of these complexes, which would give the final proof, has not been examined.

Oxalato-complexes. Titanium forms no oxalate $TiOx_2$ (Ox = C_2O_4), no titanyl oxalate O=TiOx, and no complex oxalates of the simple titanic type, such as $M_2[TiOx_3]$; but it forms a series of complex titanyl oxalates, such as $K_2[O{=}TiOx_2]$, 2 H_2O.[1063]

Zirconium may form the simple oxalate $ZrOx_2$, but this could not be purified. A series of complex 8-covalent oxalates $M_4[ZrOx_4]$, $x H_2O$ have been prepared (Na, 4 H_2O: K, 4: NH_4, 6).[1064]

Thorium, in addition to a very insoluble simple oxalate $ThOx_2$, 6 H_2O (0·11 mg./litre at 25°), gives a series of double oxalates like those of zirconium $M_4[ThOx_4]$, x H_2O (K, 4: Na 6: NH_4 7).[1036]

Catechol compounds: these are given by all three elements Ti, Zr, and Th. The titanium compounds are formed[1065-6] by dissolving titanic acid in an alkaline solution of catechol; they have the composition

$M_2[Ti(cat)_3]$, x H_2O (catH_2 =  x usually = 1);

the rubidium and caesium salts were obtained, but not the sodium,

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[1062] L. Lortie, *C.R.* 1929, **188**, 915.

[1063] E. Pechard, ib. 1893, **116**, 1513.

[1064] A. Rosenheim and P. Frank, *Ber.* 1907, **40**, 803.

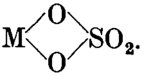
[1065] A. Rosenheim and O. Sorge, ib. 1920, **53**, 932.

[1066] A. Rosenheim, B. Raibmann, and G. Schendel, *Z. anorg. Chem.* 1931, **196**, 160.

presumably because it is too soluble (salts of strong acids); the alkaline earth salts have 8 H_2O. The acid was resolved through the cinchonine salt, and an active NH_4 salt prepared, which racemized quickly.[1066]

The zirconium salts[1066] have varying amounts of catechol 'of crystallization', as in $(NH_4)_2[Zr(cat)_3]$, H_2cat, 1·5 H_2O.

With thorium, Rosenheim[1066] got trichelate complexes such as $(NH_4)_2[Th(cat_3)]$, 1[1065] and 5[1066] H_2O, as well as more complicated types with 2 and 3 thorium atoms in the molecule. An 8-covalent form $(pyH)_2H_2[Th(cat)_4]$ has also been described.[1067]

Sulphato-compounds, 
$M{<}^{O}_{O}{>}SO_2$. Titanium forms sulphato-compounds of two types[1068-9]: (1) normal, as $K_2[Ti(SO_4)_3]$ and (2) titanyl, as

$$(NH_4)_2[O{=}Ti(SO_4)_2],\ H_2O,$$

in both of which it is 6-covalent. These are all hydrolysed by water even in the cold, and cannot be recrystallized from it.

Zirconium can be shown to form sulphato-complexes.[1070-1] The sulphate $Zr(SO_4)_2$ obtained from concentrated sulphuric acid evolves a large amount of heat on solution in water, and a compound of the composition $Zr(SO_4)_2$, 4 H_2O separates. This must be complex because on electrolysis of the solution the zirconium goes to the anode. Further oxalic acid and ammonium oxalate precipitate thorium oxalate from a solution of the chloride or nitrate, but not from one of the sulphate or one of the chloride or nitrate to which sulphuric acid has been added, showing that complex sulphato-ions are formed. The 'hydrated sulphate' is probably in fact a complex zirconyl sulphato-acid $H_2[O{=}Zr(SO_4)_2]$, 3 H_2O, the water being divided between the hydrogen ions and the sulphato-groups, which are usually hydrated. It is doubtful whether any salts of this acid have been isolated.

Cerium forms double sulphates mainly of the type $M_4[Ce(SO_4)_4]$. Thorium also gives double sulphates both of the (apparently) 6-covalent type $M_2[Th(SO_4)_3]$ (Rb, Cs, Na) and of the 8-covalent form $M_4[Th(SO_4)_4]$ (K, NH_4).[1031,1072]

Halide Complexes

Titanium. Complex halides $M_2[TiX_6]$ seem to be formed by all four halogens; but the stability falls off very rapidly with increasing atomic number of the halogen; only the fluorides have any considerable stability, and the iodides, though they appear to be formed in solution, have not been isolated.

[1067] R. Weinland and H. Sperl, *Z. anorg. Chem.* 1925, **150**, 69.

[1068] A. Rosenheim and O. Schütte, ib. 1901, **26**, 239.

[1069] R. F. Weinland and H. Kühl, ib. 1907, **54**, 253.

[1070] R. Ruer, ib. 1904, **42**, 87.

[1071] R. Ruer and M. Levin, ib. 1905, **46**, 449.

[1072] G. N. Wyrouboff, *Chem. Centr.* 1901, i. 494.

Dry hydrogen fluoride has no action on dry titanium tetrafluoride (the same is true with the chlorides, and with silicon tetrafluoride), but in water they combine with a rise of conductivity, and the production of a strong acid,[1073] which no doubt is $H_2[TiF_6]$, aq., though it cannot be isolated. The salts $M_2[TiF_6]$ are numerous and stable. The alkaline salts melt at 500–800°; in water they are very little hydrolysed, and even on addition of alkali precipitate titanium hydroxide only slowly. Ruff showed[1074] that they are more stable than the fluorosilicates. The solubilities of their alkaline salts (as salts of a strong acid) falls from 25/25° for the lithium to 0·8/25° for the rubidium salt.[1075]

A solution of titanium tetrachloride in concentrated hydrochloric acid gives Raman lines similar to those of H_2SnCl_6, indicating the presence of H_2TiCl_6 in the solution[1076]; corresponding salts are known,[1068] but they are unstable and difficult to prepare.

The bromides are similar. The yellow solution of titanium tetrabromide in water goes blood-red on addition of concentrated hydrogen bromide, and a dark red salt $(NH_4)_2[TiBr_6]$, 2 H_2O can be isolated.[1068]

The iodides are even less stable, and the only evidence for them is the dark red colour of the tetraiodide in concentrated hydrogen iodide.[1068]

Zirconium behaves very similarly in many respects. The stability of the complexes falls off very rapidly in the usual order F > Cl > Br; only one bromide is known, $(pyH)_2[ZrBr_6]$, and no iodides[1077]; this bromide loses hydrogen bromide in air, and the chlorides cannot be prepared in water but only in alcohol, so that the zirconium complexes are obviously less stable than those of titanium. The fluorides are numerous and fairly stable, though less so than their titanium analogues; they mostly decompose on heating in air, and break down on dehydration. They are of various types, with from 5 to 8 fluorine atoms to 1 Zr. The salts of the first type seem always to have 1 H_2O, and probably are aquo-salts $M[ZrF_5(OH_2)]$; the hexa-fluoro-salts $M_2[ZrF_6]$ are practically all anhydrous (Li, Na, K, Cs, NH_4). The heptafluorides $M_3[ZrF_7]$ have now been shown by X-ray analysis[1078] to be true 7-covalent compounds, the structure of the anion being derived from the octahedron by the insertion of a 7th fluorine atom, with consequent distortion. These salts are important in the separation of hafnium from zirconium (p. 648). The octofluorides, which are formed especially by divalent metals (Ni, Cu″, Zn, Cd, Mn″: Marignac 1860) have no titanium analogues, and may be true 8-covalent compounds.[1077]

For the chlorides and bromides see reference [1079].

[1073] W. V. Kovalevski, *Z. anorg. Chem.* 1900, **25**, 189.

[1074] O. Ruff and R. Ipsen, *Ber.* 1903, **36**, 1777.

[1075] See further, H. Ginsberg, *Z. anorg. Chem.* 1932, **204**, 225.

[1076] M. E. P. Rumpf, *C.R.* 1936, **202**, 950.

[1077] A. Rosenheim and P. Frank, *Ber.* 1905, **38**, 812.

[1078] G. C. Hampson and L. Pauling, *J.A.C.S.* 1938, **60**, 2702.

[1079] V. I. Spicin (Spitzin), *J. Russ. Phys.-Chem. Soc.* 1917, **49**, 357 (*J.C.S. Abstr.* 1923, ii. 427).

Thorium. Here the complex halides are little known, and seem difficult to make. This is partly due to the high ionization of the simple thorium halides. The fluorides, which are the most stable in the absence of water, are difficult to prepare in water, owing to the minute solubility of thorium tetrafluoride (0·2 mg./litre at 25°).[1079] Only the least soluble (K and Rb) double salts can be separated, not those of sodium or ammonium. The salts, so far as they are known, are of the types $M[ThF_5]$ and $M_2[ThF_6]$.

The chlorides are also few, and of the types of $Cs_2[ThCl_6]$ and $Cs_3[ThCl_7]$.[1031,1035]

Of the bromides only $(pyH)_2ThBr_6$[1031,1035] is known. There are no complex iodides.

HAFNIUM

WE may here consider the history of the discovery of hafnium[1080] and its minute differences from zirconium, which make a separation possible.

Moseley's determination of the atomic numbers from the wave-lengths of the hardest X-rays showed that element 72, preceding Ta 73, was unknown, but this gave no indication of its chemical properties. The Bohr theory, however, shows that the rare earth series is completed, with the filling up of the fourth quantum group of 32, at Lu 71, and that no. 72 must have the structure 2. 8. 18. 32. (8+2) 2, and so belong to the zirconium group IV A. Hevesy and Coster proceeded to look for no. 72 in zirconium minerals by means of the X-ray spectrum, the position of which for no. 72 could be calculated by interpolation from those of the neighbouring elements. In the very first mineral they examined[1081] they found the lines, with a strength indicating about 1 per cent. of the new element, to which they gave the name hafnium, from Hafnia, the old name for Copenhagen, since it was discovered at Copenhagen as a result of the theoretical views of a Copenhagen physicist. Further work showed that all the known zirconium minerals (with one doubtful exception) contain hafnium, usually from 1 to 20 per cent. of the zirconium; but no mineral is known which contains more hafnium than zirconium. The average value of the Hf/Zr ratio in the earth's crust is about 1·7 per cent., giving the amount of hafnium as 3·2 parts per million, about as abundant as arsenic (5·0) or boron (3·0) and far more so than cadmium or mercury (0·5) or iodine (0·3).

As zirconium was discovered by Klaproth in 1787, and the metal isolated by Berzelius in 1824, it seems remarkable that a second element invariably accompanying it, and in such considerable proportions as to cause serious discrepancies in the determination of the atomic weight (the ratio of the atomic weights is 178·6/91·2 = 1·95), should not have been dis-

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[1080] See (*a*) G. v. Hevesy, *Ber.* 1923, **56**, 1503; for a detailed description of the preparation of the element; (*b*) Hevesy, *Récherches sur les propriétés du Hafnium*, Copenhagen, 1925; see also, especially for the geophysical data, Hevesy, *J.C.S.* 1931, 1.

[1081] D. Coster and G. v. Hevesy, *Nature*, 1923, **111**, 79.

covered until in 1923 the theoretical conclusions of Bohr led to a special search being made for it. But for this there are several reasons. The two elements are more similar in properties than any other pair in the whole table; they are devoid of characteristic flame spectra, and all their compounds are extraordinarily difficult to handle. This last point is less important with modern technique; but until lately the purification of non-volatile inorganic compounds (and none of these compounds are readily volatile) depended almost wholly on recrystallization from water. Now apart from the complex fluorides, which at first were naturally neglected, scarcely any zirconium compounds except the oxy-halides crystallize at all readily; when soluble they are always largely hydrolysed, forming the colloidal hydroxide, which has an almost unparalleled power of carrying down electrolytes. Hauser[1082] says in 1904: 'The preparation of really pure zirconium salts is one of the most difficult tasks in preparative inorganic chemistry.' It is therefore not surprising that hafnium should have been overlooked for so long.

The proportion of hafnium in a zirconium compound can be determined in two ways. The first, by which it was originally discovered, depends on the X-ray spectrum; the sample is mixed with a small quantity of an element giving an X-ray line very close to that of hafnium (Ta 73 or better Lu 71), and the relative intensities of the lines are measured photometrically. It is found that 2·5 parts of lutecium give the same intensity of line as 1 part of hafnium. The second method depends on the densities of the dioxides, which are in the ratio 1:1·7 (ZrO_2 5·73; HfO_2 9·68), and as the two form mixed crystals the change of density is very nearly proportional to the hafnium content. Care is needed to get the very infusible dioxide into the proper coherent form.

The close similarity of these two elements is due in the main to their ionic radii being almost identical. The molecular volumes have been accurately determined for the metals by van Arkel,[1083] for the oxides (Hevesy), and for the heptafluorides (Hassel and Mark[1084]); the difference in radius of the ion is roughly one-third of that in volume. The results are given in the table:

Atomic and Molecular Volumes

		Metal	MO_2	$(NH_4)_3MF_7$
Molecular	Zirconium	13·97	21·50	123·9
	Hafnium	13·66	21·70	125·7
	Diff. %	−2·22	+0·93	+1·45
Linear, Diff. %		−/0·74	+0·31	+0·48

The chemical resemblances are in fact closer than those between two successive lanthanides (where the radii differ on the average by 0·016 A,

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[1082] O. Hauser, *Ber.* 1904, 37, 2024.

[1083] A. E. van Arkel, *Z. physikal. Chem.* 1927, 130, 100.

[1084] O. Hassel and H. Mark, *Z. Phys.* 1924, 27, 89.

or 15 per cent.); they approach those between two isotopes. The separation is of course easier than with the rare earths because we have only two elements to deal with instead of many. Various methods have been tried. No first-order differences are known. The zirconium fluoride and chloride are rather more volatile, but not enough to be used for separation, and we have to rely wholly on differences of solubility, which seldom exceed 50 per cent., while the difficulties are enormously increased by the salts always forming solid solutions. As an example of the care required, the final atomic weight determinations by Hönigschmid and Zintl[1085] may be quoted. After 5,000 crystallizations of the double fluoride K_2MF_6 the zirconium content was reduced to about 0·5 per cent.; two of the last fractions were shown by X-ray analysis to contain (A) 0·57 and (B) 0·16 per cent. Zr. These were converted into the tetrabromide, and the ratio of this to silver determined in the usual way.

The results were:

	% Zr	*At. wt. found*	*Corrd. for* Zr	*Mean*
Fraction A . .	0·57	177·79 177·80	178·64	
Fraction B . .	0·16	178·32 178·33	178·57	
				178·6

Numerous compounds have been tried for the separation; nearly always (e.g. double fluoride, double sulphate, double oxalate, simple oxalate, benzoate, salicylate, peroxide, hydroxide, tartrate) the hafnium salt is the more soluble; occasionally, however (oxychloride, phosphate),[1086] it is the zirconium salt. With many of the above the differences are too small to be of practical use, and the salt always employed for the separation is the hexafluoride $(NH_4)_2ZrF_6$, or rarely the heptafluoride $(NH_4)_3ZrF_7$. The following are some of the most favourable differences observed (solubilities in moles per litre):

	Zr	Hf	Hf/Zr *ratio*
$(NH_4)_2MF_6$ at 0°	0·611	0·890	1·46
$(NH_4)_3MF_7$ at 0°	0·360	0·425	1·18
K_2MF_6 in N/8 HF at 20°	0·0655	0·1008	1·54
$O{=}MCl_2$ in 11·6N HCl at 20°	0·33	0·15	0·46 (i.e. 1/2·20)

[1085] O. Hönigschmid and E. Zintl, *Ber.* 1925, **58**, 453.

[1086] E. M. Larsen, W. C. Fernelius, and L. L. Quill, *Ind. Eng. Chem.* [*Anal.*] 1943, **15**, 512.

TRIVALENT AND DIVALENT TITANIUM, ZIRCONIUM AND HAFNIUM

VALENCIES lower than 4 do not occur with thorium; but the first three members of the subgroup can assume the trivalent and divalent states, titanium much the most readily. The behaviour in these lower valencies depends very largely on whether the compounds are ionized or covalent; the tendency to ionization (basicity) is much increased by the fall in the ionic charge, while the covalent compounds have only a valency sextet in $-\overset{|}{\mathrm{M}}-$ and a quartet in $-\mathrm{M}-$, so that they may be expected to be highly polymerized like those of divalent germanium.

It is found experimentally that in the lower valency states titanium alone can form ions (Ti^{++} and Ti^{+++}) as well as covalent compounds; with zirconium both the tri- and the divalent, so far as is known, are always covalent, polymerized, and non-volatile. This difference is normal with the A elements in their lower valencies; it is opposed to the simple Fajan's rules, which, however, do not always apply to ions that are not of the inert gas numbers. The two elements are therefore discussed separately.

Trivalent Titanium (Titanous)

This state has considerable stability. Its general resemblance is to the trivalent state of transitional elements such as $\mathrm{V}^{\mathrm{iii}}$ and $\mathrm{Cr}^{\mathrm{iii}}$, rather than the third-group elements like scandium. A particular resemblance to chromium is the formation of isomeric green and violet hydrated halides.

Titanous ($\mathrm{Ti}^{\mathrm{iii}}$) compounds are obtained from titanic ($\mathrm{Ti}^{\mathrm{iv}}$) by reduction with zinc and acid, or electrolytically: in this way the reduction never goes beyond the trivalent stage. The titanous compounds are all coloured, while the titanic are colourless: this results from the extra electron in the $(8+1)$ group, which the titanic compounds have not got. The tendency of the titanous compounds to revert to the quadrivalent state is stronger than with the stannous: it is just strong enough to cause them to decompose water with evolution of hydrogen in presence of platinum; as usual, the covalent titanous atom is more unstable and more readily oxidized than the ion A solution of a titanous salt is readily oxidized by air; it shows the phenomenon of 'autoxidation'; that is, if other substances are present which are not normally oxidized by air, they take up oxygen during the oxidation of the titanium. Thus in alkaline solution (i.e. with covalent Ti''') water is oxidized to hydrogen peroxide, according to the equation

$$2\,\mathrm{Ti(OH)_3} + \mathrm{O_2} + 2\,\mathrm{H_2O} = 2\,\mathrm{Ti(OH)_4} + \mathrm{H_2O_2}.$$

Accordingly the titanous ion has a strong reducing power: it reduces sulphurous acid to sulphur, aurous and argentous ions to the metal, mercuric compounds to mercurous and to mercury, cupric and ferric solutions to cuprous and ferrous. It also reduces nitro-compounds to amines, and decolorizes azo-compounds at once. It is often used for the estimation of organic substances, especially nitro-compounds, excess of the titanous solution being added, and the excess titrated with iron alum, with thiocyanate as indicator; the titanous solution must be kept in an atmosphere of hydrogen.

The stable bronze-coloured nitride TiN has already been described (p. 634).

The black *oxide* Ti_2O_3 can be made by heating the dioxide alone to 2,000°[1087] or with carbon to 870°. It has the same crystal lattice as corundum. It is very stable, and not attacked by any acid except sulphuric.

The *hydroxide* $Ti(OH)_3$, variously described as black, red, and dark blue, has no acidic properties and is insoluble in alkali, as we should expect from the lower valency. It has very strong reducing power, and on prolonged washing with water in the absence of air changes into $Ti(OH)_4$ with evolution of hydrogen.

Of the trihalides the fluoride TiF_3 is obtained by igniting K_2TiF_6 in hydrogen. It is a purple or violet powder; the aqueous solution, which can be made by reducing K_2TiF_6 with zinc and hydrochloric acid, or sodium amalgam, is green or violet.

Titanous chloride $TiCl_3$ can be made by reducing the anhydrous tetrachloride with silver or mercury, or with hydrogen at 650°,[1088-90] or (in 100 per cent. yield) by heating $TiCl_4$ to 340° in a sealed tube with powdered antimony.[1091] It is a violet powder, subliming very slowly at 430°, and changing by 600° into $TiCl_4+TiCl_2$. In the solid state it is no doubt covalent and highly polymerized. In water it is ionized and considerably hydrolysed. It forms two hydrates $TiCl_3, 6\ H_2O$; the ordinary form is violet but is converted by ether and hydrochloric acid into a green isomer, which soon reverts. The solution is violet in water and green in alcohol; the complex salts are green. This is just like the behaviour of chromic chloride $CrCl_3\ 6\ H_2O$.

The bromide and iodide are similar, but give only violet hexahydrates.

Ti''', unlike Ti'''', is basic enough to give a normal oxalate and sulphate, and even a formate and acetate. The oxalate is very soluble and may be autocomplex.[1092-4] The sulphate forms a series of alums,[1094] of which all but the caesium and rubidium salts are too soluble to be crystallized.

Trivalent titanium has a rather weak power of forming *complexes*. The trichloride forms a colourless hexammine $[Ti(NH_3)_6]Cl_3$, which is free from ammonium chloride, and loses $4\ NH_3$ at 300° to give the diammine.[1090] There is a dichelate complex oxalate $M[Ti(C_2O_4)_2], 2\ H_2O$ ($M = K, Rb, NH_4$: all brownish-red); the salts are much decomposed in solution, and alkalies

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[1087] E. Junker, *Z. anorg. Chem.* 1936, **228**, 97.

[1088] O. Ruff and F. Neumann, ib. 1923, **128**, 84.

[1089] F. Meyer, A. Bauer, and R. Schmidt, *Ber.* 1923, **56**, 1908.

[1090] W. C. Schumb and R. F. Sundström, *J.A.C.S.* 1938, **55**, 596.

[1091] M. Billy and P. Brasseur, *C.R.* 1935, **200**, 1765.

[1092] A. Stähler, *Ber.* 1904, **37**, 4405.

[1093] Id., ib. 1905, **38**, 2619.

[1094] B. Diethelm and F. Förster, *Z. physikal. Chem.* 1908, **62**, 129.

precipitate the hydroxide $Ti(OH)_3$.[1092-3] Complex fluorides $K_2[TiF_5]$ and $(NH_4)_2[TiF_5]$ are known, and also a hexafluoride $(NH_4)_3TiF_6$ (Petersen, 1889; Piccini, 1896); it is apparently isomorphous with the hexafluorides of trivalent chromium, vanadium, and iron. These salts are green. The complex chlorides $Rb_2[TiCl_5], H_2O$ and $Cs_2[TiCl_5], H_2O$, are also known[1092-3]; the water is presumably part of the anion. They give violet solutions.

Divalent Titanium Compounds

These resemble the compounds of divalent vanadium and iron, but are less stable, and are not well known. They are practically confined to the oxide and hydroxide, and the dihalides.

Titanium monoxide TiO has long been doubtful, but has recently[1095] been made by heating the dioxide with titanium *in vacuo* for 2 hours at 1,550° to 1,750°; the product gives an X-ray diagram for a face-centred cubic form; it melts at 1,750°, and dissolves in cold hydrochloric acid with evolution of hydrogen. The hydroxide $Ti(OH)_2$ is no doubt contained in the black precipitate formed in a solution of a Ti″ salt by alkali, which is rapidly oxidized by air.

Of the dihalides[1096] the dichloride and di-iodide are known. The former, $TiCl_2$, can be made by heating the trichloride to redness, when the tetrachloride distils off, or by heating the trichloride in hydrogen at 700°.[1097] It is a deep black powder, which begins to decompose into titanium and the tetrachloride at 475°, and so has never been got pure.[1090] It oxidizes violently in air, and evolves hydrogen with acids.

The di-iodide TiI_2 is made by reducing the tetraiodide with silver or mercury at a red heat, or by heating the tri-iodide *in vacuo* at 200°.[1098] It is black and infusible. It occurs in two forms, one of which has a cadmium iodide structure like vanadium di-iodide.[1099] In a vacuum at 480° it breaks up into titanium and the tetraiodide.[1098]

A sulphate $TiSO_4$ is said to be formed when titanium dissolves in sulphuric acid.[1092-3]

The dichloride forms with liquid ammonia an ammine $TiCl_2$, 4 NH_3, which is free from NH_4Cl; it is very unstable, loses ammonia in the cold, and evolves hydrogen violently with water.[1090]

Trivalent Zirconium Compounds

The lower valency states of zirconium are much less stable than those of titanium, and our knowledge of them is confined to the chlorides,[1100] bromides,[1101] and iodides.[1102]

[1095] W. Dawihl and K. Schröter, *Z. anorg. Chem.* 1937, **233**, 178.

[1096] For the magnetic properties of the dihalides see W. Klemm and L. Grimm, ib. 1942, **249**, 209.

[1097] A. Stähler and F. Bachran, *Ber.* 1911, **44**, 2906.

[1098] J. D. Fast, *Rec. Trav.* 1939, **58**, 174.

[1099] W. Klemm and L. Grimm, *Z. anorg. Chem.* 1942, **249**, 198.

[1100] O. Ruff and R. Wallstein, ib. 1923, **128**, 96.

[1101] R. C. Young, *J.A.C.S.* 1931, **53**, 2148.

Zirconium trichloride $ZrCl_3$.[1049] The tetrachloride in presence of aluminium chloride (which seems to act partly as a solvent) is reduced at 300° by aluminium powder (less well by magnesium or mercury); the excess of tetrachloride and the aluminium trichloride are distilled off *in vacuo*, and $ZrCl_3$ remains behind; it always retains a few per cent. of aluminium and oxygen. It forms brown crystals converted by air into the oxychloride $ZrOCl_2$. It is insoluble in benzene, carbon bisulphide, and liquid sulphur dioxide. It is rapidly decomposed by water with evolution of hydrogen (with $TiCl_3$ this only occurs in presence of platinum), and the production of a brown solution of high reducing power, which soon becomes colourless and on evaporation separates $ZrOCl_2$, $8\ H_2O$. Sodium hydroxide or ammonia gives a yellow precipitate (presumably $Zr(OH)_3$), which is soon converted into $Zr(OH)_4$.

Zirconium tribromide[1101] is precisely similar.

The *tri-iodide* is made[1102] by heating zirconium with its tetraiodide at 400°; at temperatures above 310° it is partly decomposed into the di- and the tetraiodides, and wholly at 560°.

Divalent Zirconium Compounds

The dichloride $ZrCl_2$[1100] can be made in an impure state by reducing the trichloride with sodium, or better by heating it alone, removing the tetrachloride formed as quickly as possible by cooling the tube in the neighbourhood. Even then it contains all the aluminium of the original trichloride (Ruff's $ZrCl_2$ had about 8 per cent. Al). The dichloride is black and amorphous. On ignition in quartz it gives zirconium and the tetrachloride. If it is warm it catches fire in the air; it is insoluble in alcohol, ether, benzene, etc., and in liquid inorganic chlorides. With water it gives a grey insoluble product, which is gradually oxidized by the air. With warm concentrated acids it evolves hydrogen, and the zirconium becomes tetravalent.

The *dibromide* $ZrBr_2$[1101] is similar. It is made by heating the tribromide *in vacuo* at 390° for some hours. It begins to decompose into $Zr+ZrBr_4$ *in vacuo* at 350°, and the reaction is complete in a few days at 410°. It behaves with reagents exactly like the dichloride.

Zirconium di-iodide is formed[1102] from zirconium and the tetraiodide at 560°, and at all temperatures above 430° breaks up into these components again.

Tri- and Divalent Hafnium

Hafnium tribromide and dibromide have been[1103] made in the same way as Young[1101] made the zirconium compounds, by volatilizing the tetrabromide (which sublimes within 25° of $ZrBr_4$) in hydrogen over aluminium at 600–650°. The tribromide is deposited as a blue-black mass, very like $ZrBr_3$; *in vacuo* at 300° it goes to the tetrabromide $HfBr_4$ and the black

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[1102] J. D. Fast, *Z. anorg. Chem.* 1938, **239**, 145.

[1103] W. C. Schumb and C. K. Morehouse, *J.A.C.S.* 1947, **69**, 2696.

non-volatile dibromide $HfBr_2$, which changes above 400° into $HfBr_4$ and metallic hafnium. These compounds closely resemble their zirconium analogues, and like them evolve hydrogen with water, going over to the tetravalent state. The relative stabilities of the lower valencies with zirconium and with hafnium were not examined.

GROUP V

N	P	As	Sb	Bi		B	−(18)	5
		V	Nb	Ta	Pa	A	−(8+3) −(8+4)	2 1

THE resemblance between the subgroups is confined to the compounds in which the element has the group valency of 5, especially the XO_4 derivatives, the arsenates, antimonates, vanadates, etc. In these the acidity falls off markedly in both subgroups as the atomic number increases, from the highly acidic HNO_3 and HPO_3 to the very weak acids of antimony and bismuth; in the A subgroup it is clear that vanadic acid is the strongest and tantalic the weakest. In compounds where the valency is less than 5 there is really no resemblance between the subgroups.

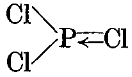
The main division, the typical and B elements, forms a very well-defined series, with a steady change of properties with the atomic number. The elements have much lower boiling-points than those of the principal series of Group IV:

C 3470°	Si 2360°	Ge ?	Sn 2362°	Pb 1755°
N −196°	P_{wh} 281°	As 633°	Sb 1645°	Bi 1560°

This difference is an obvious result of the atomic structure. In Group IV the atom cannot for stereochemical reasons satisfy all its four valencies in a diatomic molecule, and accordingly tends to form non-volatile giant molecules of the diamond type, which the trivalent Group V elements cannot do. With the first of these, nitrogen, where the formation of multiple links is much easier than in later elements of the series, the diatomic $N{\equiv}N$ molecule is formed. With phosphorus—at any rate white phosphorus—and with arsenic, the triple link is apparently too unstable to be readily formed: in its place we have tetratomic molecules P_4 and As_4, which, as has been recently shown by electron diffraction in the vapour, have the four atoms at the points of a regular tetrahedron, with single P—P and As—As links inclined at 60°—the simplest structure for trivalent atoms avoiding multiple links. In the last two elements (Sn, Pb: Sb, Bi) the metallic character predominates in both groups and the boiling-points become more alike. Unlike the elements of Group IV, the atoms cannot form the stable 4-covalent octet except by co-ordination. Their methods of direct combination are essentially two: (1) in their trivalent compounds they form the octet $2, \underline{6}$ as in ammonia. A trivalent ion X^{+++} would have the structure (core) 2, and could only be stable if these last two electrons were inert. This condition is fully realized with bismuth, which does form such ions, is much less stable with antimony, and is only just perceptible with arsenic: and the ionization is distributed accordingly. A pentavalent cation X^{5+} is of course far too highly charged to be able to exist, and so we find that only the heaviest (Sb, Bi) of these elements can ionize at all, because they alone can have two of their valency electrons inert, and so can form trivalent cations. A trivalent anion N^{---} probably occurs in the crystalline state of some AN nitrides (see below, p. 664). (2) The second method of covalency formation is that in which all five valency electrons take part, with the formation of five covalencies as in PF_5, (core) $\underline{10}$. This is impossible for nitrogen owing to the covalency rule, while it is very unusual in bismuth, owing to the inertness of two of the electrons.

In co-ordination the trivalent nitrogen atom has an unshared pair of electrons, and so can act as a donor, though not as an acceptor; the other elements in the trivalent state can act as donors, and also, since their valency group is not limited to 8, as acceptors. In the pentavalent state these later elements can act as acceptors but not as donors. Trivalent nitrogen very readily co-ordinates as a donor, thus assuming the stable form of the 4-covalent octet, taking up a univalent positively charged atom or radical, as in NH_4^+ and $N(CH_3)_4^+$. The tendency to do this is much weaker in phosphorus, and almost zero in the heavier elements. In place of the positive univalent atom or group the acceptor may be a neutral divalent atom such as oxygen or sulphur, giving the amine or phosphine oxides R_3XO; this form of co-ordination occurs as readily with phosphorus as with nitrogen, and also with arsenic. The amine oxide can only have the structure $R_3N \rightarrow O$ by the covalency rule; for the other elements the rule admits of the alternative structure $R_3P{=}O$, etc.; and so far as these atoms can form double links, this structure must at least play the part of a resonance formula.

The covalency of 5 is naturally more usual in Group V than elsewhere, since it can be formed without co-ordination: in other groups 5-co-ordination is rare. The more usual co-ordination number of 6 is curiously rare in this group, though it is commoner than was formerly supposed.

THE limitation of the covalency group of nitrogen to 4 (or of the valency group to 8) while for phosphorus the limit is 6 (12), not only cuts out from nitrogen chemistry all the 5-covalent derivatives of the type of phosphorus pentafluoride PF_5, and all 6-covalent complexes like $K[PCl_6]$, but also restricts the resonance possibilities of nitrogen: thus phosphorus trichloride (like silicon tetrachloride) may be stabilized by resonance with such forms as  (in which the phosphorus has 10 valency electrons), but this is impossible for NCl_3, as it is for CCl_4.

The relative affinities are indicated by a comparison of the heats of formation of the covalent links of nitrogen with those of carbon. These depend on the values assumed for the heats of atomization of nitrogen and of carbon, about which there has been much dispute. The value for carbon is taken (IV. 493) to be 170·4 k.cals.; that for nitrogen is half the heat of dissociation of N_2, which was previously[1-3] assumed to be 169 or 170, but has recently[4-5a] been shown to be 225·3. The half-value is thus 112·6 k.cals./g.atom. We thus get

	X—H	X—C	X—N	X—O	X—F	X—Cl
X = N	92·9	69·3	38·4	(?58)	62·9	47·6 k.cals.
X = C	98·8	81·6	69·3	81·5	103·4	78·0 ,,
Diff. (N—C)	—5·9	—12·3	—30·9	(? - 24)	—40·5	—30·4 ,,

The heats are always less for the nitrogen links, the differences being small for the links to hydrogen and carbon, but about 30 k.cals. (40 per cent.) for those to nitrogen, oxygen, and the halogens. (With phosphorus, as with silicon compared with carbon, there is a marked rise in the affinity for oxygen, and a marked fall in that for hydrogen.)

There are great differences in the relative heats of formation of multiple links. The following are the absolute and relative values for the links of carbon to carbon, nitrogen to nitrogen, and carbon to nitrogen; those of phosphorus to phosphorus (see p. 728) are added for comparison.

C—C	81·6	1	N—N	38·4	1	C—N	69·3	1	P—P	47·5	1
C=C	146·1	1·79	N=N	97·6	2·54	C=N	135	1·95	P=P	..	..
C≡C	192·1	2·35	N≡N	225	5·86	C≡N	212	3·06	P≡P	117·0	2·46

Thus while with the link of carbon to carbon the heat increases much less rapidly than the multiplicity, with that of nitrogen to nitrogen it increases much more rapidly. This may probably be due to the fact that in the

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[1] R. S. Mulliken, *Phys. Rev.* 1934, **46**, 144.

[2] G. Herzberg and H. Sponer, *Z. physikal. Chem.* 1934, B **26**, 1.

[3] A. van der Ziel, *Physica*, 1937, **4**, 373.

[4] A. G. Gaydon, *Nature*, 1944, **153**, 407.

[5] A. G. Gaydon and W. G. Penney, *Proc. Roy. Soc.* 1945, **183**, 374.

[5a] G. Glockler, *J. Chem. Phys.* 1948, **16**, 602.

carbon-to-carbon link both atoms have all their valency electrons shared, whereas the nitrogen atom has in all these states a pair that is not shared, and so is more adaptable to the state of the triple link. It has already been shown (IV. 508) that the acidity of acetylene can be explained in this way. For a further confirmation see below under the azides (p. 717). The result is that whereas in a carbon chain a multiple link, owing to its strain, is the point at which it is likely to break, a multiple link between two nitrogen atoms is a sign of strength; the chain never breaks at that point except on reduction by hydrogen, for which nitrogen has a stronger affinity than for any other element; the tendency is for the double $N{=}N$ link to turn into a triple one, i.e. for the $—N{=}N—$ group to separate as nitrogen gas (e.g. with diazo-compounds both aliphatic and aromatic, with hydrazines on oxidation with copper sulphate, with azo-compounds on heating, and in the decomposition of the hyponitrites).

Owing to the small energy content of nitrogen gas, very many of its compounds are endothermic: all the numerous oxides except the pentoxide, which is just (+5 k.cals.) exothermic, cyanogen (−71 k.cals.), and of course nitrogen trichloride (−55 k.cals.; compare PCl_3+70 k.cals.).

Elementary Nitrogen

Nitrogen N_2 boils at 77·37° K. (−195·79° C.), and melts at 65·16° K. (−208·0° C.) under 9·40 cm. pressure[6]; the solid changes into a second form at 35·5° K. (−237·7° C.).

Nitrogen has a natural isotope ^{15}N, discovered in the band spectrum of nitric oxide by Naudé in 1929[7]; the proportion is one part to 265 of ordinary ^{14}N (0·38 per cent.).[8] The concentration has been raised by Urey,[9] employing the exchange between ammonia gas and a solution of ammonium nitrate[10] or sulphate in an elaborate cascade apparatus, to 73 per cent. ^{15}N. By diffusion Clusius *et al.*[11] have obtained 800 c.c. of pure $^{14}N^{15}N$.

Owing to the large heat of formation of the triple $N{\equiv}N$ link, elementary nitrogen is a relatively inert substance. In organic life most of the N_2 acts as a mere diluent for the O_2, but the combined part is of course essential to animals and plants alike. As the decay of organic matter leads to the liberation of molecular nitrogen, this must normally be replaced, and there are micro-organisms that can absorb nitrogen gas and convert it into ammonia or nitrous or nitric acid; the most remarkable are a group that live symbiotically in nodules provided for them by certain Leguminosae.

Active nitrogen is usually produced by an electric discharge in nitrogen gas, which then gives a greenish glow for some time after the discharge

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[6] W. H. Keesom and A. Biji, *Proc. K. Akad. Amst.* 1937, **40**, 235.

[7] S. M. Naudé, *Phys. Rev.* 1929, **34**, 1498.

[8] A. L. Vaughan, J. H. Williams, and J. T. Tate, ib. 1934, **46**, 327.

[9] H. G. Thode and H. C. Urey, *J. Chem. Phys.* 1939, **7**, 34.

[10] See further, K. Clusius and E. Becker, *Z. physikal. Chem.* 1943, **193**, 64.

[11] For separation by diffusion see K. Clusius, G. Dickel, and E. Becker, *Naturwiss.* 1943, **31**, 210.

has ceased. It is very active chemically, and will combine in the cold with mercury, sulphur, and phosphorus.[12,13] There has been much dispute about its nature, probably because more than one active form is produced, including free atoms and (perhaps more than one kind of) excited molecules, with very different amounts of energy. For later work see references[14-16].

The artificial production of nitrogen compounds from atmospheric nitrogen is carried out by various methods, of which the most important are:

I. Combination with oxygen in an electric arc, spread out by a magnetic field or a stream of air (Birkland-Eyde Process, 1905).

II. 'Kalkstickstoff' Process: by heating calcium carbide to a high temperature in nitrogen (Frank and Caro, 1904):

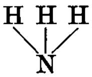
$$CaC_2 + N_2 = CaCN_2 + C.$$

III. Synthesis of ammonia from hydrogen and nitrogen with a catalyst under pressure (Haber Process, 1909).

*Ammonia**

Ammonia is formed from its elements with evolution of heat (11·0 k.cals./mole at 20°[17,18]). The percentage of ammonia at equilibrium in the mixture $N_2+3\ H_2$ under 1 atmosphere is (Haber) at 27° C. 98·5, at 327° 8·7, at 627° 0·21. Hence in its commercial synthesis[19] the temperature must be as low as is compatible with a reasonable rate of reaction, and so the rate is increased by high pressure (1,000 atm. in the Claude process) and the presence of catalysts, which are usually metallic oxides; the process is due to Haber.

Ammonia is a colourless gas with a characteristic smell perceptible at a dilution of 17 mg./m³.[20] The molecule is pyramidal, as is proved by the dipole moment of 1·44,[21] and by the absorption spectrum which shows[22] the H—N—H angle to be 116° and the N—H distance 0·94 A (theory 1·00); the molecules are in rapid oscillation between the two states



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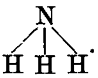

Ammonia has a considerable resemblance to water, especially in the liquid state; both, unlike methane, have one or more pairs of unshared

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* The other binary hydride hydrazine N_2H_4 is described later, p. 708.

[12] R. J. Strutt (Lord Rayleigh), *Proc. Roy. Soc.* 1911, **85**, 219.

[13] Id., ib. 1913, **88**, 539.

[14] Rayleigh, ib. 1935, **151**, 567.

[15] Id., ib. 1940, **176**, 1, 16.

[16] G. Cario and U. Stille, *Z. Phys.* 1936, **102**, 317.

[17] F. Haber and S. Tamaru, *Z. Elektrochem.* 1915, **21**, 191.

[18] S. Tamaru, *J. Soc. Chem. Ind.* 1915, **35**, 81.

[19] See Gmelin, *Stickstoff*, pp. 367–408.

[20] J. C. Olsen and W. H. Ulrich, *J. Ind. Eng. Chem.* 1914, **6**, 621.

[21] F. G. Keyes and J. G. Kirkwood, *Phys. Rev.* 1930, ii. **36**, 1573.

[22] R. M. Badger and R. Mecke, *Z. physikal. Chem.* 1929, B **5**, 352.

electrons, and are to a greater or less extent associated. The properties of liquid ammonia, both as solvent and as reagent, have been fully investigated by E. C. Franklin.[24] Some of the properties of liquid ammonia at its boiling-point are given below; those for water, at 18° unless otherwise stated, follow in square brackets.

Mol. wt.	17 [18]	Diel. const.	22 [81]
Mol. vol.	25 [18]	Dip. mom.	1·48 [1·84]
M. pt.	−77° [0°]		
B. pt.	−33·4° [100°]	Sp. ht.	1·07 [1·00]
Crit. temp.	132·5° [374°]	Ht. of fusion	81·5 kc./g. [79·7]
Trouton	23·4 [25·9]	Rel. visc.	0·241 [1]

The high boiling-point (compared with methane, −164°) and Trouton constant are evidence of considerable association; that this occurs in the gas also is shown by the infra-red absorption.[23] The specific heat and heat of fusion are abnormally high. The ionization of salts in liquid ammonia is considerable though less than in water; the mobilities of the ions are much greater (e.g. K^+2·63 times as great at 20°) owing to the smaller viscosity.

Liquid ammonia is an excellent solvent. It dissolves practically all ordinary acids, though scarcely any metallic oxides or hydroxides. Among salts, the fluorides are nearly all insoluble, but apart from these almost all the salts of monobasic acids dissolve readily—nitrites, nitrates, cyanides, thiocyanates, chlorides, bromides, iodides—but those of polybasic acids are insoluble: sulphites, sulphates, carbonates, phosphates, arsenates, oxalates, and sulphides.

The conductivities of aqueous solutions of ammonia give $1{\cdot}8\times10^{-5}$ as the apparent dissociation constant, i.e. the ratio between the product of the ionic concentrations and that of all the non-ionized ammonia, which is presumably present partly as NH_3 and partly as undissociated NH_4OH. The ratio of these last, $[NH_3]$ $[NH_4OH]$, is independent of the concentrations if they are small, and may be called B. Hence the apparent dissociation constant K′

$$= \frac{[NH_4]\cdot[OH]}{[NH_4OH]+[NH_3]} = \frac{[NH_4]\cdot[OH]}{[NH_4OH]\cdot(1+B)}$$

$$= \frac{K}{1+B}, \quad \text{where } K = \frac{[NH_4]\cdot[OH]}{[NH_4OH]},$$

and is the true (Ostwald) dissociation constant. Moore and Winmill showed[25,26] that the value of B can be determined by measuring at three temperatures at least both the ionization and the partition of the NH_3 between water and an immiscible solvent such as toluene. They thus found how much of the un-ionized ammonia was present as NH_3 and how

[23] R. Robertson and J. J. Fox, *Proc. Roy. Soc.* 1928, **120**, 189.

[24] *The Nitrogen System of Compounds*, Reinhold Pub. Corp., New York, 1935.

[25] T. S. Moore, *J.C.S.* 1907, **91**, 1373.

[26] T. S. Moore and T. F. Winmill, ib. 1912, **101**, 1635.

much as NH_4OH. The actual value of B at 25° is 0·885. Hence in a decinormal solution of ammonia at 25° we have present NH_3 46·2 per cent.; NH_4OH 52·4 per cent.; NH_4^+ 1·4 per cent.; the true dissociation constant of NH_4OH is 4×10^{-5}, about twice the apparent.*

Moore and Winmill found the alkylamines (primary, secondary, and tertiary) to be rather stronger bases than ammonia, but the highest values they got for the true dissociation constants were of the order of 10^{-3}, while the quaternary bases such as $(CH_3)_4NOH$ are strong bases, with dissociation 'constants' of the order of 10. It was formerly thought that the relative weakness of ammonia and the amines was due to their undissociated portions being nearly all in the tertiary NR_3 form, and scarcely any in the form of NR_3HOH, which was imagined to be a strong base. But we now see that this is not so. Ammonia and the amines are truly weak bases so long as there is at least one hydrogen atom attached to the nitrogen, as in $(CH_3)_3NHOH$; but as soon as this last hydrogen is replaced, as in $(CH_3)_4NOH$, the basicity increases ten thousand fold, and they become strong electrolytes. Hence the $[Alk_3NH]^+$ ion must be capable of forming a covalent compound (in some sense) with the hydroxyl ion. in a way which is impossible for the $[Alk_4N]^+$, that is, through its hydrogen atom. This was clearly expressed by Moore and Winmill,[26] in what is probably the first suggestion of the hydrogen bond; the structure was put by Latimer and Rodebush in 1920[28] in the electronic form $R_3N\!:\!H\!:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\!:\!H$, which must be modified in accordance with our present view of the hydrogen bond (I. 23).

Ammonium Salts

These are in general very similar to the salts of the alkali metals, and in particular to those of rubidium, which have nearly the same molecular volumes; according to Tutton the values for the sulphates X_2SO_4 are K_2 65·3; Rb_2 73·8; $(NH_4)_2$ 74·6; Cs_2 85·2 c.c. They are often isomorphous with the corresponding potassium and rubidium salts; almost all are very soluble in water, though the bitartrate, like its potassium analogue, is relatively insoluble. They further resemble the potassium rubidium and caesium salts in being nearly always anhydrous; when they are hydrated (e.g. the carbonate, oxalate, iodate, periodate) the potassium salts are almost always hydrated too,[29] so that the water is probably attached to the anion.

The ammonium halides have interesting peculiarities. The solid chloride, bromide, and iodide are obvious salts $[NH_4]X$. They are dimorphic, having the CsCl (8:1) lattice at low temperatures (below 184·3°, 137·8°,

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* The E.M.F. measurements of Everett and Wynne-Jones,[27] which give the thermodynamic dissociation constant, confirm in general the results of Moore and Winmill.

[27] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* 1938, **169**, 190.

[28] W. M. Latimer and W. H. Rodebush, *J.A.C.S.* 1920, **42**, 1419.

[29] See *E.T.V.*, p. 194.

and —17·6° respectively[30]) and the NaCl (6:1) at high, which is evidence of their ionic structure. The fluoride, however, has quite a different structure[31] of a wurtzite type, each N being surrounded tetrahedrally by 4F atoms at 2·66 A, and each F by 4 N's, the atoms being joined by a hydrogen bond. The H···F distance (1·66 A) being so much greater than the covalent H—F (0·94), the N—H···F bond must be due to resonance between N—H F^- and $\overset{-}{N}\ \overset{+}{H}\ \overset{-}{F}$,[32] with corresponding resonance formulae for the other 3 N neighbours of each F. The difference of the fluoride from the other halides is also shown by the much greater ease with which ammonium fluoride volatilizes, being thereby converted into ammonia and hydrogen fluoride.

The volatilization of ammonium chloride, and especially the effect of traces of moisture upon it, have been the subject of much discussion. Baker[33] stated that when it is perfectly dry, ammonia does not combine with hydrogen chloride, and ammonium chloride volatilizes as such, instead of dissociating into NH_3+HCl, as it does when moist. The vapour pressure of undried ammonium chloride is 1 atm. at 340°, and the amount of undissociated NH_4Cl in the vapour is too small to detect. Hence the concentration of NH_4Cl vapour in contact with moist solid salt at 340° must be very small. But Abegg and Johnson[34-5] showed that the vapour pressure of dry NH_4Cl, in which they claimed that there was no dissociation, was the same as that of the undried salt. These conclusions are self-contradictory. The true explanation was given by Rodebush,[36] who showed that the vapour of ammonium chloride is always completely dissociated into NH_3+HCl whether it is wet or dry, but that the dry solid is extremely slow to evaporate, and only reaches equilibrium with its vapour after a considerable time.* Hence in an apparatus of the Victor Meyer type it is easy to think that the evaporation is complete when there really is solid left, and so to get an excessive value of the vapour density, suggesting that there is no dissociation.

Hence in the solid we have only the salt $[NH_4]Cl$ and in the vapour only the mixed gases NH_3+HCl. The interconversion of solid and vapour is not a mere sublimation, but rather a chemical reaction, as is shown by the enormous value of the Trouton constant. The heat of sublimation (i.e. from NH_4Cl_{solid} to $NH_{3\,gas}+HCl_{gas}$) was found by Smits[38] to be 39·6 k.cals.

* In the same way if the two completely dry gases are mixed, the formation of the solid salt is very slow (see Hinshelwood and Burk).[37]

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[30] Wells, *S.I.C.* 258.

[31] W. H. Zachariasen, *Z. physikal. Chem.* 1927, **127**, 218.

[32] L. Pauling, *Chem. Bond.* ed. 2, 288.

[33] H. B. Baker, *J.C.S.* 1898, **73**, 422.

[34] R. Abegg, *Z. physikal. Chem.* 1908, **61**, 455.

[35] F. M. G. Johnson, ib. 457.

[36] W. H. Rodebush and J. C. Michalek, *J.A.C.S.* 1929, **51**, 748.

[37] C. N. Hinshelwood and R. E. Burk, *J.C.S.* 1925, **127**, 1105.

[38] A. Smits and W. de Lange, ib. 1928, 2944.

at 339·3°, and by Stephenson[39] to be 42·2 k.cals. at 25°. If we take the first value, and allow 4 k.cals. for the imaginary heat of fusion, the Trouton constant

$$= \frac{35{,}000}{612{\cdot}5} = 58{\cdot}1.$$

Ammonium nitrate NH_4NO_3 is interesting from its large number of polymorphic forms, which have these transition points[40]:

$$\mathrm{V} \underset{-18^\circ}{\rightleftharpoons} \mathrm{IV} \underset{+\,32{\cdot}5^\circ}{\rightleftharpoons} \mathrm{III} \underset{84{\cdot}2^\circ}{\rightleftharpoons} \mathrm{II} \underset{125^\circ}{\rightleftharpoons} \mathrm{I} \underset{169{\cdot}5^\circ}{\rightleftharpoons} \text{Liquid}$$

The crystal is of course formed of NH_4 and NO_3 ions, the former tetrahedral, the latter planar and capable of rotation in three orthogonal directions.[40] In the cubic form I all four kinds of rotation were shown to be occurring. As the temperature falls these four will obviously be quenched in succession.

Rotation of the NH_4 ions may well account for the dimorphism which is so common among ammonium salts (chloride, bromide, iodide, nitrate, sulphate, arsenite, bichromate, dihydrogen-phosphate). For further discussion of this question of ionic rotation in crystals see Beck[41]; the theory, originally suggested by Pauling,[42] is consistent with observations of the specific heats,[43-5] dielectric constants,[46-8] coefficients of expansion,[52] crystal structures,[49-51, 51a] and Raman spectra.

Metallic Amides

These are formed especially by the alkalies and the Group II metals (including zinc), by heating the metal or its hydride in ammonia; many of them can be made by the action of potassamide KNH_2 on a salt of the metal in liquid ammonia.[53] They are high-melting solids (one of the lowest melting-points is that of sodamide $NaNH_2$, 210°) which have all the characters of salts, and behave in liquid ammonia exactly like metallic hydroxides

[39] C. C. Stephenson, *J. Chem. Phys.* 1944, **12**, 318.

[40] S. B. Hendricks, E. Posnjak, and F. C. Kracek, *J.A.C.S.* 1932, **54**, 2766.

[41] C. Beck, *J. Chem. Phys.* 1944, **12**, 71.

[42] L. Pauling, *Phys. Rev.* 1930, **36**, 430.

[43] F. Simon, *Ann. d. Phys.* 1922, **68**, 241.

[44] F. Simon and R. Bergmann, *Z. physikal. Chem.* 1930, B **8**, 255.

[45] F. Simon, C. Simpson, and M. Ruhemann, ib. 1927, **129**, 339.

[46] J. H. Bruce, *Trans. Far. Soc.* 1939, **35**, 706.

[47] R. Guillien, *C.R.* 1939, **208**, 1561.

[48] G. P. Smyth, *Chem. Rev.* 1936, **19**, 329.

[49] G. Bartlett and I. Langmuir, *J.A.C.S.* 1921, **43**, 84.

[50] A. Hettich, *Z. physikal. Chem.* 1934, **168**, 353.

[51] R. W. G. Wyckoff, *Am. J. Sci.* 1922, **4**, 469.

[51a] T. H. Goodwin and J. Whetstone, *J.C.S.* 1947, 1455.

[52] A. Smits and C. H. MacGillavry, *Z. physikal. Chem.* 1933, **166**, 97.

[53] E. C. Franklin, *Z. anorg. Chem.* 1905, **46**, 1.

in water; they are clearly ionized compounds, such as $Na[NH_2]$, $Ca[NH_2]_2$, with the very unstable anion $[NH_2]^-$, which at once reacts with water to give $NH_3+[OH]^-$.

*Binary Nitrides**

The inorganic azides, such as NaN_3, are dealt with under hydrazoic acid (below, p. 716), and will not be further considered here. The other binary nitrides resemble the binary carbides (IV. 519) in many ways, and like them can be divided into (I) salt-like, (II) covalent, and (III) interstitial compounds. The position is, however by no means simple, and there is some doubt about the nature of the forces holding the nitrogen in (III), and the structure of the ions in (I).

I. *Ionic nitrides.* Compounds assigned to this class are formed by elements of Group I (M_3N) and Group II (M_3N_2). In Group I the only nitrides yet obtained in the pure state are Li_3N and Cu_3N; they are transparent but coloured; Li_3N (I. 84) is ruby-red, Na_3N (impure) is orange when cold and red when hot, Cu_3N (I. 116) is dark green, the alkaline nitrides are at once hydrolysed by water to ammonia and the hydroxides; cuprous nitride is only hydrolysed by acids. The structure of the lithium compound is peculiar (I. 85), and suggests that it may be Li [Li—N—Li]. Cu_3N may well be covalent.

In Group II, nitrides of the type M_3N_2 are formed by all the elements.† Except for the mercury compound Hg_3N_2, which is coloured and explosive (II. 317) and may well be covalent, they are all colourless and readily hydrolysed (the Zn and Cd compounds less so) but are stable up to high temperatures and have high melting-points (from Be_3N_2, 2,200° to Ba_3N_2 1,000°). If these compounds are fully ionized they must contain the N^{---} ion, which is not known outside the nitrides, and is the only trivalent monatomic anion for which there is any evidence.

II. *Covalent nitrides.* The simple volatile nitrides of hydrogen, carbon, oxygen, fluorine, and chlorine need not be further discussed here. Giant molecules are formed by the nitrides of the typical and B elements of Group III, BN (III. 380) being of the graphite type and AlN (III. 418) and GaN and InN (III. 466) wurtzite.

The nitrides of Group IV (Si_3N_4, Ge_3N_4, Sn_3N_4, Th_3N_4), to which may be added P_3N_5 and S_4N_4,‡ are probably covalent, but their structures are not quite clear. Cu_3N and Hg_3N_2 may also belong to this class.

III. *Interstitial or metallic nitrides.* These include the MN nitrides of the transitional metals of Groups III A, IV A, and V A, where M = Sc, La, Ce, Pr; Ti, Zr; V, Nb, Ta,§ all of which have the sodium chloride structures; like the corresponding carbides they are very hard and have high melting-points; for example (hardness on Moh's scale):

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* See A. F. Wells, *S.I.C.*, p. 425.

† References: Be II. 201; Mg 234; Ca, Sr, Ba 247; Zn, Cd 268.

‡ References: Si_3N_4, Ge_3N_4 IV. 498; Th_3N_4 IV. 634; P_3N_5 V. 733; S_4N_4 VI. 892.

§ References Sc, La, Pr Wells, p. 427; Ti, Zr IV. 634; V, V. 807; Nb 836; Ta 845.

Compound	*M.pt. °C.*	*M.pt. metal*	*Hardness*
TiN	2,947°	2,073°	8-9
ZrN	2,982°	1,857°	8
VN	2,300°	1,715°	. .
NbN	2,300°	1,950°	. .
TaN	3,087°	3,027°	. .

As we have seen (IV. 634), the occurrence of such stable compounds of trivalent elements in Group V A is remarkable, especially with zirconium, which is otherwise so unstable in the trivalent state; that the metal in these nitrides is trivalent is supported by the fact that thorium, which practically never is trivalent, does not form a nitride of this type but another (Th_3N_4). These peculiar valency relations may be compared with those shown by the acetylides of the rare earth metals MC_2 (IV. 519).

Other obscure nitrides, probably covalent or metallic are: Cr_3N (VI. 1002), MoN (1032), U_3N_4 (1071), Mn_3N_2, MnN_2 (VIII. 1266); Fe_2N, Fe_4N (VIII. 1325), Ni_3N (VIII. 1428).

Nitrogen and Carbon

Compounds with the C—N link are dealt with in treatises on organic chemistry, and only a few of their more general properties can be discussed here. The main classes are (1) ammonia derivatives (amines and amides), (2) cyanogen derivatives, (3) oxy-derivatives, especially the nitroso- and nitro-compounds. These last are discussed later among the N—O compounds.

Amines

These compounds, in which one or more of the hydrogen atoms of ammonia or the ammonium ion are replaced by alkyl or aryl groups, are chiefly prepared (1) by treating alkyl halides with ammonia, (2) by the hydrolysis of certain cyanogen derivatives—isonitriles, cyanates, etc., (3) by the reduction of oxy-compounds, especially the nitro-, but also cyanides and oximes.

The following are some boiling- and melting-points:

Amines: B.pts. and [M.pts.]

R	NH_2R	NHR_2	NR_3
CH_3 . .	—6·3° [—93·5]	+6·9° [—91·1]	+2·8°[a] [—117·1°][a]
C_2H_5 . .	+16·6° [—80·6°]	54° [—39°]	89° [—114·8°]
C_3H_7 . .	+48° . .	110° [—63°]	156·5° . .
n.pr.$C_{13}H_{27}$	265° [+27°]	. .	. .
Phenyl .	184·4° [—6°]	302° [54°]	365° [126°]

a = ref. [64],

The alkylamines have rather larger dissociation constants, both true[25-6] and apparent, than ammonia, though the increase is somewhat irregular. In their apparent dissociation constants (the true are not known) the arylamines are much weaker than ammonia (NH_3 2×10^{-5}, CH_3NH_2 47×10^{-5}, $C_6H_5NH_2$ $1{\cdot}26\times10^{-10}$); diphenylamine forms salts only with strong acids, and these are hydrolysed by water; triphenylamine forms no salts at all except a very unstable perchlorate. How far this is due to a fall in the true K and how far to a fall in the hydration is not known.

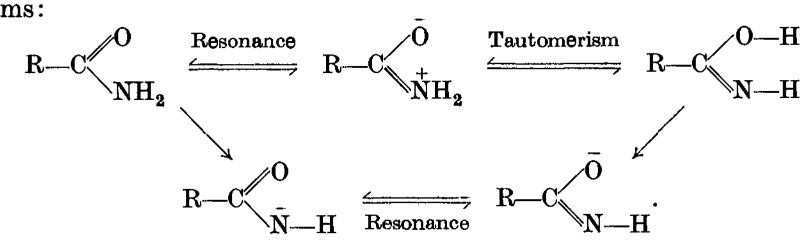
The crystal structure of $CH_3{\cdot}NH_3Cl$ has been determined[55]; the C—N distance is 1·47±00·3 A (a list of values of C—N in other compounds is given; 'theory' 1·47).

The replacement of hydrogen in ammonia by alkyl groups weakens the tendency to form ammines; aryl groups seem to have a stronger effect. The tendency to co-ordination increases with the basic dissociation constant of the amine in each (primary, secondary) class.[53a]

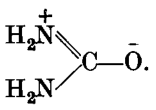
An interesting derivative is the trifluorodimethyl amine $(F_3C)_2NH$[56] made from iodine pentafluoride and cyanogen iodide (along with the azo-compounds $F_3C{\cdot}N{=}N{\cdot}CF_3$: p. 711); b.pt. −6·2°, m.pt. −130°; Trouton 21·4. It has an unpleasant smell, is easily hydrolysed, but does not attack dry glass or mercury; this last fact shows that it has no N—F group.

Organic Amides

These are sharply distinguished from the amines, as the esters are from the ethers, by their easy hydrolysis. This is no doubt due to the resonance. Amides can have two resonance forms, in addition to the tautomeric OH form; these all give the same monovalent ion, which itself has two resonance forms:



With urea the dimensions in the crystal,[57-8] and especially the value for the C—N link of 1·33 A (normally C—N is 1·47 and C═N 1·28) indicate that in the solid state it is almost entirely in the zwitterion form



[53a] R. J. Bruehlman and F. J. Verhoek, *J.A.C.S.* 1948, **70**, 1401.

[54] J. G. Aston, M. L. Sagenkahn, G. J. Szasz, G. W. Moessen, and H. F. Zuhr, ib. 1944, **66**, 1171.

[55] E. W. Hughes and W. N. Lipscomb, ib. 1946, **68**, 1970.

[56] O. Ruff and W. Willenberg, *Ber.* 1940, **73**, 724.

Amides always have higher boiling-points than their acids:

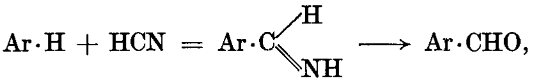
	R=H	CH_3	C_2H_5	C_6H_5
B. pt. $R\cdot CONH_2$.	194°	223°	213°	288°
$R\cdot COOH$.	101°	118°	140°	250°
Diff. . .	93°	105°	73°	38°

Imides and Imines

These compounds, containing the C=N link, offer a curious problem. The heats of formation of the links of nitrogen to carbon increase quite regularly:

	C—N	C=N	C≡N *in* HCN	C≡N *in Nitriles*
Absolute	69·3	135	206	212 k.cals.
Relative	1	1·95	2·97	3·06

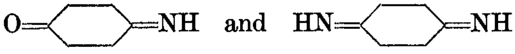
But the organic evidence shows that the double C=N link is as a rule far less stable than the single or the triple. Imides proper $R\cdot C{\langle}^{OH}_{NH}$ (cyclic imides like phthalimide are of course of a different type) are scarcely known except as possible tautomeric forms of amides; their alkyl derivatives, the imino-ethers $R\cdot C{\langle}^{O\cdot R}_{N\cdot R}$, change easily and irreversibly into the disubstituted amides $R\cdot C{\langle}^{O}_{NR_2}$. Imines of the type $^{C}_{C}{\rangle}C{=}N\cdot H$ rarely occur and are always unstable, being hydrolysed with great ease, in sharp contrast to the amines; thus $\Phi_2C{=}N\cdot H$ (made by the action of ammonia on benzophenone in alcohol) is split by cold hydrochloric acid at once to the ketone $+NH_4Cl$. Again, imines are undoubtedly intermediate products in the Gattermann synthesis of aldehydes from aromatic hydrocarbons + hydrogen cyanide in presence of $AlCl_3$:



$$Ar\cdot H + HCN = Ar\cdot C{\langle}^{H}_{NH} \longrightarrow Ar\cdot CHO,$$

but they are at once hydrolysed to the aldehydes.[59]

The quinone-imines



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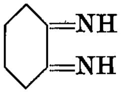
[57] R. W. G. Wyckoff, *Z. Krist.* 1932, **81**, 102.

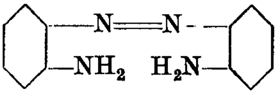
[58] R. W. G. Wyckoff and R. B. Corey, ib. 1934, **89**, 462.

[59] For the mechanism of this reaction see (*a*) L. E. Hinkel, E. E. Ayling, and W. H. Morgan, *J.C.S.* 1932, 2793; (*b*) Hinkel, Ayling, and J. H. Beynon, ib. 1936, 184; (*c*) id., ib. 339.

are similarly unstable, and the ortho-di-imine



polymerizes as soon as it is formed to ortho-azo-aniline.

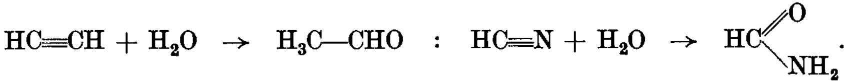


This instability of the C=N compounds may be largely due to a small heat of activation, especially in comparison with the nitriles; but the irreversibility of the change of the imino-ethers shows that it is partly at least a thermodynamic effect. No explanation of it has yet been offered.

Cyanogen Compounds

The further dehydration of an amide gives a nitrile, one of the large group of cyanide derivatives. This includes cyanogen $N\equiv C—C\equiv N$; hydrogen cyanide $H—C\equiv N$ with its salts, simple and complex, and its two series of esters, the nitriles $R\cdot C\equiv N$ and the carbylamines $R\cdot \overset{+}{N}\equiv \overset{-}{C}$; the cyanogen halides, as $CN\cdot Cl$; cyanic acid HOCN and thiocyanic HSCN and their normal and iso-derivatives; and the cyanurates $R_3C_3N_3$.

The analogy between the $C\equiv N$ and the $C\equiv C$ compounds—between HCN and acetylene, and between the nitriles and the alkyl-acetylenes—is obvious.[60] In both series the hydrogen attached to the triply linked carbon is to some extent acidic, though acetylene ($K = 10^{-14}$) is far weaker than hydrogen cyanide ($K = 10^{-9}$). They both have a strong tendency to form addition compounds, either with themselves by polymerization—acetylene giving the trimer benzene as cyanogen chloride gives the trimer cyanuric chloride—or with other molecules such as water, which converts acetylene into acetaldehyde, and a nitrile into an amide:



$$HC\equiv CH + H_2O \rightarrow H_3C—CHO \;:\; HC\equiv N + H_2O \rightarrow HC\begin{smallmatrix}\nearrow O\\ \searrow NH_2\end{smallmatrix}.$$

Cyanogen $(CN)_2$

Cyanogen $N\equiv C—C\equiv N$ is an endothermic compound with a heat of formation H_f of -71 k.cals.* Hence H_a the heat of formation from the atoms is 495 k.cals.,[75] which gives for the $C\equiv N$ group 207, agreeing with the value 206 got from HCN. It melts at $-27{\cdot}8°$ and boils at $-21{\cdot}1$: the Trouton constant is $22{\cdot}1$.[63-4] Its hydrolysis to oxamide shows that the two carbon atoms are united. The molecule $N\equiv C—C\equiv N$ must be linear,

* This is Bichowski and Rossini's mean value.[61-2]

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[60] See G. Bähr, *Z. physikal. Chem.* 1934, **168**, 363.

[61] H. v. Wartenberg and H. Schütza, *Z. physikal. Chem.* 1933, **164**, 386.

[62] J. McMorris and R. M. Badger, *J.A.C.S.* 1933, **55**, 1952.

[63] J. H. Perry and D. C. Bardwell, ib. 1925, **47**, 2629.

[64] R. A. Ruehrwein and W. F. Giauque, *J.A.C.S.* 1939, **61**, 2940.

and this agrees with its having a dipole moment of zero,[65-6] and with the results of electron diffraction. This last shows[67] the distances to be N—C 1·16 (theory for the triple link 1·15) and C—C 1·37 (theory 1·54: in benzene 1·39), indicating very considerable resonance with a C═C form; the structure closely resembles that of diacetylene H—C≡C—C≡C—H, for which the distances have been shown[67] to be C≡C 1·21 (theory 1·20) and C—C 1·43.

The stability of cyanogen to heat is remarkable, especially for an endothermic substance. It is not affected below about 1,000°; from there to 1,500° it is partly broken up into CN radicals[68]: the heat absorbed in this dissociation is 77±4 k.cals.[69-71] (the normal value for C—C is 82 k.cals.). The CN radicals so produced are even more stable to heat, and dissociate into their elements only at a much higher temperature. Their presence has been detected spectroscopically in many stellar spectra,[72-4] and they are indeed the first compound molecules to be thus detected as the temperature of the stellar atmosphere falls.

*Hydrogen Cyanide**

Hydrogen cyanide boils at +25·6° and melts at −13·4°; the Trouton constant is 20·17[77] (Giauque 1939; Bredig[78] gave 22·6 and Perry[79] 22·4). It has a very high dielectric constant, especially at low temperatures[80] (194·4 at −13° and 116 at 20°, where the D.E.C. of water is 80·3: the former is the highest value of this constant hitherto found for any substance). Accordingly it has a high dipole moment, 2·6 D in benzene solution[81] and 2·93 D in the vapour.[82]† The state of association of HCN is

* According to Briner[76] this can be made (up to 120 g. per watt-hour) by the action of a carbon arc on a mixture of nitrogen gas with the paraffins from CH_4 upwards.

† This last value of Smyth's is much higher than those previously given for the vapour, but it seems to have been determined with exceptional care. It is confirmed by Watson and Ramaswamy,[83] who found 3·03.

[65] H. Braune and T. Asche, *Z. physikal. Chem.* 1931, B **14**, 18.
[66] H. E. Watson and K. L. Ramaswamy, *Proc. Roy. Soc.* 1936, **156**, 130.
[67] L. Pauling, H. D. Springall, and K. J. Palmer, *J.A.C.S.* 1939, **61**, 933.
[68] J. U. White, *J. Chem. Phys.* 1940, **8**, 459.
[69] G. B. Kistiakowsky and H. Gershinowitz, ib. 1931, **1**, 432.
[70] Id., ib. 885. [71] But see H. D. Springall, *Trans. Far. Soc.* 1947, **43**, 177.
[72] P. Swings and O. Struve, *Phys. Rev.* 1932, ii. **39**, 142.
[73] N. Morguleff, *C.R.* 1938, **207**, 967.
[74] D. Hoffleit, *Astrophys. J.* 1939, **90**, 621 (*B.C.A.* 1940, i. 144).
[75] H. D. Springall, *Trans. Far. Soc.* 1947, **43**, 177.
[76] E. Briner and H. Hoefer, *Helv. Chem. Acta,* 1940, **23**, 1054.
[77] W. F. Giauque and R. A. Ruehrwein, *J.A.C.S.* 1939, **61**, 2626.
[78] G. Bredig and L. Teichmann, *Z. Elektr.* 1925, **31**, 449.
[79] J. H. Perry and F. Porter, *J.A.C.S.* 1926, **48**, 299.
[80] K. Fredenhagen and J. Dahmlos, *Z. anorg. Chem.* 1929, **179**, 77.
[81] O. Werner, *Z. physikal. Chem.* 1929, B **4**, 371.
[82] C. P. Smyth and K. B. McAlpine, *J.A.C.S.* 1934, **56**, 1697.
[83] H. E. Watson and K. L. Ramaswamy, *Proc. Roy. Soc.* 1936, **156**, 130.

obscure. At the boiling-point and 1 atm. the association in the vapour seems to be about 18 per cent.[77,84-5] The very low value of the Trouton constant given by Giauque's results suggests that the molecular weight is much the same in the liquid as in the gas, and that the relatively high boiling-point (25·6°: compare C_2H_6 −93°; CH_3F −78° [mol. wts. HCN 27; C_2H_6 30; CH_3F 34]; $CH_3\cdot O\cdot N{=}O$ −12°; CH_3NO_2 101°) is largely due to dipole attraction. In the solid state—whether through hydrogen bondage or dipole attraction—the positions of the molecules are fixed, and they do not rotate even at the melting-point of −13°[86-7] (arsine molecules rotate above −250°, H_2Se, HCl, and HBr above −170°).

Hydrogen cyanide is a typical example of an inseparable tautomeric substance. Through its salts it gives rise to two isomeric series of esters, the nitriles $R\cdot C{\equiv}N$ and the isonitriles or carbylamines $R\cdot\overset{+}{N}{\equiv}\overset{-}{C}$. Itself it is only known in one form, and all efforts to separate it into two—even by 'aseptic' distillation[92]—have failed.* At the same time it cannot be a resonance hybrid since the position of the hydrogen is different in the two formulae. On thermal grounds we should expect the HCN form to be the more stable; according to Pauling H_a for —C≡N in the nitriles is 212 k.cals., while for —N≡C (below, p. 678) it is 207; this would give 311 k.cals. for HCN and 300 for HNC; the observed value[94] for hydrogen cyanide is 304 k.cals.

The spectra of hydrogen cyanide are much more like those of nitriles than those of isonitriles (see, for example, ref. [95]). Dadieu[96] ascribed the weak Raman line at 2,062 cm.$^{-1}$ (accompanying the line 200 times as strong at 2,092) to the presence of 0·5 per cent. of HNC, but it was pointed out by Herzberg[97] that the isotopic $HC^{13}N$, of which about 1 per cent. is present, must give a line at this place, so that Dadieu's results really only show that the amount of the $H{-}\overset{+}{N}{\equiv}\overset{-}{C}$ form is much less than 0·5 per cent.

The ions derived from the two forms are identical:

$$\begin{array}{ccc} : & : & : \\ \text{H:C:N:} & \text{:C:N:} & \text{:C:N:H.} \\ : & : & : \end{array}$$

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* Coates *et al.*[93] have shown that the supposed isomer described by Enklaar, *Rec. Trav.* 1923–5–6, does not exist.

[84] J. R. Partington, *J.C.S.* 1926, 1559.

[85] W. A. Felsing and G. W. Drake, *J.A.C.S.* 1936, **58**, 1714.

[86] C. P. Smyth and C. S. Hitchcock, ib. 1933, **55**, 1830.

[87] C. P. Smyth and S. A. McNeight, ib. 1936, **58**, 1723.

[88] J. E. Coates and N. H. Hartshorne, *J.C.S.* 1931, 657.

[89] J. E. Coates and E. G. Taylor, ib. 1936, 1245.

[90] Id., ib. 1495.

[91] H. P. S. Britton and E. N. Dodd, ib. 1931, 2332.

[92] K. H. Meyer and H. Hopf, *Ber.* 1921, **54**, 1709.

[93] J. E. Coates, L. E. Hinkel, and T. H. Angel, *J.C.S.* 1928, 540.

[94] A. R. Gordon, *J. Chem. Phys.* 1937, **5**, 30.

[95] T. M. Lowry and S. T. Henderson, *Proc. Roy. Soc.* 1932, **136**, 471.

[96] A. Dadieu, *Naturwiss.* 1930, **18**, 895.

[97] G. Herzberg, *J. Chem. Phys.* 1940, **8**, 847.

Arguments about the structure of true salts of prussic acid are therefore futile. We have seen that one covalent metallic derivative, silver cyanide, actually has both forms at once in the solid state, being formed of strings of atoms $-\mathrm{Ag}-\mathrm{C}\equiv\mathrm{N}-\mathrm{Ag}-\mathrm{C}\equiv\mathrm{N}-\mathrm{Ag}-\mathrm{C}\equiv\mathrm{N}-\mathrm{Ag}-\mathrm{C}\equiv\mathrm{N}-$.

Hydrogen cyanide, as we should expect from its high dielectric constant, is a fairly good solvent for salts, many of which behave in it as strong electrolytes[89]; the ionic mobilities are very nearly 5 times as great as in water, which is the ratio of the fluidities of the two solvents.[80] The cryoscopic constant is found experimentally to be[98] 1·786/1000 g.; the melting-point and heat of fusion give 1·805. Freezing-points show that dichloracetic acid, sulphuric acid, and sulphur trioxide are not dissociated in the solution, but amines (triethylamine and propylamine) are 20–50 per cent. ionized.[98] Ammonium salts behave as strong electrolytes, but tetra-alkyl ammonium salts show large negative deficiencies,[90] suggesting polymerization such as these salts exhibit in solvents like chloroform. For details of chemical reactions in liquid hydrogen cyanide see Jander and Scholtz.[98]

Hydrogen cyanide is miscible with water. At lower temperatures the system (Coates and Hartshorne)[88] is rather like that of salicylic acid and water. There is no solid compound, but a eutectic at $-23{\cdot}4°$ C. and 74·5 mols. per cent. HCN. The ice branch of the curve becomes nearly horizontal at $-16°$ and 35 mols. per cent. HCN; below this curve is a metastable two-liquid area, with a critical solution temperature of about $-24°$ and 35 mols. per cent. With ether HCN forms a 1:1 compound of small stability, m.pt. $-87°$.[99]

In water hydrogen cyanide is a very weak acid, with a dissociation constant of $4{\cdot}9 \times 10^{-10}$ [91] (less than 0·001 per cent. ionized in decinormal solution). It is slowly hydrolysed to ammonia and formic acid (for the kinetics of this hydrolysis see ref. [100]).

Hydrogen cyanide is remarkable for the large number of complex salts that it forms. This is no doubt partly due, as it is with the nitrites, to the weakness of the acid, which implies a strong tendency of the ion to go over into the covalent state. With both prussic and nitrous acids one particular size of complex tends to prevail with any given central atom, often to the exclusion of others; thus we have the tetra-cyanide ions $\mathrm{A(CN)_4}$ formed by Ni'', Pd'', and Pt''; the hexacyanide ions $\mathrm{A(CN)_6}$ by Mn'', Mn''', Fe'', Fe''', Co'', Co''', $\mathrm{Os}^{\mathrm{vi}}$, $\mathrm{Rh}^{\mathrm{iv}}$, $\mathrm{Ir}^{\mathrm{iii}}$, and $\mathrm{Pt}^{\mathrm{iv}}$; and octocyanides—the most remarkable—$\mathrm{A(CN)_8}$ by $\mathrm{Mo}^{\mathrm{iii}}$, $\mathrm{Mo}^{\mathrm{iv}}$, Mo^{v}, and W^{iv}, and W^{v}; more than 30 elements (counting 2 valency states as 2) form complex cyanides, many of quite exceptional stability.

Considering their number and importance it is remarkable that we do not know for certain whether the cyanide radical is attached to the central atom through the carbon as $\mathrm{A}-\mathrm{C}\equiv\mathrm{N}$ or through the nitrogen as

[98] G. Jander and G. Scholtz, *Z. physikal. Chem.* 1943, **192**, 163.

[99] L. Birckenbach and E. Büchner, *Ber.* 1940, **73**, 1163.

[100] V. K. Krieble, F. C. Duennebier, and E. Colton, *J.A.C.S.* 1943, **65**, 1479.

$\mathrm{A{-}\overset{+}{N}{\equiv}\overset{-}{C}}$.[101] Both are clearly possible: alkyl nitriles and alkyl isocyanides both form complexes. The carbon and nitrogen atoms are so near in atomic number that only the most accurate X-ray measurements can distinguish between them. Wherever such accurate measurements have been made (with the argenticyanides, Hoard, 1933[102]; the octacyanides of tetravalent molybdenum, Hoard and Nordsieck, 1939[103]; the ferrocyanides, Powell[104]) the results indicate that the central atom is attached to carbon. With the ferrocyanides this structure is supported by chemical evidence; the products of their methylation which have the compositions $[(CH_3)_6Fe(CN)_6]X_2$ and $(CH_3)_4Fe(CN)_6$ all split off on heating the alkyl isocyanide and not the nitrile, so they must contain the grouping CH_3—N—C—Fe, and the ferrocyanide itself must presumably have N—C—Fe.

Again, divalent platinum forms complex cyanides $M_2[Pt(CN)_4]$, and also addition compounds both with nitriles and with isonitriles, and the complex cyanides resemble in stability the isonitrile much more than the nitrile complexes.

So far all the evidence seems to be in favour of the A—C—N structure. But if we compare the tendency of various acceptors to form complex cyanides with their power of co-ordination in other (non-cyanide) complexes to carbon and nitrogen respectively, the results point rather in the opposite direction. Those elements (especially in Groups VIII and I B) which can co-ordinate with unsaturated hydrocarbons show no peculiar tendency to form complex cyanides, while elements in these groups which can add on the CN ions cannot always add on the hydrocarbons. On the other hand, nearly all the strong cyanide builders (Cu', Ag', Au', Cu'', Fe'', $\mathrm{Co}^{\mathrm{iii}}$, Ni'', Pd'', Pt'', $\mathrm{Pt}^{\mathrm{iv}}$) are atoms which have a strong tendency to form ammines, though even here there are marked exceptions; tetra- and pentavalent molybdenum and tungsten, forming some of the stablest known cyanides, seem to give no ammines. Again the nitro-complexes (which must have the nitrogen attached to the central atom, since the nitrito- are also known) have a considerable resemblance to the complex cyanides.

It is of course possible that some of the complex cyanides are linked through the carbon and the others through the nitrogen, but if so it is curious that their properties have not been found to show any corresponding differences. On the whole we may conclude that the complex cyanides have the carbon attached to the central atom; this is the conclusion from the crystal structure data, and also from the chemical evidence so far as it goes. The comparison with other co-ordination compounds of carbon and nitrogen is no doubt misleading, because the presence of the triple C≡N link must very greatly modify the properties of the donor atom.

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[101] N. V. Sidgwick, *J.C.S.* 1941, 433.

[102] J. L. Hoard, *Z. Krist.* 1933, 84, 231.

[103] J. L. Hoard and H. H. Nordsieck, *J.A.C.S.* 1939, 61, 2853.

[104] H. M. Powell and G. W. R. Bartindale, *J.C.S.* 1945, 799.

Nitriles and Carbylamines

A comparison between these two isomeric series is interesting; the justification for the formulation of the carbylamines as $R—\overset{+}{N}{\equiv}\overset{-}{C}$ has already been given under divalent carbon; the presence of a triple bond is shown by the position of the characteristic Raman line, which is 2,245 cm.$^{-1}$ for the nitrile and 2,180 for the carbylamine.[105]

The nitriles have slightly higher boiling-points than the isomeric carbylamines, which agrees with their rather larger dipole moments:

Boiling-points[106-7]

$CH_3.CN$ 81·6° C.	Et.CN 98°	*n*-Pr·CN 118·5°	*Iso*-Am·CN 155°	C_6H_5·CN 191°
CH_3·NC 59°	Et·NC 79°	*n*-Pr·NC 98°	*Iso*-Am·NC 140°	C_6H_5.NC 166°
Diff. +23°	+19°	+20·5°	+15°	+25°

The mean difference is 20·5°, which for a Trouton constant of 21 means that the heat of evaporation of the nitrile is greater than that of the carbylamine by 0·43 k.cals., or about 5 per cent.

Dipole Moments in Solution[108-11]

Et.CN 3·57	C_6H_5·CN 3·94	CH_3—⬡—CN 4·37	Cl—⬡—CN 2·61
Et·NC 3·47	C_6H_5·NC 3·53	CH_3—⬡—NC 3·35	Cl—⬡—NC 2·07
Diff. 0·10	0·41	1·02	0·54

The larger differences with the aromatic compounds may be ascribed to the resonance of the ring being greater with the —CN than with the —NC group.

The energy-content of the nitriles is smaller than that of their isomers, as is shown by these values of the heats of combustion of the gas:

CH_3·CN 312·1 k.cals.	C_2H_5·CN 471·5 k.cals.
CH_3·NC 325·7 ,,	C_2H_5·NC 487·1 ,,
Diff. —13·6 ,,	—15·6 ,,

Thus the mean difference is about 15 k.cals.; the normal values of the C—C and C—N links are 81·6 and 69·3 respectively, so that the heat of formation of the —C≡N link seems to be only 15—12 = 3 k.cals. greater than that of the $\overset{-}{C}{\equiv}\overset{+}{N}—$ in the isocyanides.

In consequence of this difference of stability the carbylamines will change over into the nitriles: the alkyl carbylamines are completely con-

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[105] K. W. F. Kohlrausch, *Der Smekal-Raman Effekt*, 1931, p. 319.

[106] L. Reichel and O. Strasser, *Ber.* 1931, **64**, 1997.

[107] M. J. Copley, G. F. Zellhoefer, and C. S. Marvel, *J.A.C.S.* 1940, **62**, 227.

[108] E. Bergmann and M. Tschudnowski, *Z. physikal. Chem.* 1932, B **17**, 116.

[109] H. Poltz, O. Steil, and O. Strasser, ib. 155.

[110] E. G. Cowley and J. R. Partington, *J.C.S.* 1935, 604.

[111] R. G. A. New and L. E. Sutton, ib. 1932, 1415.

verted into nitriles by heating to 140–240°[112] and phenyl isocyanide behaves in the same way at 220°.

As to their chemical properties, the nitriles are hydrolysed by both acids and alkalies:

$$\mathrm{R\cdot CN + 2\,H_2O = R\cdot COOH + NH_3.}$$

Carbylamines hydrolyse to the monamine and formic acid:

$$\mathrm{R\cdot NC + 2\,H_2O = R\cdot NH_2 + H\cdot COOH.}$$

But it is remarkable (and so far unexplained) that this last reaction, though it goes rapidly (sometimes even explosively) in presence of acids, is not caused by alkalies, which have no effect. The unstable state of the carbon in the isocyanides is shown by the ease with which it goes over to the normal tetravalent condition, the isocyanides being oxidized to isocyanates $\mathrm{R\cdot N{=}C{=}O}$ and taking up sulphur to form mustard oils $\mathrm{R\cdot N{=}C{=}S}$.

Cyanic Acid

Cyanic acid $\mathrm{H{-}O{-}C{\equiv}N}$ or $\mathrm{H{-}N{=}C{=}O}$ is best made by passing the vapour of its trimer cyanuric acid through a red-hot tube. It is a liquid freezing at $-86\cdot8°$[114] and boiling at $+23\cdot5°$, with a Trouton constant of 23·4.[113] It is very unstable, and even at 0° soon goes over to the solid polymer cyamelide, or at higher temperatures to a mixture of cyamelide and cyanuric acid; in water at 0° it soon hydrolyses to ammonia and carbon dioxide. It is a fairly strong acid, with a dissociation constant at 0°[115] of 12×10^{-5} (acetic $1\cdot8\times10^{-5}$, monochloracetic 155×10^{-5}). It forms very stable salts, the cyanates, and one series of esters, which must have the structure $\mathrm{R\cdot N{=}C{=}O}$ since they are hydrolysed to the amine $\mathrm{R\cdot NH_2{+}CO_2}$; the O-esters $\mathrm{R\cdot O\cdot CN}$ are unknown, though their sulphur analogues, the normal thiocyanic esters, exist.

The free acid gives no indications of being a mixture, and all the evidence supports the iso-structure $\mathrm{H{-}N{=}C{=}O}$. Thus the Raman[116] and ultra-violet[117] spectra of the acid are very like those of its esters (and of the silver and mercuric 'salts'), and quite unlike those of the potassium, tetramethyl ammonium, and plumbous salts, which are no doubt ionized, while the silver and mercuric derivatives contain the covalent $\mathrm{Ag{-}N}$ and $\mathrm{N{-}Hg{-}N}$ links.

Eyster, Gillette, and Brockway[118] find by electron diffraction that the $\mathrm{N{-}C{-}O}$ group is linear both in cyanic acid and in methyl isocyanate, the $\mathrm{N{-}C}$ and $\mathrm{C{-}O}$ distances being $1\cdot19\pm0\cdot02$ in both (calculated $\mathrm{N{=}C}$ 1·26, $\mathrm{N{\equiv}C}$ 1·15; $\mathrm{C{=}O}$ 1·21, $\mathrm{C{\equiv}O}$ 1·10); this shows that the acid has (at least

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[112] H. Guillemard, *C-R.* 1907, **144**, 141.

[113] M. Linhard, *Z. anorg. Chem.* 1938, **236**, 200.

[114] Id., ib. 1938, **239**, 155.

[115] R. Naumann, *Z. Elektr.* 1910, **16**, 770.

[116] J. Goubeau, *Ber.* 1935, **68**, 912.

[117] S. C. Woo and T. K. Liu, *J. Chem. Phys.* 1935, **3**, 544.

[118] E. H. Eyster, R. H. Gillette, and L. O. Brockway, *J.A.C.S.* 1940, **62**, 3236.

mainly) the imide structure, and also that there is much resonance in the molecule.

The salts of cyanic acid, the cyanates, are of exceptional stability, especially those of the alkali metals. They can be made by oxidizing the cyanides (or the ferrocyanides) with lead oxide or dioxide, manganese dioxide, or dichromate, at temperatures little below a red heat; the use of potassium cyanide for inorganic reductions depends on this reaction. They do not decompose in the dry state below redness, but in water or even aqueous alcohol they are rapidly hydrolysed to carbonate and ammonia.

The cyanate ion, presumably a resonance hybrid of $\bar{N}{=}C{=}O$ and $N{\equiv}C{-}\bar{O}$, is isoelectronic with the azide ion $\bar{N}{=}\overset{+}{N}{=}\bar{N}$, and like the latter is found[119] to be linear. The alkaline cyanates resemble the alkaline azides closely in density, refractivity, solubility, and in conductivity in alcohols, etc.[120]

Cyanic Esters, $R\cdot N{=}C{=}O$

Only this class of esters has been isolated. The O-esters may well be the primary products of the action of Na·O·Alk on cyanogen halides, but the actual product is the trimer alkyl cyanurate (an O-ester). The isocyanates can be made by distilling the metallic cyanates with alkyl hydrogen sulphate (Wurtz, 1854) and in other ways. They are volatile liquids (b.pts. CH_3 44°; Et 60°; phenyl 166°), readily hydrolysed by alkali to primary amine $+CO_2$, and converted by ammonia or amines to alkylureas.

Thiocyanogen and the Thiocyanic Compounds

Thiocyanogen $(CNS)_2$

Thiocyanogen ('Rhodan') is best made by the action of bromine in ether on lead thiocyanate, or by oxidizing thiocyanic acid with lead tetraacetate[121]; it is a fairly volatile liquid which melts about -3[122]; it is monomeric in bromoform by the freezing-point.[123] At the ordinary temperature it very soon polymerizes in various ways; in water it is rapidly hydrolysed to thiocyanic acid, H_2SO_4, and HCN.

Its chemical behaviour is very like that of a halogen; it forms thiocyanates with many metals, and reacts with aniline just like bromine:

$$(SCN)_2 + \Phi\cdot NH_2 = HSCN + H_2N\cdot C_6H_4\cdot SCN.$$

The structure of thiocyanogen is almost certainly $N{\equiv}C{-}S{-}S{-}C{\equiv}N$ (with resonance forms); thus with cold concentrated hydrochloric acid it

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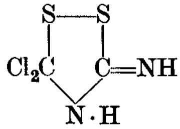
[119] S. B. Hendricks and L. Pauling, ib. 1925, **47**, 2904.
[120] J. A. Cranston and A. Y. Livingstone, *J.C.S.* 1926, 501.
[121] H. P. Kaufmann and F. Kögler, *Ber.* 1925, **58**, 1553.
[122] H. Kerstein and R. Hoffmann, ib. 1924, **57**, 491.
[123] H. Lecher and A. Goebel, ib. 1921, **54**, 2223.

gives the 'dihydro-chloride', a dichlorimino-dithiazolidine of the structure given here,[124] and other reactions support this.



The selenium analogue can also be made.[125] The oxy-analogue $(CNO)_2$ may exist in solution, but it has never been isolated.[126]

Thiocyanic Acid and its Salts

Thiocyanates are readily formed from cyanides by the addition of sulphur, as are cyanates by that of oxygen.

Thiocyanic acid HSCN is best made by the action of potassium hydrogen sulphate on potassium thiocyanate[127]; its properties have been re-examined lately by Birckenbach[128]; it is a gas at the ordinary temperature, and can be condensed in liquid air to a white enamel-like solid which melts at −110°, but if heated above −90° polymerizes, and at −55° changes further. The molecular weights of these polymers could not be determined: they evolve the (monomeric) HCNS gas at any temperature slowly. It is quickly hydrolysed in water, especially in presence of acids.

It behaves as a tautomeric mixture of two forms, giving indistinguishable (resonance hybrid) ions:

$$\mathrm{H{-}S{-}C{\equiv}N} \longrightarrow \bar{\mathrm{S}}\mathrm{{-}C{\equiv}N} \text{ or } \mathrm{S{=}C{=}}\bar{\mathrm{N}} \longleftarrow \mathrm{S{=}C{=}N{-}H}.$$

The comparison of its Raman spectrum with those of the isothiocyanic esters (mustard oils) indicates[129] that in carbon tetrachloride solution the acid is wholly $\mathrm{H{-}N{=}C{=}S}$, but that in ether (where no doubt it is present as the ionized oxonium salt) there is a hybrid of the two resonance forms of the ion. In water it is a strong acid.[130]

The ion like the cyanate and azide ions is linear, and[131] seems to be $\bar{\mathrm{S}}\mathrm{{-}C{\equiv}N}$ rather than $\mathrm{S{=}C{=}}\bar{\mathrm{N}}$, since the Raman spectrum shows a line assignable to the triple link, but none for the double C=S link.[132]

The conductivities[133] of very dilute solutions ($V = 500$ to 10,000) of the salts in methyl alcohol show that in this solvent the alkaline thiocyanates behave as strong electrolytes; with salts of the metals of Group II A there

[124] E. Söderbäck, *Ann.* 1919, **419**, 217.

[125] L. Birckenbach and K. Kellermann, *Ber.* 1925, **58**, 787.

[126] H. Hunt, *J.A.C.S.* 1932, **54**, 907.

[127] U. Rück and H. Steinmetz, *Z. anorg. Chem.* 1912, **77**, 51.

[128] L. Birckenbach and E. Büchner, *Ber.* 1940, **73**, 1153.

[129] J. Goubeau and O. Gott, ib. 127.

[130] M. Gorman and J. Connell, *J.A.C.S.* 1947, **69**, 2063.

[131] M. Strada, *Gaz.* 1934, **64**, 400.

[132] A. Langseth, J. R. Nielsen, and J. U. Sörensen, *Z. physikal. Chem.* 1934, **B 27**, 100.

[133] A. Unmack, D. M. Murray-Rust, and H. Hartley, *Proc. Roy. Soc.* 1930, **127**, 228.

is some association [de-ionization] in the stronger solutions, while the thiocyanates of zinc and cadmium behave as weak electrolytes. The alkaline salts, which have rather low melting-points (KSCN 176·6° C.),[134] are very soluble: 100 g. of water at 25° will dissolve 58·8 of NaCNS and 70·9 of KCNS[135]; 100 g. of ethyl alcohol at 25° will dissolve 20·7 g. of NaSCN.[136] Ferric thiocyanate is famous for its intense red colour, which makes it a delicate test for ferric or thiocyanate ions (see VIII. 1350).

Unlike cyanic acid, thiocyanic gives two series of esters, derived from the two tautomeric forms. The heats of formation of the esters and acids, calculated from the normal heats of their links, are:

	Cyanic		*Thiocyanic*	
	Normal	*Iso*	*Normal*	*Iso*
Esters	*C—O—C≡N^a	O=C=N—C*	*C—S—C≡N^b	S=C=N—C*^{c}
	290 k.cals.	292·6	259	245·6
Acids	H—O—C≡N	O=C=N—H	H—S—C≡N	S=C=N—H
	330	327·7	292	280·7

* Attached carbon of the alkyl. ^{a} Non-existent. ^{b} Unstable. ^{c} Stable.

From these results (which take no account of resonance) it would seem that in the cyanate series the *iso*-forms are slightly more stable, and in fact the only known esters are of this form. In the thiocyanates the normal forms appear to be definitely more stable; as a fact, however, it is the isothiocyanic esters that are the more stable; they are often formed from their isomers on heating; thus methyl thiocynate goes over completely at 180°. The reason must be that the stability of the *iso*-form is increased by resonance.

The structures of these esters are clear from their reactions. The normal thiocyanic esters are reduced to mercaptans +HCN, and are oxidized by nitric acid to alkyl sulphonic acids; the mustard oils are reduced to primary amine and methyl mercaptan:

$$R\cdot N{=}C{=}S + 3\,H_2 = R\cdot NH_2 + CH_3\cdot SH.$$

The following list of boiling-points is taken from Beilstein: compounds marked O/- are not known to exist.

	H—O—C=N	H—N=C=O	H—S—C=N	H—N=C=S	
	O/-	+23·5°	O/.	?	
	R—O—C=N	R—N=C=O	R—S—C=N	R—N=C=S	*Diff.*
R = Me	O/.	43°	131·5°	118·0°	—12·5°
Et	O/-	60°	145°	131°	—14°
n-Pr	O/.	84°	163°	153°	—10°

B. pt. R—NCS—b. pt. R—NCO (75°, 71°, 69°); mean 72°.

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[134] P. Dingemans, *Rec. Trav.* 1939, **58**, 559.

[135] V. J. Occleshaw, *J.C.S.* 1931, 55.

[136] J. R. Partington and R. J. Winterton, *Trans. Far. Soc.* 1934, **30**, 1104.

Cyanogen Halides, X·CN

All four of these acid halides of normal cyanic acid HO·CN are known (Cl·CN Berthollet, 1787; I·CN Dàvy, 1816; Br·CN Serullas, 1827; F·CN Cosslett, 1931). They are usually made by the action of the halogen on prussic acid or its salts; the fluoride is made from silver fluoride and cyanogen iodide. Some of their physical properties are[137-40]:

	F.CN	Cl·CN	Br·CN	I.CN
B. pt. . .	Subl. 1 atm.	+13·0°	+61·3°	Subl. 1 atm.
	at −72°	−6·9°	+51·3	at *circa* 146°
M. pt. . .	. .			146°
Sol^y in water	Alm. none	Easily sol.	Sol.	Slightly sol.

The spectral and electron diffraction evidence show that the molecules are linear, and the resemblance of their spectra[141-2] that the chloride, bromide, and iodide have structures of the same type. Hence the possible structures are $X—C\equiv N$ and $C\equiv N—X$. The chemical evidence is ambiguous; the compounds react with ammonia to give cyanamide $H_2N \cdot CN$, and with potassium hydroxide to give a halide and a cyanate:

$$Cl \cdot CN + 2\,KOH = KCl + KOCN + H_2O.$$

These reactions are to be expected for $X \cdot C\equiv N$. On the other hand, they are very easily reduced to hydrogen cyanide—by SO_2, by H_2S, and by H_2NOH—a characteristic of compounds with halogen attached to nitrogen, such as nitrogen chloride. The physical evidence is, however, conclusive in favour of the first ($X \cdot C\equiv N$) structure. The absorption spectrum[141] gives heats of dissociation which are too small to be due to the triple $C\equiv N$ link, too large for the attachment of the halogen to nitrogen, and the right size for its linkage to carbon. Indeed, the known values of the heats of linkage show that the X—CN form must be much the most stable. The difference in heat of formation will be practically that between the heats of linkage of the halogen to carbon and to nitrogen, since the CN value is (V. 672) the same within 5 k.cals. for —CN and for —NC. The differences are:

$$\text{For F·CN : C—F } 107{\cdot}0 - \text{N—F } 68{\cdot}8 = +\ 38{\cdot}2$$

$$\text{For Cl·CN : C—Cl } 66{\cdot}5 - \text{N—Cl } 38{\cdot}4 = +\ 28{\cdot}1.$$

They are too great to be overcome by any probable differences in the resonance energies. The values of the heats of the links N—Br and N—I are unknown; but from the spectra the iodide and bromide must have the same type of structure as the chloride.

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[137] V. E. Cosslett, *Z. anorg. Chem.* 1931, **201**, 75.

[138] R. P. Cook and P. L. Robinson, *J.C.S.* 1935, 1001.

[139] A. Klemenc and G. Wagner, *Z. anorg. Chem.* 1938, **235**, 427.

[140] J. A. A. Ketelaar and S. Kruyer, *Rec. Trav.* 1943, **62**, 550.

[141] R. M. Badger and S. C. Woo, *J.A.C.S.* 1931, **53**, 2572.

[142] W. West and M. Farnsworth, *J. Chem. Phys.* 1933, **1**, 402.

The oxidizing power of the halogen does not prove that it is joined to nitrogen: this property is shared by halogen atoms attached to carbon in many compounds as in the α-bromoketones R·CHBr·CO·R and elsewhere.

There is evidence of resonance between the structures X—C≡N and $\overset{+}{X}{=}C{=}\overset{-}{N}$; electron diffraction shows[143] that while the C≡N link has its normal length of 1·13 A the X—C link is much shortened, the values being (C—I is got by a careful extrapolation by Stevenson[144]):

Link	*Obs.*	*Calc.*	*% Diff.*
C—Cl .	1·67	1·76	5·1
C—Br .	1·79	1·91	6·3
C—I .	1·96	2·10	6·7

From these lengths (assuming the same relation as with the C—C link) the C—Cl link should have 24 per cent. and the C—Br 33 per cent. of double-bond character.[143]

Cyanogen fluoride F·CN, made[137] by distilling cyanogen iodide over dry silver fluoride at 220°, is a colourless gas; at low temperatures it forms a white powder which sublimes without melting under 1 atmosphere at −72°; like the other cyanogen halides it is a strong lachrymator. It is monomeric in the vapour. It is very stable, and can be kept for weeks in glass vessels without attacking the walls. Its exceptionally small solubility in water is no doubt connected with its low boiling-point. The rate of reaction of the gas with sodium vapour was measured by Cosslett[137] by the method of v. Hartel and Polanyi, and he found that the relative rates of the three cyanogen halides were

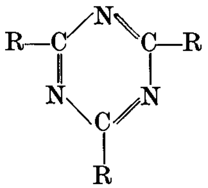
$$F{\cdot}CN : Cl{\cdot}CN : Br{\cdot}CN = 1 : 1{\cdot}7 : 120.$$

For the ultra-violet absorption see reference [145].

Other volatile compounds of carbon, nitrogen, and fluorine, mostly obscure, but including $CF_3{\cdot}NF_2$, are formed when fluorine acts on silver cyanide diluted with calcium fluoride.[146-7]

Cyanuric Compounds

The cyanogen compounds readily polymerize, and in particular tend to form trimers with the 1, 3, 5-triazine ring,



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[143] J. Y. Beach and A. Turkevich, *J.A.C.S.* 1939, **61**, 299.

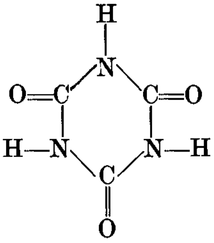
[144] D. P. Stevenson, *J. Chem. Phys.* 1939, **7**, 171.

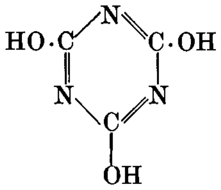
[145] C. F. White and C. F. Goodeve, *Trans. Far. Soc.* 1934, **30**, 1049.

[146] O. Ruff and M. Giese, *Ber.* 1936, **69**, 598.

[147] Id., ib. 604.

known as cyanuric compounds. In this way we should expect hydrogen cyanide to form the parent triazine (R = H), but this reaction does not occur; for the other polymerization products of HCN see Hinkel *et al.*[148] Other nitriles will polymerize to cyanuric compounds, benzonitrile, for example, giving the triphenyl triazine (R = phenyl) as methyl acetylene gives mesitylene. Various derivatives of this ring-system are known; cyanuric chloride and bromide[149] are formed by the polymerization of the cyanogen halides, and with water yield cyanuric acid, which can be written either as an OH or as an N—H compound, and which reacts as both, giving two series of esters, the O-esters changing at their boiling-points (trimethyl O-ester, b.pt. 265°) into their N-isomers. Cyanuric acid gives signs of being a pseudo-acid,[150-1] and so Hantzsch[150] ascribes to it the N·H structure, which appears to be supported by X-ray examination of the solid.[152-3]





Cyanuric triazide $C_3N_3(N_3)_3$ (= C_3N_{12}) has been shown by X-ray analysis (Miss Knaggs)[155] to have a curious plane structure like a 3-legged swastika (see W. H. Bragg's picture[154]); her further conclusion that the successive links in the ring are of different sizes (1·38 and 1·31 A) is difficult to accept, since this would imply the absence of resonance, while only very slight interaction between the ring and the azide groups is possible. No such difference was found in the X-ray examination of cyanuric acid,[152-3] which gave C—N 1·36±0·01 A (theory C—N 1·47, C=N 1·27).

Thiocyanuric acid and its derivatives are also known; they are similar to the oxygen compounds, except that here the N esters are much less stable than their sulphur isomers.

Amine-oxides, $R_3N{\rightarrow}O$

These were first obtained by Dunstan and Golding[156] by the action of methyl iodide on hydroxylamine; they are usually made by oxidizing tertiary amines, for example with hydrogen peroxide. They are high-melting and relatively non-volatile substances; thus trimethylamine

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[148] L. E. Hinkel *et al.*, *J.C.S.* 1937, 1432; 1939, 492; 1940, 1206.

[149] A. Perret and R. Perrot, *Bull. Soc.* 1940, [v] **7**, 743.

[150] A. Hantzsch, *Z. anorg. Chem.* 1932, **209**, 218.

[151] E. Agallidis, H. Fromherz, and A. Hartmann, *Ber.* 1938, **71**, 1391.

[152] E. H. Wiebenga and N. F. Moerman, *Nature*, 1938, **141**, 122.

[153] Id., *Z. Krist.* 1938, **99**, 217.

[154] W. H. Bragg, *Nature*, 1934, **134**, 138.

[155] I. E. Knaggs, *Proc. Roy. Soc.* 1935, **150**, 576.

[156] W. R. Dunstan and E. Golding, *J.C.S.* 1899, **75**, 792.

oxide $(CH_3)_3N{\rightarrow}O$ melts at 208° and sublimes under low pressure at 180°, in marked contrast to the isomeric trimethyl hydroxylamine,

$$(CH_3)_2N{-}O{-}CH_3,$$

which boils at 30°.[157] They dissolve readily in water, in which they are weak monacid bases (K for $(CH_3)_3N{\rightarrow}O$ about 10^{-10}), forming with strong acids salts such as $[(CH_3)_3N{\cdot}OH]I$. Since a solid hydrate can be isolated, the hydration to $R_3N(OH)_2$ must be fairly complete, and the weak basicity must be due to the large extent to which the ions combine to form $R_3N{-}O{-}H{\cdot\cdot}O{-}H$, the hydrogen bond being stronger between two oxygens than between an oxygen and a nitrogen as in $R_3N{-}H{\cdot\cdot}O{-}H$.

The low volatility is related to the high dipole moment, which for trimethylamine oxide was found to be 5·04 in dioxane at 25°, 5·02 in benzene at 45°,[158] and 4·95 in benzene at 25°[159]; this gives 4·3 D for the co-ordination link $\overset{+}{N}{-}\overset{-}{O}$, which is two-thirds of the value

$$(4{\cdot}8 \times 1{\cdot}36 = 6{\cdot}53)$$

for complete separation of the ionic charges; this large value is no doubt due to the impossibility of resonance with a form $R_3N{=}O$.

Electron diffraction showed[160] that the N—O distance is 1·36 (theory for N—O 1·36), while the C—N link is lengthened to 1·54 (theory 1·47).

Hydroxylamine, NH_2OH

This was discovered by Lossen in 1865, but was not isolated until thirty years later. It is formed by the reduction of the more highly oxidized compounds of nitrogen, such as nitric oxide, nitrites, and nitric acid, often electrolytically; or by the hydrolysis of oximes (isonitroso-compounds), which can be made by the action of nitrous acid on acidic methylene groups. It is usually made by Tafel's method, by the electrolytic reduction of nitric acid, using a lead cathode.

The pure base can be obtained from the chloride by treating it with an equivalent of sodium methylate in methyl alcohol, and fractionating,[161-2] or by distilling the phosphate at 136° under 13 mm. pressure.[163]

Hydroxylamine is a solid melting at 33° and boiling at 57° under 22 mm. It dissolves readily in water and alcohol, but only slightly in ether or benzene. These facts, and the relatively high boiling-point (as compared with $(CH_3)_2N{-}O{-}CH_3$ b.pt. 30°/760 mm.),[157] are signs of association, due to the hydroxyl group.

It resembles ammonia in many of its properties, though the basicity is very much weakened by the OH group; it can be alkylated and acylated

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[157] L. W. Jones and R. T. Major, *J.A.C.S.* 1928, **50**, 2742.

[158] E. P. Linton, ib. 1940, **62**, 1945.

[159] G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J.C.S.* 1945, 146.

[160] M. W. Lister and L. E. Sutton, *Trans. Far. Soc.* 1939, **35**, 495.

[161] C. A. Lobry de Bruyn, *Rec. Trav.* 1891, **10**, 100; 1892, **11**, 18.

[162] Id., *Ber.* 1894, **27**, 967.

[163] R. Uhlenhuth, *Ann.* 1900, **311**, 117.

like NH_3, and it forms a series of co-ordination compounds corresponding to the ammines.

It is an unstable substance. The solid base (the salts are more stable) begins to decompose above 15°, mainly thus:

$$3\,NH_2OH = NH_3 + N_2 + 3\,H_2O$$

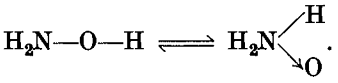
but partly also thus:

$$4\,NH_2OH = 2\,NH_3 + N_2O + 3\,H_2O.$$

It is also readily oxidized, and differs from ammonia in its strong reducing power. It is oxidized by air—violently on heating—and by all oxidizing agents, forming nitrogen and oxides of nitrogen. Ferric salts convert it quantitatively into nitrous oxide. Silver, gold, and mercury salts are readily reduced to the metal: cupric compounds (e.g. Fehling's solution) are reduced to the cuprous state even in great dilution.

Under certain conditions hydroxylamine can act as an oxidizing agent, being reduced to ammonia. This happens, for example, with ferrous hydroxide, and trivalent compounds of vanadium, titanium, and molybdenum.

The formula of hydroxylamine has the possibility of tautomerism:



$$H_2N{-}O{-}H \rightleftharpoons H_2N\begin{matrix}\diagup H\\ \searrow O\end{matrix}.$$

There is no evidence how far either form predominates. The suggestion of Haber that the oxidation of ferrous to ferric hydroxide is due to the $H_3N \rightarrow O$ form (since trimethylamine oxide oxidizes ferrous hydroxide very readily) has been disproved; ferrous hydroxide is oxidized by $H_2N \cdot O \cdot CH_3$ as rapidly as by $CH_3 \cdot NH \cdot OH$, which could give $CH_3H_2N \rightarrow O$.[164]

OXIDES OF NITROGEN

Eight oxides of nitrogen have been described:

1. Nitrous oxide, N_2O.
*2. Nitric oxide, NO.
3. Nitrogen sesquioxide, N_2O_3.
*4. Nitrogen dioxide, NO_2.
5. Nitrogen tetroxide, N_2O_4.
6. Nitrogen pentoxide, N_2O_5.
*7. Nitrogen trioxide, NO_3.
8. Nitrogen hexaoxide, N_2O_6.

* Odd molecule.

Of these 1, 3, and 6 can be regarded as the anhydrides of hyponitrous, nitrous, and nitric acid respectively, though nitrous oxide cannot be rehydrated to hyponitrous acid.

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[164] P. Baumgarten and H. Erbe, *Ber.* 1938, 71, 2603.

5·N_2O_4 is not the mixed anhydride of nitrous and nitric acids; 8·N_2O_5 is probably the peroxide derivative of N_2O_5, $O_2N—O—O—NO_2$. The remaining oxides, NO, NO_2, and NO_3 are 'odd molecules', that is, they have an odd number of electrons. The power of forming such odd molecules is very marked with nitrogen. We have a series of similar types among the organic compounds, such as the free radicals Ar_2N, and the compound Ar_2NO, as well as the lower fluoride NF_2.

The odd molecules (like the hydrides of boron) cannot be formulated with the ordinary symbols, and with nothing but doublet links and complete octets; they are best represented with doublet links but incomplete octets. This would normally be a sign of unsaturation and instability: the unexpected stability which is actually observed is clearly due to resonance, and it is often possible to infer what the resonance formulae actually are. It must be remembered that the spatial positions of the atoms (which have sometimes been determined experimentally) must agree with both of the resonance structures, and also that the atoms of the first short period can never hold more than 8 valency electrons, even, as we know from $Al(BH_4)_3$ (III. 367), when they have a covalency greater than 4.

The various oxides may be treated in order, beginning with those in which the percentage of oxygen is the lowest.

Nitrous Oxide, N_2O

This is formed by the suitable reduction of nitrites and nitrates, or by heating hydroxylamine, which breaks up into nitrous oxide and ammonia. It is usually made by heating ammonium nitrate:

$$NH_4NO_3 = N_2O + 2\ H_2O.$$

The reaction, which is exothermic, begins at 185°, and becomes violent at 250°. The gas so made is impure: it contains NO_2, NO, N_2, O_2, CO_2, and water, and must be specially purified before it can be used as an anaesthetic.

Nitrous oxide boils at $-88{\cdot}46°$ and melts at $-90{\cdot}81°$; the Trouton constant is 21·4.[165] It is a very stable substance at the ordinary temperature; it is not acted on in the cold by oxygen, ozone, hydrogen, halogens, alkali metals, phosphine, hydrogen sulphide, or aqua regia. At higher temperatures it is a strong oxidizing agent, being reduced to elementary nitrogen. It reacts with alkali metals at their boiling-points to form nitrites (and nitrogen), and it oxidizes organic compounds at temperatures above 300°.

Nitrous oxide has the composition of an anhydride of hyponitrous acid HO·N=N·OH, and is formed from that acid on standing, but it is not reconverted into hyponitrite by alkali, and its aqueous solution does not conduct electricity any better than pure water (compare the relation of carbon monoxide to formic acid).

The absorption spectrum of the gas and the X-ray examination of the

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[165] H. J. Hoge, *J. Res. Nat. Bur. Stand.* 1945, 34, 281.

solid[166] (and even of the liquid)[167] show that the molecule is linear, so that it must have either two double links or a single and a triple. It has the same crystal lattice as carbon dioxide, and forms a continuous series of mixed crystals with it.[168] It was, however, shown by Plyler and Barker[169,170] from the infra-red absorption bands, supported by the Raman spectrum, that the gaseous molecule, though it is linear, is not symmetrical. In confirmation of this the dipole moment in the gas was found on very careful measurement[171] not to be zero, though it is very small (0·17 D). Hence the molecule must be N—N—O, and we have two possible structures $\overset{\longleftarrow\!\!+}{\mathrm{N}\overset{\leftarrow}{=}\mathrm{N}=\mathrm{O}}$ and $\overset{+\!\!\longrightarrow}{\mathrm{N}\equiv\mathrm{N}\rightarrow\mathrm{O}}$. Both are highly polar but in opposite senses, so that the low moment can only be explained by resonance between the two. Pauling[172] has shown that the moment of inertia deduced from the measurements of Plyler and Barker[169] when correctly interpreted (Badger, quoted by Pauling,[172] p. 498) agrees with this resonance, if we assume that each link has its smallest value (N≡N and N=O). More recently[173] electron diffraction results have confirmed the linearity of the molecule, and shown that the distance between the two terminal atoms is 2·32 A (theory for N≡N + N=O 2·24; for $\overset{-}{\mathrm{N}}=\overset{+}{\mathrm{N}}=\mathrm{O}$ 2·35; for $\mathrm{N}\equiv\overset{+}{\mathrm{N}}-\overset{-}{\mathrm{O}}$ 2·45 A).

Nitric Oxide, NO

This is formed by the direct combination of nitrogen and oxygen at very high temperatures, as in the electric arc. The reaction being endothermic, the proportion at equilibrium rises rapidly with the temperature. With air at atmospheric pressure it is 1·2 per cent. by volume at 2,000° and 5·3 at 3,000°. This formation of nitric oxide is the foundation of the fixation of atmospheric nitrogen by the arc. In the laboratory it is commonly made by the reduction of nitric acid (for example, by copper) or of nitrites.

It is a colourless gas, which boils at −151·8° and freezes at −163·7°. The pure substance in the liquid and solid states is a deeper blue than liquid oxygen.[174] The Trouton constant is 27·1. The gas shows faint signs of association at high pressures, and in the liquid association is clearly indicated by the high Trouton constant (see ref. [175]) and the parachor[176]; and in the solid by the entropy,[174] the magnetic susceptibility,[177-8] and the heat of sublimation.[179]

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[166] J. de Smedt and W. H. Keesom, *Proc. K. Akad. Amst.* 1924, **27**, 839.

[167] P. C. Sharrah, *J. Chem. Phys.* 1943, **11**, 435.

[168] L. Vegard, *Z. Phys.* 1931, **71**, 465.

[169] E. K. Plyler and E. F. Barker, *Phys. Rev.* 1931, [2] **38**, 1827.

[170] E. F. Barker, *Nature*, 1932, **129**, 132.

[171] H. E. Watson, G. G. Rao, and K. K. Ramaswamy, *Proc. Roy. Soc.* 1934, **143**, 558.

[172] L. Pauling, *Proc. Nat. Acad.* 1932, **18**, 293, corrected ib. 498.

[173] V. Schomaker and R. Spurr, *J.A.C.S.* 1942, **64**, 1184.

[174] H. L. Johnston and G. F. Giauque, ib. 1929, **51**, 3207.

[175] F. A. Henglein and H. Krüger, *Z. anorg. Chem.* 1923, **130**, 186.

[176] G. H. Cheesman, *J.C.S.* 1932, 889.

The internuclear distance in NO is 1·14 A[180] (calculated:

$$\mathrm{N{-}O}\ 1{\cdot}36,\ \mathrm{N{=}O}\ 1{\cdot}15,\ \mathrm{N{\equiv}O}\ 1{\cdot}05).$$

The formula is evidently that of molecular oxygen with one electron missing; it is no doubt a resonance hybrid of the two structures in which the oxygen and the nitrogen respectively have the complete octet:

$$\cdot\overset{\cdot 7}{\underset{\cdot}{\mathrm{N}}}\,\overset{\cdot}{\underset{\cdot}{:}}\,\overset{\cdot}{\underset{\cdot}{\mathrm{O}}}\!: \quad \text{or} \quad \mathrm{N{=}O} \quad \text{and} \quad :\!\overset{\cdot}{\underset{\cdot}{\mathrm{N}}}\,\overset{\cdot}{\underset{\cdot}{:}}\,\overset{\cdot 7}{\underset{\cdot}{\mathrm{O}}}\cdot \quad \text{or} \quad \overset{-}{\mathrm{N}}{=}\overset{+}{\mathrm{O}} \quad \text{or} \quad \mathrm{N}\overset{\leftarrow}{=}\mathrm{O}.$$

The resonance explains why the dipole moment of nitric oxide is so small: it is 0·16 D[171]; in N=O the sharing of the four electrons is such as to make the oxygen negative, while in $\overset{-}{\mathrm{N}}{=}\overset{+}{\mathrm{O}}$ the electronic transfer will outweigh this, and the oxygen will be positive.

Chemically, nitric oxide is a reactive substance with an unsaturated behaviour. It combines with oxygen to form NO_2, and with chlorine and bromine to the nitrosyl halides, such as NOCl. Burning phosphorus or carbon continue to burn in the gas, though feebly burning sulphur is extinguished. As a free radical (though an unusually stable one) nitric oxide will combine with other free radicals such as methyl; the inhibiting effect of small quantities of nitric oxide in many gaseous reactions is the most direct evidence we have of the participation in them of radical chains.[181]

The nitric oxide molecule resembles that of carbon monoxide except that it has one electron more; this electron it has a remarkable tendency to get rid of, which it can do in two ways. If it is removed by ionization we get a univalent cation $[NO]^+$, with the same structure as a neutral CO molecule ($[\mathrm{N}\overset{\leftarrow}{=}\mathrm{O}]^+$, $\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$). The existence of this ion was established by Hantzsch and Berger,[182] who showed that nitrosyl perchlorate is anhydrous, and gives a conducting solution in nitromethane: it must therefore be a true salt, $[NO](ClO_4)$. A similar salt is the fluoroborate $[NO](BF_4)$.[183] The crystal structure of the perchlorate and fluoroborate has been examined,[184] and shows that they are true salts, isomorphous with $[NH_4](ClO_4)$, $[NH_4](BF_4)$, and $[H_3O](ClO_4)$. $[NO]^+$ is about the same size as $[H_3O]^+$, and rather smaller than $[NH_4]^+$. Other nitrosyl salts are $[NO](SbF_6)$, formed by the direct combination of NOF with SbF_5,[185] and $[NO](FeCl_4)$ made by passing NOCl over $FeCl_3$ (VIII. 1367). The so-called nitrosulphonic acid (lead chamber crystals) made by dissolving

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[177] E. Lips, *Helv. Phys. Acta*, 1934, **7**, 663; 1935, **8**, 247, 263.

[178] H. Bizette and B. Tsai, *C.R.* 1938, **206**, 1288. They calculate that there is 97 per cent. of $(NO)_2$ at −163° C.

[179] F. London, *Z. physikal. Chem.* 1931, B **11**, 240.

[180] See Pauling, *Chem. Bond.*, ed. 2, p. 267.

[181] See Hinshelwood, *Kinetics of Chemical Change*, 1940, p. 92.

[182] A. Hantzsch and K. Berger, *Z. anorg. Chem.* 1930, **190**, 321.

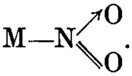
[183] E. Wilke-Dörfurt and G. Balz, ib. 1927, **159**, 197.

[184] L. J. Klingenberg, *Rec. Trav.* 1937, **56**, 749.

[185] O. Ruff, *Z. anorg. Chem.* 1908, **58**, 325.

oxides of nitrogen in concentrated sulphuric acid, and usually written $O_2N \cdot SO_3H$, was shown by Hantzsch to be ionized in absolute sulphuric acid (which an acid would not be) and hence to be nitrosyl hydrogen sulphate $[NO](HSO_4)$. For more on $[NO]^+$ see references [186-7].

*Metallic Nitrosyls**

The nitrosyls resemble the carbonyls (IV. 547) in many ways, but have NO in place of CO. The idea that they are derivatives of hyponitrous acid HON=NOH was disproved by Manchot.[188-9] They are formed from nitric oxide and not from hyponitrous acid (except under conditions where the latter forms nitric oxide), and they readily liberate NO (as the carbonyls CO) with acids, whereas the hyponitrites with acids give nitrous oxide. Also if they were hyponitrous acid derivatives we should have to double the formulae of many of these nitrosyls, such as the nitroprussides and all those with only one NO to a metallic atom; and there is no evidence for this, and much against it. Hence each NO group must be separately attached to the central atom; moreover this must be through the nitrogen (M—N—O) and not the oxygen, since the NO can often be oxidized to a nitro-group  $\mathrm{M{-}N}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{O}}$.

For the M—N—O group thus established there are three possible structures. (1) It might contain a true nitroso-group M—N=O as in nitrosobenzene C_6H_5—N=O. This, however, can be disproved; the nitrosyls are devoid of the characteristic tendency of the nitroso-compounds to polymerize with a change of colour, and also this structure would involve very improbable valencies for many of the metallic atoms, such as tetravalency for the iron in the nitroprussides. Further, some complexes are known which probably are true nitroso-derivatives, such as $[Co(NH_3)_5{-}N{=}O]X_2$, corresponding to $[Co(NH_3)_5Cl]Cl_2$, and like it diamagnetic; this has an unusual red colour, and a black isomer; another is $M_3[Fe(CN)_5{-}N{=}O]$, which is dark yellow in neutral solution and violet in acid, and clearly of a different type from the nitrosyl compound which has the isomeric anion, the nitroprusside $M_2[Fe(CN)_5NO]$. Moreover, it has been shown by electron diffraction that the M—N—O groups in $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ are linear like the M—C—O; since the NO group is known to occupy one co-ordination place, this shows that the linkage is M—N≡O, for M—N=O would involve an angle at the nitrogen of about 125°.

(2) The nitric oxide molecule might merely share a lone pair of electrons

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* References: Gp. I, Cu″ 160; Gp. VII, Mn 1288; Gp. VIII A, Fe 1372, Ru 1484, Os. 1510; Gp. VIII B, Co 1423; Gp. VIII C, Ni 1452; Pd 1577; Pt 1628.

[186] W. R. Angus and A. H. Leckie, *Proc. Roy. Soc.* 1935, **149**, 327.
[187] Id., *Trans. Far. Soc.* 1935, **31**, 958.
[188] W. Manchot and H. Schmid, *Z. anorg. Chem.* 1933, **216**, 99.
[189] W. Manchot and S. Davidson, *Ber.* 1929, **62**, 681.

with the metal, the peculiar 'odd' structure of the N—O link being maintained. But this link is only known in nitric oxide and a few organic derivatives; it is obviously unstable, and likely to change to a more normal bond. If it did not do so the replacement of CO by NO should involve no other change in the molecule, whereas it always causes a change in valency (compare $K_3[Fe(CN)_5CO]$ and $K_2[Fe(CN)_5NO]$).

(3) If we assume that the N—O link in the nitrosyls is an ordinary triple link $M—N\equiv O$, corresponding to $M—C\equiv O$, then since NO has one more electron than CO it must get rid of it somehow. We know that it can do so by forming the $[NO]^+$ cation, of which many salts have been prepared, and in the nitrosyls we may suppose that the electron is transferred to the central atom, giving the structure $\overset{=}{M}—\overset{+}{N}\equiv\overset{+}{O}$, in which both the nitrogen and the oxygen have complete octets. If we accept this structure* we can explain the valency relations of the carbonyls and nitrosyls and show that the inert gas rule established for the carbonyls (IV. 548) holds for the nitrosyls as well. The following series of salts, all of which give the inert gas number for the central atom, exemplify this:

EAN 36	$K_3[Mn(CN)_5NO]$		$K_5[Mn(CN)_6]$
	$K_2[Fe(CN)_5NO]$	$K_3[Fe(CN)_5CO]$	$K_4[Fe(CN)_6]$
		$K_3[Fe(CN)_5(OH_2)]$	
EAN 54	$K_2[Ru(CN)_5NO]$		$K_4[Ru(CN)_6]$
	$K_2[RuCl_5NO]$		
EAN 86	$K_2[OsCl_5NO]$		$K_4[Os(CN)_6]$
			$K_4[OsCl_6]$

Perhaps the most striking series is that of the carbonyl-nitrosyls:

	$Ni(CO)_4$	$Co(CO)_3NO$	$Fe(CO)_2(NO)_2$
B. pts.	43°	78·6°	110°
F. pts.	−23°	−1·1°	+18°

in which the electron given by the NO to the metal compensates for the drop in atomic number, so that the E.A.N. is in all cases 36.

The inert gas rule (IV. 548) holds for the nitrosyls if we count each NO as 3, each CO being 2; for the compound $M_x(CO)_y(NO)_z$ (where G is the atomic number of the next inert gas, and m that of M) it takes the form

$$G-\frac{x\cdot m+2y+3z}{x}=x-1.$$

In many of the nitrosyls the molecular weight is unknown, so that we can only say they do not disagree with the rule, and as with the carbonyls some (but not many) seem definitely to depart from it.

The elements which form nitrosyls are on the whole much the same as those which form carbonyls, though fewer nitrosyls exist (or are known)

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* The probability of this view is greatly increased by the evidence that the carbonyl hydrides (IV. 549) have the very similar grouping $\overset{=}{M}—C\equiv\overset{++}{O}—H$.

than carbonyls; they are Mn: Fe, Ru [this forms a more varied selection than any other element, all (save the binary $Ru(NO)_5$) with only one NO group]: Os (one type); Co: Ni, Pd, Pt; Cu (cupric but not cuprous). The formal valencies (as with the carbonyls) have little relation to those in other compounds: except for a possible tetravalent iron compound $(NO)\cdot[Fe(NO)_3]$ (compare $Fe_2(CO)_9$) they are all (taking the most probable structures) 0, 1, or 2; Ru and Os are all 2; Co all 1; and Ni, Pd, and Pt all 0.

The nitrosyls are divisible generally into the same classes as the carbonyls: 'binary', halides, ammines, complexes with only one NO; hydrides, as we might expect, do not occur. Two 'binary' nitrosyls have been described: $Fe(NO)_4$, a black non-volatile compound made by NO acting under pressure on $Fe(CO)_5$; it may be the nitrosyl salt

$$[NO]\cdot[Fe(NO)_3]:$$

with E.A.N. $26+1+3\times 3 = 36$, but with the unusual valency for the iron of 4; $Ru(NO)_5$ has also been described, but the composition is uncertain. The mixed carbonyl nitrosyls $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ have already been mentioned.

The nitrosyl halides are numerous, with 1 or 2 or in one case 3 nitrosyl groups, and 1, 2, or 3 halogen atoms: $M(NO)X_2$ is formed by Ru; $M(NO)X_3$ by Ru and Os, with complex salts; $M(NO)_2X$ by Fe and Co; $M(NO)_2X_2$ by Pd and Pt, the last forming complex salts. The unstable compound $Fe(NO)_3Cl$ is exceptionally volatile, no doubt being monomeric, as the E.A.N. of the iron is 36.

Ammines occur, but the NO group is never replaced (as CO can be) by the amine; we have, for example, $Fe(NO)_2(phn)$ and $Co(CO)(NO)(phn)$ (phn = *o*-phenanthroline), and the compounds $[Ru(NO)(NH_3)_4OH]X_2$, which are the salts of a strong base.

The compounds in which one NO forms part of a recognized complex are numerous, including all the many ruthenium compounds except $Ru(NO)_5$, and the only osmium nitrosyls, as well as the pentacyano- and pentachloro-compounds in the list given above (p. 685).

Nitrosyls of copper have not been isolated; but a cupric solution containing anionic cupric complexes absorbs NO readily, up to 3·6 NO to one Cu″, and this has an obvious resemblance to the absorption of CO by *cuprous* solutions, the NO filling up the gap in the third quantum group of the cupric atom.

Nitrogen Sesquioxide, N_2O_3

This is usually made by the reduction of nitric acid with arsenic trioxide or starch.

Pure N_2O_3 exists only as a solid, which is pale blue and melts at −102°. In the liquid it is partially dissociated into $NO_2 \rightleftharpoons N_2O_4$ and nitric oxide; the dissociation increases with temperature, and so the liquid, which is deep blue at −30°, is greenish (from the colour of the brown NO_2) at the ordinary temperature. In the gas the dissociation is almost complete, the percentage of undissociated N_2O_3 being at 1 atmosphere 10·5 at 25° and 1·2 at 100°.[190]

According to Baker[191] and B. M. Jones[192] the dissociation of N_2O_3 is prevented by the complete removal of water; the liquid then remains blue up to the ordinary temperature, and the density of the vapour is almost equal to that of N_2O_3[192] or is that of N_4O_6[191]; this recalls the behaviour of dry ammonium chloride (p. 661).

Nitrogen trioxide is obviously the anhydride of nitrous acid, with a structure O=N—O—N=O. Liefer[193] showed that if ordinary ^{14}NO is mixed with NO_2 made from nitrogen rich in ^{15}N, there is a quick exchange of the isotopes, evidently through the anhydride, which can break up in two symmetrical ways:

$$^{14}NO + {}^{15}NO_2 \rightleftharpoons O{}^{14}N{-}O{-}{}^{15}N{=}O \rightleftharpoons {}^{14}NO_2 + {}^{15}NO.$$

The chemical properties entirely support this. Nitrogen trioxide dissolves in alkalies with complete conversion into nitrite; in water it forms a blue solution which obviously contains nitrous acid, but is rapidly decomposed into nitric acid and nitric oxide.

Nitrogen Peroxide, $NO_2 \rightleftharpoons N_2O_4$

This can be made by oxidizing nitric oxide with oxygen or nitrogen pentoxide, or by heating nitric acid or a nitrate; it is commonly made by heating lead nitrate.

The gas is reddish-brown; the liquid boils at 21·1° and is then brown; it becomes paler on cooling, and freezes at −11·2° to a colourless solid; the heat of fusion is 3·50 k.cals., of evaporation 9·11 k.cals./mole, and the Trouton constant 30·9.[194] It is evident that N_2O_4 is colourless and NO_2 brown, and that the solid is pure N_2O_4 which is partly dissociated in the liquid, and more as the temperature rises. The density of the gas shows the degree of dissociation under 1 atmosphere to be 20 per cent. at 27°, 53 per cent. at 60°, and 90 per cent. at 100°. At higher temperatures the NO_2 dissociates further into nitric oxide and oxygen, and the colour fades again.

The degree of dissociation in various solvents was determined by Cundall[195] by means of the colour, on the assumption that this was proportional to the concentration of NO_2: the results gave reasonably constant values of the dissociation constant.

The rate of dissociation in the gas was calculated by Einstein[196] from the

[190] M. Bodenstein *et al.*, *Z. physikal. Chem.* 1922, **100**, 75.

[191] H. B. Baker and M. Baker, *J.C.S.* 1907, **91**, 1862; H. B. Baker, ib. 1912, **101**, 2339.

[192] B. M. Jones, ib. 1914, **105**, 2310.

[193] E. Liefer, *J. Chem. Phys.* 1940, **8**, 301.

[194] W. F. Giauque and J. D. Kemp, *J. Chem. Phys.* 1938, **6**, 10.

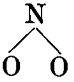
[195] J. T. Cundall, *J.C.S.* 1891, **59**, 1076; 1895, **67**, 808.

[196] A. Einstein, *Berl. Ber.* 1920, 380.

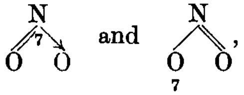
velocity of sound, as being at 1 atmosphere and 25° between $1-5\times 10^4$/sec. Brass and Tolman[197] measured it by the change of temperature on expansion of the gas through a small hole: they found 2×10^4/sec.

Nitrogen peroxide is a powerful oxidizing agent. With water it is first converted into nitric acid and N_2O_3, and then the latter changes as usual into more nitric acid and nitric oxide. It is absorbed by alkaline solutions with complete conversion into nitrite and nitrate.

We have two separate structural problems, that of NO_2, which is an odd molecule, and that of N_2O_4 which is not.

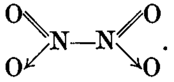
The structure of NO_2 was deduced by Sutherland and Penney[198] from the fine structure of the absorption bands: this shows that the molecule is not linear, and that the  angle is about 110–20°. Electron diffraction measurements on NO_2[199,199a] give the angle as 132±2°, and the N—O distance as 1·20 A (theory N—O 1·36, N=O 1·15), in agreement with the predictions of Pauling (*Chem. Bond*, p. 270) of 140° and 1·18 A.

The possible formulae are

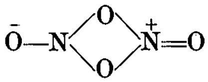


in which we should expect the angle to be not far from 125°; it is no doubt a resonance hybrid of the two.

For N_2O_4 the most obvious structure, especially in view of its behaviour with alkalies, is that of a mixed anhydride of nitrous and nitric acids, O=N—O—NO_2. This, however, does not seem to be correct. From the infra-red and Raman spectra of N_2O_4 Sutherland[200] finds that the structure must be the symmetrical



The same conclusion is reached by Hendricks[201] from the X-ray examination of the solid. Similarly Giauque and Kemp[194] find that the entropy value for solid N_2O_4 suggests a symmetrical molecule in which the NO_2 groups cannot rotate freely. A planar 'bridge' structure



has also been suggested,[202] and is found to agree with the Raman and infra-red spectra.

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[197] P. D. Brass and R. C. Tolman, *J.A.C.S.* 1932, **54**, 1003.

[198] G. B. B. M. Sutherland and W. G. Penney, *Nature*, 1935, **136**, 146.

[199] L. R. Maxwell and V. M. Mosley, *J. Chem. Phys.* 1940, **8**, 738.

[199a] S. Claesson, J. Donohue, and V. Schomaker, ib. 1948, **16**, 207.

[200] G. B. B. M. Sutherland, *Proc. Roy. Soc.* 1933, **141**, 342.

[201] S. B. Hendricks, *Z. Phys.* 1931, **70**, 699.

[202] H. C. Longuet-Higgins, *Nature*, 1944, **153**, 408.

The 'Nitronium' ion, $[NO_2]^+$

It has long been known (mainly through a series of papers by Hantzsch from 1907 onwards) that nitric acid reacts with concentrated sulphuric or perchloric acid to form a salt with nitrogen in the cation. A solution of nitric acid in absolute sulphuric acid, as compared with one in 80 per cent. aqueous acid, has scarcely any vapour pressure of nitric acid; it has different ultraviolet and Raman spectra, a high conductivity, and a great nitrating power. The positive charge of the nitrogen is shown by the migration of the nitric acid to the cathode when the perchlorate is electrolysed in nitromethane solution, or nitric acid in absolute sulphuric.[202b–c] Hantzsch assumed that the cation was $[H_2NO_3]^+$ or $[H_3NO_3]^{++}$; he isolated perchlorates with the compositions of

$$[H_2NO_3](ClO_4) \text{ and } [H_3NO_3](ClO_4)_2.$$

Recent work, mainly of Westheimer and Kharasch,[202a] of Bennett,[202b–e] and of Ingold and Hughes[202f–k] and their respective co-workers, has shown that while this $H_2NO_3^+$ may well occur in presence of larger quantities of water,[202j–k] in more concentrated acid the cation is NO_2^+, as was suggested by v. Euler in 1922.[202l] The main evidence for this is (1) the enormous increase in the rate of nitration as the water is removed: it is about 1,000 times as great in 90 per cent. as in 80 per cent. aqueous sulphuric acid[202a]; the relation of the rate to the water concentration supports this view quantitatively. (2) the van 't Hoff factor i determined cryoscopically[202g] is 4, as required by the equation

$$HNO_3 + 2\ H_2SO_4 = NO_2^+ + H_3O^+ + 2\ HSO_4^-$$

($H_2NO_3^+$ would require $i = 2$, and H_3NO_3 $i = 3$). (3) The Raman spectrum also supports the formula NO_2^+; it is very like that of the isoelectronic CO_2.

Still stronger evidence for the occurrence of this cation was obtained by Ingold *et al.*[202h] from the perchlorate; they failed to get Hantzsch's $H_2NO_3 \cdot ClO_4$, which must have been a mixture, but they isolated his other perchlorate, with the composition $H_3NO_3(ClO_4)_2$. They showed, however,[202m]

[202a] F. H. Westheimer and M. S. Kharasch, *J.A.C.S.* 1946, **68**, 1871.

[202b] G. M. Bennett, J. C. D. Brand, and G. Williams, *J.C.S.* 1946, 869.

[202c] Id., ib. 875.

[202d] J. C. D. Brand, ib. 880.

[202e] G. M. Bennett, J. C. D. Brand, D. M. James, T. G. Saunders, and G. Williams, ib. 1947, 474.

[202f] E. D. Hughes, C. K. Ingold, and R. I. Reed, *Nature*, 1946, **158**, 448.

[202g] R. J. Gillespie, J. Graham, E. D. Hughes, C. K. Ingold, and E. R. A. Peeling, ib. 480.

[202h] D. R. Goddard, E. D. Hughes, and C. K. Ingold, ib. 480.

[202i] C. K. Ingold, D. J. Millen, and H. G. Poole, ib. 480.

[202j] E. S. Halberstadt, E. D. Hughes, and C. K. Ingold, ib. 514.

[202k] C. A. Bunton, E. D. Hughes, G. J. Minkoff, and R. I. Reed, ib. 514.

[202l] H. v. Euler, *Angew. Chem.* 1922, **35**, 580.

[202m] C. K. Ingold, unpublished.

that this was an equimolecular mixture of $[NO_2]^+(ClO_4)^-$ and the well-known 'hydrate' $[H_3O]^+(ClO_4)$; the nitronium salt can be separated by recrystallization from nitromethane, or by decomposing the hydrate with nitrogen pentoxide, and its structure is established by analysis, and supported by the Raman spectrum.

The final proof that this NO_2 cation exists is given by the X-ray structure of solid nitrogen pentoxide. Ingold showed that this is nitronium nitrate, $[NO_2]^+(NO_3)$, rather like phosphorus pentachloride, which has been shown to be $[PCl_4]^+(PCl_6)$.

Nitrogen Pentoxide, N_2O_5

This can be made by treating the lower oxides with ozone, or by distilling nitric acid with phosphorous pentoxide.

It is a colourless solid which sublimes without melting. Since it begins to decompose into N_2O_4 and oxygen at any temperature above 0°, its melting-point cannot be very exactly determined; but it appears to have a vapour pressure of 1 atmosphere at 32·5° and to melt at 41°; the vapour density is normal; the half-life, in the change to $N_2O_4+O_2$, is 10 days at 0° and 10 hours at 20°.[203] The kinetics of this decomposition have given a great deal of trouble; the unimolecular rate appears to remain constant down to a pressure of 0·002 mm., which is inconsistent with the ordinary Lindemann theory of unimolecular reactions. It is probable that some other reactions occur which have an appreciable effect at these very low pressures.[204,204a]

Nitrogen pentoxide is converted by water into nitric acid with considerable evolution of heat. It has no action in the cold and in absence of catalysts on hydrogen, chlorine, or bromine, but it at once converts iodine into the pentoxide I_2O_5.[205] Nitric oxide or nitrogen trioxide converts it into N_2O_4.

There seems no reason to doubt that in the vapour it has the obvious structure $O_2N—O—NO_2$. Electron diffraction measurements[206] gave the N—O—N angle as 180°, but Lewis and Smyth[207] find that in carbon tetrachloride solution it has the moment of 1·39 D, which indicates very roughly a more probable angle of 145°.

Nitrogen Trioxide, NO_3

The formation of an oxide of nitrogen with a larger proportion of oxygen than the pentoxide was noticed in 1881[208]; the compound was further

[203] F. Daniels and E. H. Johnston, *J.A.C.S.* 1921, **43**, 57.

[204] See Hinshelwood, *Chem. Change in Gaseous Systems*, ed. 3, p. 172; *Kinetics of Chemical Change*, p. 118.

[204a] R. A. Ogg, *J. Chem. Phys.* 1947, **15**, 337.

[205] F. Daniels and H. Eyring, *J.A.C.S.* 1930, **52**, 1489.

[206] L. R. Maxwell, V. M. Mosley, and L. S. Deming, *J. Chem. Phys.* 1934, **2**, 331.

[207] G. L. Lewis and C. P. Smyth, *J.A.C.S.* 1939, **61**, 3067.

[208] P. Hautefeuille and J. Chappuis, *C.R.* 1881, **92**, 80.

investigated by Warburg and Leithäuser,[209] who noticed the very characteristic absorption spectrum (see further, [211]), and by Schumacher and Sprenger[210]; they made it by the action of ozone on nitrogen pentoxide. Schumacher and Sprenger[210] showed that it is produced in the gas when the pentoxide decomposes in the presence of ozone, and has the formula NO_3. It is very unstable; its existence, like that of sulphur monoxide, can only be established in great dilution by means of the absorption spectrum: it cannot be condensed. The statement that it is got as a white solid by exposing a mixture of nitrogen pentoxide and oxygen to the electric discharge at a low temperature[212] has been disproved.[213] Lowry[214] has shown that the vapour of the pentoxide, if mixed with (7-8 per cent.) ozonized oxygen, contains a blue gas, which is probably NO_3. On heating, this mixture ignites below 100°, and burns with a brown flame to nitrogen peroxide and oxygen.

Nitrogen trioxide dissolves in water, and the solution is more stable than the pure gas; it has a strong oxidizing power, which only disappears after a day or two. The trioxide can be extracted from the water with ether, the partition coefficient being 3:1 in favour of the ether. On standing in water it goes to nitric acid and oxygen; with NaOH it evolves oxygen, forming a nitrate and nitrite. In none of these reactions is any hydrogen peroxide formed, so that it seems certain that it does not contain a peroxide —O—O— link, and it cannot be an anhydride of pernitric acid HNO_4; it is also clearly distinct from the next oxide N_2O_6.

N_2O_6

This is formed by the action of fluorine on nitric acid[215]; it appears to be the mixed anhydride of nitric and pernitric acid, $O_2N—O—O—NO_2$; it rapidly decomposes with loss of oxygen. The corresponding pernitric acid $H—O—O—NO_2$ is said to be formed by the action of hydrogen peroxide on nitric acid.[216]

Constitution of NO_3 *and* N_2O_6

The formation of N_2O_6 makes it probable that it contains the peroxide group, and the anhydride formula above may be accepted.

NO_3, as we have seen, cannot contain such an anhydride link, or it would form H_2O_2. In default of any evidence, we can give it various

[209] E. Warburg and G. Leithäuser, *Ann. Phys.* 1906, **20**, 743; 1907, **23**, 209.

[210] H. J. Schumacher and G. Sprenger, *Z. physikal. Chem.* 1928, **136**, 77; 1929, **140**, 281; 1929, B **2**, 267.

[211] G. Sprenger, *Z. Elch.* 1931, **37**, 674.

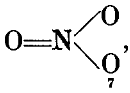
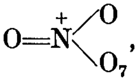
[212] R. Schwarz and H. Achenbach, *Ber.* 1935, **68**, 343.

[213] A. Klemenc and W. Neumann, *Z. anorg. Chem.* 1937, **232**, 216.

[214] J. T. Lemon and T. M. Lowry, *J.C.S.* 1936, 1409; T. M. Lowry and R. V. Seddon, ib. 1937, 1461; id., ib. 1938, 626.

[215] F. Fichter, E. Brunner, *Helv. Chim. Acta*, 1929, **12**, 306.

[216] I. Trifonow, *Z. Anorg. Chem.* 1922, **124**, 133.

structures, of which the most probable is , otherwise written , with resonance between the three O atoms.

OXY-ACIDS OF NITROGEN

Hyponitrous Acid, $(NOH)_2$

This acid can be made (1) by the action of nitrous acid on hydroxylamine

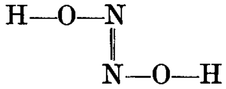
$$H—O—N{=}O + H_2N—OH = HO—N{=}N—OH + H_2O,$$

(2) by the oxidation of hydroxylamine with copper oxide, silver oxide, or mercuric oxide, (3) by the reduction of nitric or nitrous acid, best with potassium amalgam. The yield is always very small. It is best made by treating hydroxylamine in methyl alcohol with sodium methylate and then with a solution of amyl nitrite in ether, when a 13 per cent. yield of sodium hyponitrite is obtained.[217] It is usually separated as the slightly soluble silver salt.

By removing the silver with hydrochloric acid in methyl alcohol, and evaporating, pure hyponitrous acid $H_2N_2O_2$ can be obtained. It is an extraordinarily explosive solid. It is more stable in solution in water, where it slowly decomposes to nitrous oxide and water. The molecular weight in water is normal. It is a very weak acid.

The salts are also unstable and explode on heating; the sodium salt explodes at 260°, giving $NaNO_3$, Na_2O, and nitrogen.

A series of esters have been obtained which have the normal molecular weight for $R_2N_2O_2$ in benzene. They also are unstable, and give off nitrogen slowly at any temperature above 15°, or on treatment with acids or alkalies.

There is no reason to doubt that hyponitrous acid has the structure HO—N=N—OH (apart from tautomeric possibilities), and that the esters, which are certainly O-esters, are Alk—O—N=N—O—Alk. Hantzsch[218] concludes, no doubt rightly, from the properties of the acid, that it is the trans-compound 

$$\begin{array}{l} H—O—N \\ \qquad\ \ \| \\ \qquad\ \ N—O—H \end{array}$$

The strong tendency to decompose with evolution of nitrogen is characteristic of compounds with the N=N group.

Acid or salts apparently isomeric with the hyponitrites have been obtained from nitric oxide and atomized hydrogen at —180°,[219] from nitric oxide and a solution of sodium in liquid ammonia,[220] and by the action of a mixture of nitrogen and nitric oxide in heated sodium.[221]

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[217] A. W. Scott, *J.A.C.S.* 1927, **49**, 986.

[218] A. Hantzsch, *Ber.* 1933, **66**, 1566.

[219] P. Harteck, ib. 423.

[220] E. Zintl and A. Harder, ib. 760.

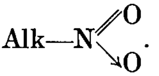
[221] H. Gehlen, *Ber.* 1939, **72**, 159.

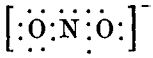
Nitrous Acid

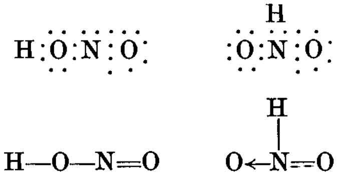
The acid only exists in solution. Nitrites are formed (1) by the reduction of nitrates, by heating them with lead, copper, etc., or sometimes (alkaline nitrates) alone (see below); (2) by the oxidation of ammonia with hydrogen peroxide, or even by air in presence of certain metals, especially copper and platinum. The reaction in presence of platinum is part of the commercial process for making nitric acid by burning ammonia.

Nitrous acid is a weak acid; $k = 4{\cdot}5 \times 10^{-4}$ (about half-way between acetic and chloracetic acids); this means that it is about 6·5 per cent. ionized in decinormal solution.

In water it changes rapidly into nitric oxide and nitric acid. It is very readily oxidized to nitric acid, but it can also be reduced, for example by stannous chloride, to all the reduction products from nitric oxide to ammonia. It is remarkable for the extraordinary rapidity with which its esters are both formed and hydrolysed, the heat of activation being for some reason very small.

The acid and its derivatives are a familiar example of tautomerism. The salts give two series of alkyl derivatives, the true nitrites Alk—O—N=O and the nitro-compounds  $\text{Alk—N}\begin{smallmatrix}\nearrow \text{O} \\ \searrow \text{O}\end{smallmatrix}$. The alkaline salts usually give nitrites, but sometimes (e.g. with chloracetic acid) nitro-compounds: silver nitrite with an alkyl halide gives a mixture of the two, in which the proportion of nitrite is greater the larger the alkyl, and is also greater for secondary halides than for primary, and much greater for tertiary. The ion is the same whichever form of acid it is derived from:





Resonance between these two forms is impossible, as the hydrogen has different positions in the two, but there will be tautomeric equilibrium in solution between the two undissociated forms. The Raman spectrum shows[222] that the ion is triangular, like ozone and SO_2.

Salts of Nitrous Acid

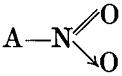
Nitrous acid being weak, and unstable in the free state, does not form salts with weak polyvalent cations like beryllium or aluminium; its simple salts are almost confined to those of the alkalies and alkaline earths, but

[222] A. Langseth and E. Walles, *Z. physikal. Chem.* 1934, B 27, 209.

these are very stable, and also very soluble in water. The solubilities (in g. anhydrous salt to 100 g. water at 25°) are (the irregularities of the series are no doubt connected with the formation of hydrates):

Li	103·6	Ca	83·1	Ag	0·414
Na	91·7	Sr	139·6 (20°)		
K	312·3	Ba	72·4		

The Na and K salts are usually described as anhydrous, but are said[223] to form hydrates with 1/2 H_2O.

The nitrite ion has a strong tendency to form complex salts. These can of course be of two kinds, with the groupings A—O—N=O (nitrito) and  $A\text{—}N\begin{matrix}\nearrow O\\ \searrow O\end{matrix}$ (nitro-); compounds of the former type are rare and unstable, and readily change over into the stable nitro-salts.[224] These nitro-complexes resemble the complex cyanides in preferring particular (sometimes rather peculiar) co-ordination numbers; this number (n in the ion $A(NO_2)_n$ is 2 for Ag', 3 for Hg'', 4 for Pd'' and Pt'' (not for Ni''), 5 for Cu'' (also 6), rare earth metals, Ru''', Os'''; and 6 for Cu'', Bi''', Fe'', Co'', Co''', Ni'', Os^{vi}, Rh^{vi}, Ir''', Pt^{iv}. The nickel compounds are in striking contrast to the nickelicyanides $M_2[Ni(CN)_4]$.

Organic Derivatives: Nitrites R—O—N=O

These esters can be made by the action of nitrous fumes, nitrosyl chloride NOCl, or an alkaline nitrite in presence of acid, on the alcohols. The alkyl nitrites[225] are very volatile pleasant-smelling liquids, with a remarkable power of enlarging the blood-capillaries and lowering the blood-pressure, which makes them of great value in certain affections of the heart, such as angina pectoris. They are remarkable for the extreme rapidity with which they are formed and hydrolysed in presence of hydrogen ion (their hydrolysis by alkalies is no quicker than that of carboxylic esters). Skrabal[226] finds that the rate of hydrolysis is proportional to the concentration of hydrogen ion, and that even when this is reduced to $0{\cdot}7\times10^{-6}$ (in a solution buffered with acetic acid and sodium acetate), the hydrolysis of methyl nitrite is half completed in 4 minutes, giving a half-life in normal acid of less than 1/6000 second. This exceptional velocity may be due to the presence of the unshared pair of electrons on the nitrogen, which makes it a possible donor to co-ordinate with a hydrogen though not with a hydroxyl ion.

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[223] J. Bureau, *Ann. Chim.* 1937, [xi] 8, 5–142.

[224] See for this isomerism Gmelin, *Cobalt B*, p. 7, 1930.

[225] F. Rogowski (*Z. Elch.* 1941, **47**, 152) has shown by electron diffraction that in $CH_3\text{—}O\text{—}N\text{=}O$ the distances are $C\underset{1\cdot44}{\text{——}}O\underset{1\cdot37}{\text{——}}N\underset{1\cdot22}{\text{——}}O$ (theory C—O, 1·43, O—N 1·36, N=O 1·15).

[226] A. Skrabal, A. Zahorka, and K. Weimann, *Z. physikal. Chem.* 1939, **183**, 345.

Nitro-compounds, $\mathrm{R{-}N}\begin{matrix} \nearrow\!\!\!\!{/}\,\mathrm{O} \\ \searrow \mathrm{O} \end{matrix}$

These compounds (whose structure is proved by their being reduced to amines, while the alkyl nitrites on reduction give alcohols and reduction products of nitrous acid) are much more stable, like most compounds which have nitrogen linked to carbon. Rogowski[225] finds in $CH_3\cdot NO_2$ by electron diffraction the distances C—N 1·47, N—O 1·22, O—N—O 135±5°[227] (theory C—N 1·47, N—O 1·36, N=O 1·15 A). They have high dipole moments: $CH_3\cdot NO_2$ 3·19[228]; $CH_3—O—N{=}O$ 2·27 D[229]: which is in accordance with their high boiling-points (some 100° higher than those of the isomeric nitrites):

					Diff.
B.pts.	$CH_3\cdot ONO$	−18°[a]	$CH_3\cdot NO_2$	101°	119°
	Et·ONO	+17°	$Et\cdot NO_2$	114°	97°
	n-Pr·ONO	+47°	*n*-$Pr\cdot NO_2$	131°	84°

a = [230]

Nitromethane has a high dielectric constant of 37 at 25°,[231] but it is not so good an ionizing solvent as this would lead us to expect.[232] This is partly because the range of even slightly soluble salts is limited. Apart from the tetra-ethyl-ammonium salts, all of which are very soluble, only iodides, thiocyanates, and perchlorates could be used. But even of these only the tetra-ethyl-ammonium salts acted as strong electrolytes; the rest gave large negative deviations from the Debye-Hückel curves, indicating imperfect dissociation. The same was true (at least qualitatively) of the acids such as hydrogen chloride that were examined, with the exception of perchloric acid, which proved a reasonably strong electrolyte. The hydrogen ion does not show in this solvent its usual excessive mobility.

Nitrobenzene, with nearly the same dielectric constant (35 at 25°), behaves similarly, but causes rather more ionization.[233]

The crystal structure of *p*-dinitrobenzene[234] shows the whole molecule to be planar, with the N—O distances all 1·23 A and C—N 1·41 (theory N—O 1·36, N=O 1·15, C—N 1·47).

It has been suggested that the reason why these nitro-compounds are so relatively inefficient as ionizing solvents is that ionization in solution depends on both ions being solvated, and that nitro-methane (or nitrobenzene), though it is a strong donor, has no atom that can act as an acceptor and so attach itself to the anions.

[227] J. N. van Niekerk (*Proc. Roy. Soc.* 1943, **181**, 314) gives an X-ray structure for 4, 4′-dinitrodiphenyl, and he says the C—N links are at 22° to the plane of the 2 rings. No parallel case is known.

[228] E. C. E. Hunter and J. R. Partington, *J.C.S.* 1933, 309.

[229] A. Weissberger and R. Sängewald, *Ber.* 1932, **65**, 701.

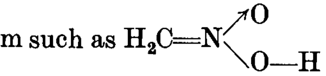
[230] H. W. Thompson and C. H. Purkis, *Trans. Far. Soc.* 1936, **32**, 674.

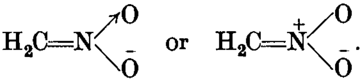
[231] R. T. Lattey and O. Gatty, *Phil. Mag.* 1929, **7**, 985.

[232] C. P. Wright, D. M. Murray-Rust, and H. Hartley, *J.C.S.* 1931, 199.

[233] D. M. Murray-Rust, H. J. Hadow, and H. Hartley, ib. 215.

[234] F. J. Llewellyn, *J.C.S.* 1947, 884.

The nitroparaffins (except the tertiary) behave in water as pseudo-acids; they go over more or less rapidly into equilibrium mixtures with an acidic hydroxyl form such as  $H_2C{=}N\begin{smallmatrix}\nearrow O\\ \searrow O{-}H\end{smallmatrix}$; sometimes, as with phenyl-nitromethane and bromophenyl nitromethane, the two forms can be isolated. The hydroxy-form gives an ion which can be written as



$$H_2C{=}N\begin{smallmatrix}\nearrow O\\ \searrow \bar{O}\end{smallmatrix} \quad \text{or} \quad H_2C{=}\overset{+}{N}\begin{smallmatrix}\diagup O\\ \diagdown \bar{O}\end{smallmatrix}.$$

The acidity of the nitroparaffins increases with the number of nitro-groups present; thus nitroethane $CH_3 \cdot CH_2 \cdot NO_2$ has a dissociation constant of $4 \cdot 1 \times 10^{-5}$ [235]—about twice as great as that of acetic acid—while nitroform $CH(NO_2)_3$ is quite a strong acid.[236]

The organic nitro-compounds, especially the aromatic, have a remarkable power of forming addition compounds with a variety of other substances, even aromatic hydrocarbons; the nature of these compounds is still obscure.[237] Their formation in solution is in many cases indicated by the production of colour; often too, solid phases can be isolated with the composition of addition compounds; these solids are likewise often highly coloured. It is not necessary to the phenomenon, either in the solid or in the liquid, that the nitro-compound used should be aromatic or that the hydrocarbon should contain unreplaced aromatic hydrogen: both tetra-nitromethane and hexa-methyl benzene are very efficient components. The nature of the linkage, either in the solid or in the liquid, is doubtful. The production of colour, with such highly polar and highly polarizable components, is not necessarily a proof of chemical linkage; but Hammick and Young,[238] using it as a measure of the amount of combination, get satisfactory reaction constants; often[239] the stability of the complex is found to increase with the number of methyl groups in the hydrocarbon. Sometimes[240] the rate of formation of the complex is slow, indicating that there is a heat of activation.

In the solid state the best evidence should be afforded by the crystal structure; in the few cases where this has been applied it has shown that there is no chemical combination. Thus Powell[241] found that in the solid compound of picryl chloride $C_6H_2(NO_2)_3Cl$ with hexamethyl benzene there

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[235] S. H. Maron and T. Shedlovsky, *J.A.C.S.* 1939, **61**, 753.

[236] See further, G. W. Wheland and J. Farr, ib. 1943, **65**, 1433.

[237] See D. Ll. Hammick in Taylor and Baker, *Organic Chemistry of Nitrogen* (1937), p. 261.

[237a] D. E. Palin and H. M. Powell, *J.C.S.* 1947, 208.

[237b] H. M. Powell, ib. 1948, 61.

[237c] D. E. Palin and H. M. Powell, ib. 815.

[238] D. Ll. Hammick and G. P. Young, ib. 1936, 1463.

[239] T. T. Davies and D. Ll. Hammick, ib. 1938, 763.

[240] D. Ll. Hammick and G. Sixsmith, ib. 1935, 580.

[241] H. M. Powell and G. Huse, *Nature*, 1939, **144**, 77; *J.C.S.* 1943, 435.

is no valency linkage between the two components; the crystal consists of successive layers of picryl chloride and the hydrocarbon, and these layers are 3·5 A apart, the usual distance for two non-linked neighbours in a crystal which are held together only by van der Waals forces. With the 1:1 complex of *p*-iodoaniline and symmetrical trinitrobenzene they find[242] no evidence of covalent union; the shortest distances from the N of the NH_2 to the nearest oxygen of the next molecule are 3·1, 3·2, and 3·3 A, which they say cannot be hydrogen bonds (but weak hydrogen bonds of 2·98 and 3·03 A have been found in urea). Crystal structures indicate the same absence of linkage between the components in the 1:1 addition compound of 4,4′-dinitrodiphenyl with 4,4′-dihydroxy-diphenyl.[243] The same is true of the complexes formed by this nitro-compound with N-tetramethyl benzidine, 4-iodo- and 4-bromo-diphenyl.[244]

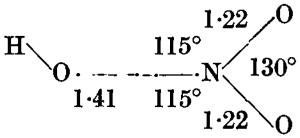
For further examples of solid addition products where there are no chemical links between the components, and especially for evidence that molecules of one component may be mechanically entangled in a giant molecule of the other ('clathrate' compounds), see Powell.[237a–c]

Nitric Acid, HNO_3

This is the ultimate product of the action of water and air on the lower oxides of nitrogen; it is also formed by the decay of organic matter. Commercially it is made either from Chili saltpetre ($NaNO_3$) or from air by the action of the electric arc, or by the burning of synthetic ammonia.

It melts at −41·4° and boils at 86°, but with some decomposition into water and nitrogen pentoxide. The constant boiling mixture with water boils at 123° and contains 69·8 per cent. of HNO_3: this is the ordinary 'concentrated' acid, of density 1·42. (Ordinary 'strong' sulphuric, nitric, and hydrochloric acids contain roughly 3/3, 2/3, and 1/3 of pure acid respectively.)

The electron diffraction of HNO_3 in the vapour has been examined by L. R. Maxwell and V. M. Mosley.[245] They find the most probable structure to be



The distances are long—the normal values are N—O 1·36, N=O 1·15. The molecule is planar.

In water nitric acid is one of the strongest acids, but in solvents of lower dielectric constant it assumes the covalent form much more readily than hydrochloric, and still more than perchloric acid. Hantzsch has shown[246] that aqueous solutions of nitric acid and its salts have an absorption

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[242] H. M. Powell, G. Huse, and P. W. Cooke, ib. 1943, 153.

[243] D. H. Saunder, *Proc. Roy. Soc.* 1946, **188**, 31.

[244] Id., ib. 1947, **190**, 508.

[245] *J. Chem. Phys.* 1940, **8**, 738.

[246] *Z. physikal. Chem.* 1930, **149**, 161.

spectrum in the near ultra-violet which is absent from the 100 per cent. acid, its ethereal solution, and its esters. This must be the spectrum of the (perhaps hydrated) ion NO_3'. The high conductivity of the 100 per cent. acid, which should thus contain no NO_3' ions, is ascribed by Hantzsch to the formation of a base $[ON(OH)_2]OH$, of which he has obtained the perchlorate $[ON(OH)_2]ClO_4$. See further, Redlich[247] and Bennett.[248-50]

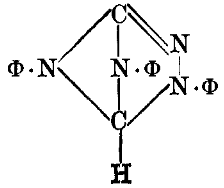
An idea of the way in which the strength of nitric acid in water falls off as the concentration increases (as compared with hydrochloric acid) is given by the results of B. Blaser[251] on its influence on the rate of hydrolysis (which is proportional to the hydrogen-ion concentration) of hypophosphoric acid $H_4P_2O_6$ into phosphoric+phosphorous acids $H_3PO_4+H_3PO_3$. The relative values are:

Normality of acid	1·9	5·75	8·39
Rate with HCl	0·32	4·6	14·0
Rate with HNO_3	0·31	2·1	4·1

Ortho-nitric Acid. A possible form of nitric acid is the fully hydrated ortho-acid $O \leftarrow N(OH)_3$, corresponding to ortho-phosphoric acid H_3PO_4. Though no salts of this acid have been established, there is some reason to think that the acid exists. Zintl and Haucke[252] conclude from the X-ray powder diagram of the monohydrate HNO_3,H_2O that it is not improbably the ortho-acid $ON(OH)_3$. The same conclusion is reached by Biltz[253] from the volume increments on adding water and the thermal expansion; he further concludes that the trihydrate is really H_3NO_4, 2 H_2O.

The reactions of nitric acid are mostly familiar, it is a powerful oxidizing agent: it is reduced by hydrogen in the cold in presence of platinum sponge to ammonia. It dissolves all the metals except chromium, rhodium, platinum, and gold; it converts tin into the dioxide SnO_2.

Nitrates, inorganic. The nitrates of all simple inorganic bases are readily soluble in water; for example, 100 g. of water will dissolve the following amounts in grammes (as anhydrous salts) at 20°: $LiNO_3$ 72·4; $NaNO_3$ 88·0; KNO_3 31·6; $RbNO_3$ 53·4; $CsNO_3$ 23·0; and at 25° $AgNO_3$ 254·6 g.; $Cu(NO_3)_2$ 150·0; Mg 77·2; Ca 132·6; Sr 383·0; Ba 10·2; Zn 126·7; Cd 135·0. The nitrates of especially weak bases like mercuric oxide, or of metals with valencies of 3 or 4, are often hydrolysed by water to give basic salts or even (as with stannic nitrate) the oxides of the metals. The nitrates of organic bases are also as a rule readily soluble, but a few are not; that of diphenyl-endo-anilino-dihydrotriazol or 'nitron' (to which the sterically improbable structure is commonly ascribed) is practically insoluble, and can be used for the estimation of nitrate ion.



The nitrates of the alkali metals and of ammonium are all polymorphic, and it is at least probable that this is due to the fact that at the lower temperatures the NO_3 ion is at rest, while at the higher it is rotating. See above, p. 662 and reference [254].

Complex Nitrates

The nitrate ion, like those of other strong monobasic oxy-acids, is very reluctant—almost as much so as the perchlorate ion—to assume the 'ato' form, in which it is covalently linked to an atom other than hydrogen (or carbon). A moderate number of double nitrates are known, such as the isomorphous series $3\,M''(NO_3)_2$, $M'''(NO_3)_3$, $24\,H_2O$ (III. 449), where $M'' = Co''$, Ni, Zn, Cd, and $M''' =$ Bi or any of the rare earth metals La, Ce, Pr, Nd, Sm, and Gd; but in these salts there is no sign of complexity: in fact their formulation as complexes $M''[M'''(NO_3)_9]$, $24\,H_2O$ would involve the improbable co-ordination number of 9.

In some complexes, however, the nitrate group is beyond doubt linked covalently to the central atom. This happens with trivalent chromium in the salt $[Cr(NH_3)_5NO_3]X_2$, and with auric gold (I. 189) in the salts $M'\,Au(NO_3)_4$, $3\,H_2O$ ($M' =$ H, K, Rb, NH_4); but it is chiefly found with the elements of Group VIII, such as Co'', Rh^{iii}, Ir^{iii}, Pt'', Pt^{iv} (VIII. 1524, 1620; see also Werner, N. A., ed. 5 (1923), pp. 191, 192, 193, 218, 271, 279, 339).

Thermal Decomposition

On heating to rather high temperatures the metallic nitrates decompose, some to give nitrites and oxygen, others to give the metallic oxides (or the free metals) and the oxides of nitrogen.* Centnerszwer[255] points out that the general type of thermal decomposition of the nitrates is

$$2\,MNO_3 \xrightarrow{T_a} 2\,MNO_2 \xrightarrow{T_i} M_2O + NO + NO_2.$$

The melting-points and decomposition temperatures (T_a) of the nitrates increase with the atomic weight of the metal, but with all the alkaline nitrates T_a is lower than T_i, the decomposition temperature of the nitrite

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* This makes it impossible to prepare the anhydrous nitrates of many polyvalent cations with a strong affinity for water, such as Be (II. 206), Zn (276), Hg'' (325), and divalent Cu'' (I. 155).

[247] O. Redlich, *Z. physikal. Chem.* 1938, **182**, 42.

[248] G. M. Bennett, J. C. D. Brand, and G. Williams, *J.C.S.* 1946, 869, 875.

[249] G. M. Bennett, J. C. D. Brand, D. M. James, T. G. Saunders, and G. Williams, ib. 1947, 474.

[250] Id., ib. 1185.

[251] *Z. physikal. Chem.* 1933, **166**, 59.

[252] E. Zintl and W. Haucke, ib. 1935, **174**, 312.

[253] W. Biltz, O. Hülsmann, and W. Eicholz, *Nachr. Ges. Wiss. Gött.* 1935, [ii] **1**, 95.

[254] C. Finbak and O. Hassel, *J. Chem. Phys.* 1937, **5**, 460; *Z. physikal. Chem.* 1937, B **35**, 25; B **37**, 75, 468.

[255] M. Centnerszwer, *Rocz. Chem.* 1938, **19**, 419; *B.C.A.* 1939, i. 263.

and both of these temperatures are above the melting-points. Hence the nitrate first melts and then changes into the nitrite. With the alkaline earth nitrates, T_a is again lower than T_i, but the melting-points are higher than both. With silver and lead, T_a is higher than T_i, and so the products are not the nitrite and oxygen, but metallic silver or lead oxide along with the oxides of nitrogen and oxygen itself.

Halides of the Oxyacids of Nitrogen

Nitrous and nitric acids both form a series of acid halides, the nitrosyl halides O═N·hal, and the nitroxyl halides O_2N·hal.

Nitrosyl Fluoride, O═N·F

This can be made by distilling nitrosyl chloride over silver fluoride in a platinum vessel at 200-250°,[256-7] or better by the combination of nitric oxide and fluorine. It is a colourless gas, boiling at −59·9°, and melting at −132·5. Vapour density normal: Trouton constant 21·6. It is very reactive. It slowly attacks glass, with the production of N_2O_3 and SiF_4; it is at once hydrolysed by water, giving the usual blue solution, which evolves nitric oxide, leaving nitric and hydrofluoric acids. Its action on most elements is like that of elementary fluorine: silicon, bismuth, red phosphorus, arsenic, and antimony catch fire in the gas. In most of its reactions it behaves like nitroxyl fluoride NO_2F, but it differs from it in that it is not reactive with iodine.

A singular reaction[257] is that on mixing, even at low temperatures, with the relatively inactive oxygen fluoride OF_2 it explodes; if the gases are slowly mixed, they react thus:

$$NOF + OF_2 = O_2 + NF_3.$$

Nitrosyl Chloride, O═N·Cl

This is formed by the combination of nitric oxide and chlorine at −80°,[258] or at the ordinary temperature in presence of charcoal; from hydrogen chloride and nitrogen peroxide, together with some nitroxyl chloride; and from the action of phosphorus pentachloride on potassium nitrite or of nitrogen peroxide on moist potassium chloride.[259] It is one of the gases evolved, along with nitroxyl chloride, chlorine, and the oxides of nitrogen, from aqua regia. B.pt. −5·8°, m.pt. −61·5°, vapour density normal.

Electron diffraction[260] shows the distances in nitrosyl chloride and bromide to be Cl—N 1·95, Br—N 2·14, N═O 1·15 (theory 1·69, 1·84, 1·15). The surprisingly large halogen-nitrogen distances are ascribed to resonance

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[256] O. Ruff and K. Staüber, *Z. anorg. Chem.* 1905, 47, 190.

[257] O. Ruff, W. Menzel, and W. Neumann, ib. 1932, 208, 293.

[258] For the kinetics of this reaction see E. M. Stoddart, *J.C.S.* 1944, 388.

[259] C. N. Whittaker, F. O. Lundstrom, and A. R. Merz, *Ind. Eng. Chem.* 1931, 23, 1410.

[260] J. A. A. Ketelaar and K. J. Palmer, *J.A.C.S.* 1937, 59, 2629.

with an ionic structure. The dipole moments in carbon tetrachloride solution are 1·83 and 1·87 D.[261] The liquid (D.E.C. 18·2/12°, conductivity $2{\cdot}88 \times 10^{-6}/-20°$) is a good ionizing solvent for salts of the nitrosyl cation, such as $[NO]FeCl_4$.[261a]

It is very reactive; with water at 0° it forms HCl and HNO_2; with alkalies, a chloride and a nitrite. It reacts with most organic compounds, and in various ways, chlorinating, diazotizing, oxidizing, and 'nitrositing', i.e. forming nitro-compounds and nitrous esters.

It has a strong tendency to form addition compounds with a variety of inorganic chlorides either X, NOCl (X = CuCl, $AuCl_3$, $ZnCl_2$, $BiCl_3$, $AlCl_3$, $TiCl_2$, $SnCl_2$, $SbCl_5$) or Y, 2 NOCl (Y = $TiCl_4$, $SnCl_4$, $PbCl_4$, $PtCl_4$). In all these compounds it is obvious that the NOCl acts as a donor.

Jahn[262] has calculated the thermodynamical values for nitrosyl chloride from the electron diffraction and the absorption spectrum; Beeson and Yost[263] on the whole agree. Jahn thus gets the heat of formation of 2 NOCl from $N_2+O_2+Cl_2$ as −25·9 k.cals. (endothermic); this gives H_a 186·1, and allowing 47·6 for N—Cl, N=O = 138·5 k.cals., a remarkably high value, owing presumably to resonance.

Nitrosyl Bromide, O=N—Br

This is slowly formed by the action of bromine on nitric oxide[264]; it is little known. B.pt. +25°, m.pt. −55·5°; it behaves like the chloride.

Nitrosyl iodide O=N—I does not seem to be known.

Nitroxyl Fluoride, $O_2N \cdot F$

Formed from nitrogen peroxide and excess of fluorine, with slight evolution of heat.[257,265] B.pt. −72·4°; m.pt. −166°; Trouton constant 21·5. Vapour density normal. It is colourless; it attacks glass less quickly than nitrosyl fluoride. Water converts it into nitric and hydrofluoric acids; chlorine has no action, but iodine is converted into IF_5. In general it resembles NOF.

Nitroxyl Chloride, $O_2N \cdot Cl$

This is formed from nitrogen peroxide and chlorine at a low red heat; from silver nitrate and phosphorus oxychloride; from phosphorus pentachloride and nitric acid; by the action of ozone on nitrosyl chloride.[266] It decomposes on heating into nitrogen peroxide and chlorine (for kinetics see ref. [267]). With water it gives hydrochloric and nitric acids, and with acetic anhydride acetyl chloride and acetyl nitrate. Steinkopf and Kuhnel[268]

[261] J. A. A. Ketelaar, *Rec. Trav.* 1943, **62**, 289.

[261a] A. B. Burg and G. W. Campbell, *J.A.C.S.* 1948, **70**, 1964.

[262] F. P. Jahn, *J. Chem. Phys.* 1938, **6**, 335.

[263] C. M. Beeson and D. M. Yost, ib. 1939, **7**, 44.

[264] See M. Trautz and V. P. Dalal, *Z. anorg. Chem.* 1920, **110**, 34.

[265] H. Moissan and P. Lebeau, *C.R.* 1905, **140**, 1573, 1621.

[266] H. J. Schumacher and G. Sprenger, *Z. Elektrochem.* 1929, **35**, 653.

[267] Id., *Z. physikal. Chem.* 1931, B **12**, 115.

[268] W. Steinkopf and M. Kuhnel, *Ber.* 1942, **75**, 1323.

have shown that it adds on to unsaturated carbon compounds, converting C=C either into CCl—CCl or into CCl—C·NO_2.

Nitroxyl Bromide, NO_2Br

This is said to be formed from nitrogen peroxide and bromine at 200-50°,[269] but it seems doubtful whether it exists.

Boiling-points of these acyl halides:

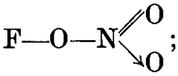
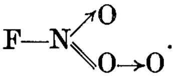
	F	Cl	Br	$NOBr_3$
NO·hal.	−59·9°	−5·8°	+25°	+32°
NO_2·hal.	−72·4°	−15°	?	..

Nitrosyl Tribromide, $NOBr_3$

Early work on this compound (Landolt, 1860; Roozeboom, 1885) is rather doubtful; but Trautz and Dalal[264] isolated from the system NO+Br_2 a solid compound $NOBr_3$, m.pt. −40°, which begins to boil at 32° with some decomposition, but on rapid distillation suffers little loss. See also reference [270]. This is the only known nitrogen analogue of the phosphoryl halides, such as $POCl_3$.

'*Fluorine Nitrate*', NO_3F

This remarkable compound was discovered in 1934 by Cady,[271] who made it by the action of fluorine on 3-normal nitric acid; later Ruff[272] showed that it is better to use 100 per cent. nitric acid at the ordinary temperature in a quartz apparatus; it can also be made by the action of fluorine on potassium nitrate.[273] It is a colourless gas, of density corresponding to NO_3F, which condenses to a colourless liquid and solid; m.pt. −175°, b.pt. −45·9°; Trouton constant 20·8.[272] Either as solid liquid or gas it explodes readily and violently on heating, on shock, and often for no apparent reason. It is stable in a dry glass vessel; water converts it (rather slowly) into oxygen, oxygen difluoride[272] [and some unspecified nitrogen compound}. Two per cent. sodium hydroxide gives OF_2 and 20 per cent. gives O_2.[272] It is a very strong oxidizing agent; it converts vanadyl (VO^{++}) salts into vandates, silver salts into a black peroxide Ag_2O_3, and manganous salts in the presence of silver ions into permanganates.[273]

Ruff[272] suggested on chemical grounds the structure  $F—O—N\begin{smallmatrix}\nearrow\!\!\!\!/\,O\\ \searrow O\end{smallmatrix}$; the only other reasonable possibility seems to be  $F—N\begin{smallmatrix}\nearrow O\\ \searrow\!\!\!\!\backslash\, O\rightarrow O\end{smallmatrix}$. Pauling and

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[269] N. Zuskine, *Bull. Soc. Chim.* 1925, [4] **37**, 187.

[270] R. L. Datta and N. R. Chatterjee, *J.A.C.S.* 1923, **45**, 481.

[271] G. H. Cady, ib. 1934, **56**, 2635.

[272] O. Ruff and W. Kwasnik, *Angew. Chem.* 1935, **48**, 238.

[273] D. M. Yost and A. Beerbower, *J.A.C.S.* 1935, **57**, 782.

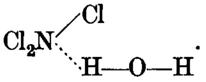
Brockway[274] found by electron diffraction results that agree best with Ruff's formula: O—N—O angle 125±5°; F—O—N 105±5°; and the rather unusual values of the distances (the theoretical values follow each in brackets): N—O terminal 1·29, N—O of N—O—F 1·39 (theory N—O 1·36, N=O 1·15), O—F 1·42 (1·30)—all these distances ±0·05 A.

The preparation and general properties were confirmed by Hill and Bigelow.[275]

Nitrogen Halides

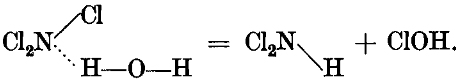
Nitrogen fluoride NF_3 was first made by Ruff in 1928,[276] by the electrolysis of ammonium acid fluoride NH_4F_2H. It is a gas, b.pt. −129°, m.pt. −208·5°[280-1]: Trouton constant 19·9. It is surprisingly inactive: it is insoluble in water, and is not acted on, except at high temperatures, by water, alkalies, sulphuric acid, silver, or manganese dioxide; ammonia, methane, and carbon monoxide do not react below a red heat, and acetylene and sulphur dioxide not at all. If its mixture with steam is sparked, it explodes feebly, forming HF and oxides of nitrogen. It is said[277] to be poisonous to animals, causing cyanosis at a dilution of 1/200 in air, but this may be due to an impurity.

The inactivity with water is easily accounted for. Nitrogen chloride is readily decomposed by water into ammonia and hypochlorous acid, presumably through the intermediate formation (no doubt only to a small extent) of a co-ordination product with the water, linked through the hydrogen, since the nitrogen can only act as a donor:



$$\mathrm{Cl_2N}\begin{array}{l}\diagup\mathrm{Cl}\\ \cdots\mathrm{H{-}O{-}H}\end{array}.$$

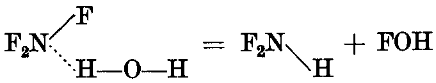
The N—H link being more than twice as strong as N—Cl (83 as against 39 k.cals.), the OH breaks off with a chlorine atom as HOCl:



$$\mathrm{Cl_2N}\begin{array}{l}\diagup\mathrm{Cl}\\ \cdots\mathrm{H{-}O{-}H}\end{array} = \mathrm{Cl_2N}\begin{array}{l}\\ \diagdown\mathrm{H}\end{array} + \mathrm{ClOH}.$$

By the repetition of this process the NCl_3 is converted into NH_3.

Now NF_3 must have much the same power of co-ordinating with the water as NCl_3, and must do so; but the second stage of the reaction



$$\mathrm{F_2N}\begin{array}{l}\diagup\mathrm{F}\\ \cdots\mathrm{H{-}O{-}H}\end{array} = \mathrm{F_2N}\begin{array}{l}\\ \diagdown\mathrm{H}\end{array} + \mathrm{FOH}$$

is impossible, because hypofluorous acid does not exist. The inactivity of nitrogen fluoride shows that this is the only mechanism by which hydrolysis

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[274] L. Pauling and L. O. Brockway, ib. 1937, **59**, 13.

[275] D. G. Hill and L. A. Bigelow, ib. 2127.

[276] O. Ruff, J. Fischer, and F. Luft, *Z. anorg. Chem.* 1928, **172**, 417.

[277] O. Ruff, ib. 1931, **197**, 273.

[278] See also O. Ruff and E. Hanke, ib. 395.

[279] O. Ruff and L. Staub, ib. **198**, 32.

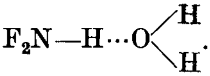
[280] O. Ruff and W. Menzel, ib. 1934, **217**, 93.

occurs at the ordinary temperature, i.e. without a very large heat of activation.

The other striking difference, that the trichloride is violently explosive by itself, and the trifluoride is not, is due to the trichloride being an exothermic and the trifluoride an endothermic substance; the heats of decomposition are:

$$2\,NF_3 = N_2 + 3\,F_2 \quad -\ 53{\cdot}0 \text{ k.cals.}$$
$$2\,NCl_3 = N_2 + 3\,Cl_2 \quad +110{\cdot}8 \quad ,,$$

The trifluoride is not the only product of the electrolysis of $[NH_4]F_2H$; NH_2F and NHF_2 are formed at the same time, and also a very remarkable lower fluoride NF_2.[279] This last has not been obtained in the pure state, as its b.pt. (*circa* −125°) is too near that of NF_3 (−129°).[279] These compounds are all more reactive than NF_3; when there is a hydrogen on the nitrogen, a hydrogen bond can be formed, as in



$$F_2N\text{—}H\cdots O\begin{matrix}\diagup H\\ \diagdown H\end{matrix}.$$

NH_2F.[278] Vapour density normal. It is a solid subliming under 1 atmosphere at −77°. This is the most stable after NF_3, but it reduces Fehling's solution at once.

NHF_2. B.pt. about −65°, m.pt. about −125°. This has not been obtained pure. It is at once absorbed by water.

NF_2. This is formed in the smallest yield in the electrolysis of $[NH_4]F_2H$, and has not been purified. B.pt. about −125°. Its vapour density was found to be 27 (mol. wt. 54: NF_2 = 52). It is presumably to be regarded as a substitution product of nitric oxide.

N_2F_2. This has recently been made by the decomposition of N_3F; it is a colourless gas smelling like NO_2, and condensing to a colourless solid at about −100°.[281a] Electron diffraction shows[281b] that it consists of about equal parts of the *cis* and *trans* forms of F—N=N—F, with the distances F—N 1·44, N=N 1·25 (both ±0·04: theory F—N 1·34, N=N 1·20).

Nitrogen Chloride, NCl_3

This was discovered by Dulong in 1811. It is formed by the action of chlorine on ammonia. The solution must be kept feebly acid, or we get the reaction

$$NCl_3 + 4\,NH_3 = N_2 + 3\,NH_4Cl.$$

It can also be made by the electrolysis of ammonium chloride, or by the action of phosphorus pentachloride on nitrosyl chloride:

$$NOCl + PCl_5 = NCl_3 + POCl_3.$$

It is a dense pale yellow oil, b.pt. 71°, m.pt. about −27° (Porret, 1813: no later determinations seem to have been made).

Its chief characteristic is the violent explosions which it gives on heating

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[281] W. Menzel and F. Mohry, *Z. anorg Chem.* 1933, **210**, 257.

[281a] J. F. Haller, *Diss. Cornell*, 1942.

[281b] S. H. Bauer, *J.A.C.S.* 1947, **69**, 3104.

above its boiling-point, or on exposure to sunlight or even diffuse daylight, or on coming into contact with many organic substances, especially unsaturated compounds such as turpentine.

It is decomposed by water into ammonia and hypochlorous acid[282-3]; in presence of hydrochloric acid the solution evolves chlorine. Dry hydrogen converts it quantitatively into ammonium chloride and chlorine.[285] All these reactions are in accordance with the above formulation of the hydrolytic mechanism.

The lower chlorination products of ammonia, NH_2Cl and $NHCl_2$, can both be formed, though only the former has yet been isolated.[283-5] Chapin[286-7] finds that when chlorine acts on aqueous ammonia, if p_H is greater than 8·5, the only product is NH_2Cl: at p_H 4·5–5·0 it is practically only $NHCl_2$, and at p_H less than 4·4 only NCl_3.

$NHCl_2$ has not been isolated, but its presence was detected, and its amount determined, by Chapin by partition between water and other solvents. The values found for $p = C$ (solvent)/C (water) were chloroform 1·88, CCl_4 0·85, ether 47·3. The value for the partition of NCl_3 in CCl_4 is very high, so that the NCl_3 can be separated from the $NHCl_2$ in this way.

NH_2Cl. It is formed by the action of sodium hypochlorite on ammonia, and comes off with the first portions of the distillate under reduced pressure.[288] The vapour can be dried by passing it over potassium carbonate. At −65° it forms a colourless liquid with very low vapour pressure: it freezes at −66°. It is liable to change explosively into NCl_3 and NH_4Cl. It is very slightly soluble in benzene, chloroform, or CCl_4: it is about as soluble in alcohol or ether as in water. The kinetics of its reactions have been examined by Bodenstein.[289-90] The chief reaction is

$$3\,NH_2Cl = NH_4Cl + N_2 + 2\,HCl$$

which is made up of two reactions:

$$(a)\ NH_2Cl + NH_3 = H_2N{-}NH_2 + HCl;$$

$$(b)\ H_2N{-}NH_2 + 2\,NH_2Cl = N_2 + 2\,NH_4Cl.$$

The purpose of the various catalysts used in the preparation of hydrazine (glue, copper, *pure* water: see below, p. 709) is to delay reaction *b*.

Alkalies decompose chloramine thus:

$$3\,NH_2Cl + 3\,KOH = NH_3 + N_2 + 3\,KCl + 3\,H_2O.$$

It is to be noticed that chloramine does not under any circumstances give hydroxylamine.

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[282] T. Selivanov, *Ber.* 1894, **27**, 1012.

[283] W. Hentschel, ib. 1897, **30**, 1434.

[284] Id., ib. 1792.

[285] W. A. Noyes, *J.A.C.S.* 1920, **42**, 2173.

[286] R. M. Chapin, ib. 1929, **51**, 2112.

[287] Id., ib. 1931, **53**, 912.

[288] W. Marckwald and M. Wille, *Ber.* 1923, **56**, 1319.

[289] M. Bodenstein, *Z. physikal. Chem.* 1928, **137**, 131.

[290] Id., ib. **139**, 415.

Nitrogen Bromide

NBr_3 is said to be a dark red explosive liquid (Millon, 1838), but it is very doubtful whether it has ever been prepared.

A dark purple solid NBr_3, 6 NH_3 is formed[291-2] when bromine acts on ammonia under 1–2 mm. pressure at $-95°$; it decomposes explosively at $-70°$ to nitrogen, ammonium bromide, and ammonia.

The intermediate compounds NH_2Br and $NHBr_2$ are formed by the action of bromine on ammonia in ether, the latter at $-50°$, but they have not been isolated.[293-4] They behave like the chloramines.

Nitrogen Iodides

The constitution of these compounds is uncertain, because they are solids, and highly explosive. The ordinary product, obtained by the action of iodine on aqueous ammonia, has the composition $N_2I_3H_3$.[282,295] But if the reaction is carried out at low temperatures in liquid ammonia, solid compounds of the compositions NI_3, NH_3 up to NI_3, 12 NH_3 are formed. Pure NI_3 has never been isolated. There seems to be no doubt that the ordinary iodide is NI_3, NH_3 (whatever may be the precise co-ordination); it is the ultimate product when the higher ammoniates are left *in vacuo* at temperatures above $-25°$,[296] and it has been shown by Silberrad[297] that when it is treated with zinc ethyl in ether, triethylamine is formed, with no traces of mono- or diethylamine; he concludes that all three iodine atoms are attached to the same nitrogen, but he only got a 3·5 per cent. yield.

It has the reactions to be expected of NI_3: with water alone it decomposes to nitrogen sesquioxide and hydrogen iodide; with acids or alkalies it forms ammonia and hypoiodous acid.

For further work on the dynamics of the formation and hydrolysis of nitrogen iodide all compatible with the formula NH_3, NI_3, see references [298-300].

Substituted Nitrogen Halides

A large number of nitrogen halides derived from amines and amides (especially chlorides) are known, which in their general behaviour resemble the simple halides.

The electron diffraction of dimethyl chloramine $(CH_3)_2N \cdot Cl$ and methyl dichloramine $CH_3 \cdot NCl_2$ has been measured[301]; the N—Cl distances are 0·08 and 0·05 A, respectively, longer than the calculated 1·69, a lengthening

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[291] L. Birckenbach and M. Linhard, *Ber.* 1929, **62**, 2265, Anm. 1.

[292] M. Schmeisser, *Naturwiss.* 1940, **28**, 63.

[293] W. Moldenhauer and M. Burger, *Ber.* 1929, **62**, 1615.

[294] G. H. Coleman, C. B. Yager, and H. Soroos, *J.A.C.S.* 1934, **56**, 965.

[295] F. D. Chattaway and K. J. P. Orton, *Am. Chem. J.* 1900, **24**, 344.

[296] O. Ruff, *Ber.* 1900, **33**, 3025.

[297] O. Silberrad, *J.C.S.* 1905, **87**, 55.

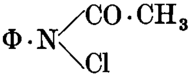
[298] E. Roederer, *Z. anorg. Chem.* 1936, **226**, 145.

[299] F. R. Meldrum, *Trans. Far. Soc.* 1938, **34**, 947.

[300] Id., *Proc. Roy. Soc.* 1940, **174**, 410.

[301] D. P. Stevenson and V. Schomaker, *J.A.C.S.* 1940, **62**, 1913.

that is found elsewhere in links between two highly electronegative elements.

Of the simple aniline derivatives $C_6H_5\cdot NHCl$ has not been isolated, and $C_6H_5\cdot NCl_2$ is explosive. The acetyl derivative  $\Phi\cdot N\begin{matrix}\nearrow CO\cdot CH_3\\ \searrow Cl\end{matrix}$ is more stable, and can be made by treating acetanilide with bleaching powder. The chlorine readily migrates to the ortho- and para- positions on the ring, this change being catalysed by acids, and specifically by hydrogen chloride. The change might be due to direct migration, or to the reaction of the chlorine on the nitrogen with that of the acid to give free chlorine (reverse substitution), and the chlorination of the nucleus by the latter. Recent work by Olson *et al.*,[302-3] in which the hydrogen chloride used contained radioactive chlorine, has shown that the reaction goes mainly if not wholly through the free chlorine formed in this way. This 'reverse substitution' ($A—Cl+HCl = A—H+Cl_2$, as with B—Cl and Si—Cl) is explained by the heats of the reactions, which are:

$$C—H + Cl—Cl = C—Cl + H—Cl + 24{\cdot}1 \text{ k.cals.}$$
$$N—H + Cl—Cl = N—Cl + H—Cl - 0{\cdot}4 \text{ k.cals.}$$

Chloramine-T is made from the amide of toluene-*p*-sulphonic acid; the chloramines of sulphonamides resemble those of carboxylamides, but are much more stable. Chattaway has shown[304] that a sulphonamide gives with bleaching powder $Ar\cdot SO_2\cdot NCl_2$, which with sodium hydroxide forms a salt $Ar\cdot SO_2\cdot NCl[Na]+NaOCl$. This salt is chloramine-T, a strong germicide used for the treatment of wounds.

COMPOUNDS WITH N—N GROUPS

Nitrogen has a relatively small power of forming chains, and these are always unstable if they contain more than two nitrogens, although among organic compounds chains of as many as 8 nitrogen atoms are known. Their instability is largely due to the much greater energy evolved in forming the N≡N link, which promotes decomposition of the chain with the evolution of nitrogen gas.

Among the inorganic nitrogen compounds, the only chains that occur are those of two nitrogens in hydrazine and its derivatives, and those of three in hydrazoic acid and the azides; Dimroth[305] has obtained evidence of the existence in solution of triazene $H_2N—N{=}NH$, the parent of the diazo-amino-compounds, but it has not been isolated.

Hydrazine, $H_2N—NH_2$

Hydrazine was first obtained by Curtius in 1887[306] from organic sources. It is formed in small quantity by the combination of hydrogen with

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[302] A. R. Olson, C. W. Porter, F. A. Long, and R. S. Halford, *J.A.C.S.* 1936, **58**, 2467.

[303] A. R. Olson, R. S. Halford, and J. C. Hornel, ib. 1937, **59**, 1613.

[304] F. D. Chattaway, *J.C.S.* 1905, **87**, 145.

[305] O. Dimroth and K. Pfister, *Ber.* 1910, **43**, 2757.

[306] T. Curtius, *Ber.* 1887, **20**, 1632.

nitrogen in the presence of certain catalysts, or by the action of an incandescent tungsten wire in liquid ammonia.[307] It is best prepared by Raschig's method[308-9] of oxidizing ammonia with sodium hypochlorite in presence of gelatine or glue. The first effect is the production of chloramine:

$$NH_3 + NaOCl = NaOH + H_2NCl.$$

The chloramine then reacts in two ways:

$$(1)\ 2\ NH_2Cl + HOCl = N_2 + 3\ HCl + H_2O$$

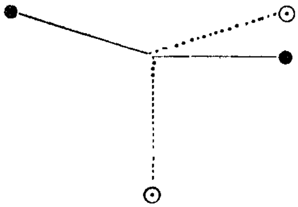
$$(2)\ H_2N{\cdot}Cl + H{\cdot}NH_2 = H_2N{-}NH_2 + HCl.$$

The presence of gelatine or glue retards the first reaction. The same result can be attained in the absence of catalysts by using specially purified water, free from traces of metals.[309]

Anhydrous hydrazine can be obtained by treating the hydrochloride with a solution of sodium methylate in methyl alcohol, or the hydrate with barium oxide. It boils at 113·5° and melts at +1·8°; the Trouton constant is 25·8. According to Eucken[310] the vapour is largely dimeric; but other work does not confirm this.[311-12] Liquid hydrazine must be associated, as it has so high a boiling-point and Trouton constant. For the heat of formation see Roth.[313]

Electron diffraction[312] gives the N—N distance in the vapour as 1·47 A (theory 1·40), the same as the O—O in H_2O_2 (theory 1·32).

The structure of the gaseous hydrazine molecule has been worked out by Penney and Sutherland[314-15] with the help of the Raman spectrum and the dipole moment. They show that the NH_2 groups can have no freedom of rotation, owing no doubt to the steric repulsion of the hydrogen atoms, so that the molecule must be unsymmetrical, with an arrangement of the groups looking like this as seen from above. Fresenius and Karweil[316] agree; they say that such a structure alone can explain the Raman and



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[307] D. H. Howard and A. W. Browne, *J.A.C.S.* 1933, **55**, 1968.

[308] F. Raschig, *Ber.* 1907, **40**, 4587.

[309] Id., *Schwefel und Stickstoff-Studien*, Leipzig-Berlin, 1924, 61.

[310] A. Eucken and H. Krome, *Z. physikal. Chem.* 1940, B **45**, 175.

[311] P. A. Giguère and R. E. Rundle, *J.A.C.S.* 1941, **63**, 1135.

[312] P. A. Giguère and V. Schomaker, ib. 1943, **65**, 2025.

[313] W. A. Roth, *Z. Elektrochem.* 1944, **50**, 111.

[314] W. G. Penney and G. B. B. M. Sutherland, *Trans. Far. Soc.* 1934, **30**, 898.

[315] Id., *J. Chem. Phys.* 1934, **2**, 492.

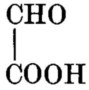
[316] W. Fresenius and J. Karweil, *Z. physikal. Chem.* 1939, B **44**, 1.

infra-red results, and that it is also supported by the molar heats. Further confirmation is obtained by West and Killingsworth[317] from the Raman spectrum of symmetrical dimethyl hydrazine $CH_3NH \cdot NHCH_3$, which implies a similar unsymmetrical structure: also the observed dipole moment of 1·35±0·15 D agrees with this, the calculated value for it being 1·47.

As a solvent anhydrous hydrazine behaves like liquid ammonia.[318] It has a high dielectric constant of 53 at 22°, and is an excellent ionizing solvent[319] for many salts.

Hydrazine is very soluble in water, from which it is obtained as a hydrate $H_2N \cdot NH_2,H_2O$, which holds its water very firmly, melting at $-40°$ and boiling at 120°.

Hydrazine is an endothermic (liquid $-12·0$, solid $-22·25$ k.cals.)[320] and somewhat unstable compound. At 250°, or when the vapour is sparked,[321] it decomposes to ammonia and nitrogen. It is oxidized even by air in the cold, and reacts violently with halogens. In these reactions nitrogen is always eliminated. The hydrogen can be replaced, as in ammonia, by metals, giving, for example, $NaNH \cdot NH_2$.

Hydrazine is practically only a monacid base, and even so is only about a fifth as strong as ammonia, K being about 1×10^{-6}.[322] The salts are nearly all, except the sulphate, very soluble in water. The fluoride $H_2N—NH_2$, 2 HF, or $[H_3N—NH_3]F_2$ has[323] a crystal lattice not unlike that of $NH_4[F]$ (p. 661), with the NH_3 groups of the cation staggered, and the distances N—N 1·42 (the same N—N distance was found by X-ray analysis in the chloride),[324] N—H··F 2·62 (theory N—N 1·40, N—H··F in $[NH_4]F$ 2·66 A); in water it dissociates mainly into two ions, so that (there) it is $[H_2N—NH_3]F_2H$. Like hydrogen peroxide hydrazine can sometimes act as an oxidizing agent; thus with glyoxylic acid  $\begin{array}{l}CHO\\ |\\ COOH\end{array}$, it gives oxalic acid and ammonia.

Of its organic derivatives the most famous is phenyl hydrazine $C_6H_5 \cdot NH \cdot NH_2$ (V. Meyer and Lecco, 1883[325]); this is usually made by the reduction of diazobenzene derivatives; b.pt. 241°, m.pt. 19·6°, Trouton constant 26·7[326] (N_2H_4 25·8). It is used as a reagent for aldehydes and ketones, for the synthesis of antipyrine, and for many other purposes. The properties of the tetra-alkyl and tetra-aryl hydrazines, and especially their dissociation to divalent NR_2 radicals, are discussed on p. 719.

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[317] W. West and R. B. Killingsworth, *J. Chem. Phys.* 1938, 6, 1.

[318] See L. F. Audrieth, *Z. physikal. Chem.* 1933, **165**, 323.

[319] P. Walden and H. Hilgert, ib. 241; 1934, **168**, 419.

[320] A. M. Hughes, R. J. Corruccini, and E. C. Gilbert, *J.A.C.S.* 1939, **61**, 2639.

[321] C. H. Bamford, *Trans. Far. Soc.* 1939, **35**, 1239.

[322] G. C. Ware, J. B. Spulnik, and E. C. Gilbert, *J.A.C.S.* 1936, **58**, 1605.

[323] M. L. Kronberg and D. Harker, *J. Chem. Phys.* 1942, **10**, 309.

[324] J. Donohue and W. N. Lipscomb, ib. 1947, **15**, 115.

[325] V. Meyer and M. T. Lecco, *Ber.* 1883, **16**, 2976.

[326] G. E. Williams and E. C. Gilbert, *J.A.C.S.* 1942, **64**, 2776.

Di-imide HN=NH, the parent substance of the very stable azo-compounds, has never been prepared, nor have its mono-alkyl or mono-aryl derivatives R·N=NH, though the dialkyl and diaryl (azo-) compounds R·N=N·R are so well known. All attempts to prepare di-imide only give nitrogen and ammonia, as we should expect, since the reaction

$$3\ HN{=}NH\ =\ 2\ NH_3 + 2\ N_2$$

should evolve 155 k.cals. It is true that the same amount of heat should be evolved if azobenzene changes into triphenylamine and nitrogen; but a hydrogen atom is always more ready to react, and has a much smaller heat of activation, than an alkyl or aryl group.

Azo-compounds

Though di-imide HN=NH is too unstable to be isolated, its dialkyl and still more its diaryl substitution products, the azo-compounds, are remarkably stable.

Azomethane $CH_3 \cdot N{=}N \cdot CH_3$, which can be made by oxidizing symmetrical dimethyl hydrazine $CH_3NH{-}NHCH_3$, is a colourless gas giving a pale yellow liquid and colourless crystals: m.pt. −78°, b.pt. +1·5°. Its structure is discussed below (p. 712). It does not decompose on heating below 200°; it then gives, like most compounds with the N=N group, free nitrogen together with ethane. The kinetics of this reaction, which can be either thermal or photochemical, have been much studied. The thermal decomposition goes at a reasonable rate at 250-300°[327-8]; the reaction is homogeneous and of the first order, with a heat of activation of 51·2 k.cals.[329] Azoisopropane behaves similarly, but its heat of reaction is 40·9 k.cals. The primary reaction involves the production of free alkyl radicals, as can be shown by their effect in removing metallic mirrors, and in catalysing various reactions. For further work on the thermal reaction see references [330-2], and for the photochemical references [333-4].

A remarkable derivative of azomethane is the hexafluoro-compound (dicyanohexafluoride) $F_3C \cdot N{=}N \cdot CF_3$. This was first obtained by Ruff[335] among the products of the action of fluorine on silver cyanide. Later he got it in a much purer form (along with $(CF_3)_2NH$, *v.* p. 665) by the action of iodine pentafluoride on cyanogen iodide at 125–45°.[336] It melts at −133° and boils at −31·6°; the Trouton constant is 22·6. It has no smell and is relatively inert. It is not attacked by 50 per cent. aqueous NaOH or by 15–20 per cent. HCl at 100°. It is very slightly soluble in water; it

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[327] See C. N. Hinshelwood, *Kinetics of Chemical Change*, 1940, p. 123.

[328] H. C. Ramsperger, *J.A.C.S.* 1927, **49**, 912, 1495.

[329] F. P. Jahn and H. A. Taylor, *J. Chem. Phys.* 1939, **7**, 474, find 52·5 k.cals.

[330] D. V. Sickman and O. K. Rice, ib. 1936, **4**, 239.

[331] Id., ib. 242.

[332] Id., ib. 608.

[333] G. S. Forbes, L. J. Heidt, and D. V. Sickman, *J.A.C.S.* 1935, **57**, 1935.

[334] M. Burton, T. W. Davis, and H. A. Taylor, ib. 1937, **59**, 1038.

[335] O. Ruff and M. Giese, *Ber.* 1936, **69**, 598, 604.

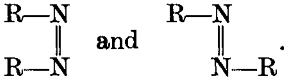
[336] O. Ruff and W. Willenberg, ib. 1940, **73**, 724.

explodes on sparking, mainly to hexafluoroethane and nitrogen. It reacts quickly with ammonia, but the reaction is complicated and obscure.

The mixed alkyl-aryl compounds seem to be rather less stable; thus benzene-azomethane $C_6H_5\cdot N{=}N\cdot CH_3$ boils with some decomposition at 150°, and the ethyl compound does the same at 175–85°.[337]

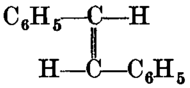
The diaryl azo-compounds are very stable. Azo-benzene $\Phi\cdot N{=}N\cdot\Phi$, made by the alkaline reduction of nitrobenzene and in other ways, forms orange plates melting at 68° and boiling without decomposition at 297°; at high temperature it gives carbon, nitrogen, diphenyl, etc. It is of course the parent of the enormous class of azo-dyes. It scarcely decomposes below a red heat. The azo-group is chemically very inert; almost its only reaction is its reduction to the symmetrical diaryl hydrazine $Ar\cdot NH{-}NHAr$ and to the amine $Ar\cdot NH_2$, but it can be oxidized to the azoxy-compound $Ar\cdot\underset{\substack{\downarrow\\ O}}{N}{=}N\cdot Ar$; it has scarcely any basic properties.

Stereochemistry. A molecule $R\cdot N{=}N\cdot R$ can obviously occur in *cis* and *trans* forms



$$\begin{array}{c} R{-}N \\ \| \\ R{-}N \end{array} \quad \text{and} \quad \begin{array}{c} R{-}N \\ \| \\ N{-}R \end{array}.$$

With azomethane the *trans* structure is established by the zero dipole moment of the substance in heptane[338] and by its Raman and infra-red spectra[338]; it is compatible with the electron diffraction,[339] which shows the C—N—N—C chain not to be linear, and gives the distances as C—N 1·47, N—N 1·24 (theory 1·47, 1·20). Many years ago Hantzsch pointed out that in general the *trans* form must be more stable than the *cis* for steric reasons, and that the only known form of azobenzene must, from its surprising stability, belong to the *trans* series; this was confirmed by its dipole moment of zero,[340] and by the crystal structure,[341] which is very like that of (*trans*) stilbene



$$\begin{array}{l} C_6H_5{-}C{-}H \\ \qquad\ \ \| \\ \qquad H{-}C{-}C_6H_5 \end{array}$$

Cis-azobenzene. The true *cis*-azobenzene was discovered by G. S. Hartley in 1937[342]; he found that an acetone solution of ordinary (*trans*) azobenzene on exposure to light became more strongly coloured; by extracting the product with water, and then extracting the excess of *trans* compound from the water with ligroin, he was able to isolate the *cis* compound in bright red crystals (not unlike the *trans* in appearance) which

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[337] See Beilstein, vol. xvi, p. 7.

[338] W. West and R. B. Killingsworth, *J. Chem. Phys.* 1938, **6**, 1.

[339] H. Boersch, *Mon.* 1935, **65**, 311.

[340] E. Bergman, L. Engel, and S. Sandór, *Ber.* 1930, **63**, 2572.

[341] J. M. Robertson, M. Prasad, and I. Woodward, *Proc. Roy. Soc.* 1936, **154**, 187.

[342] G. S. Hartley, *Nature*, 1937, **140**, 281.

melt at 71·4° (*trans* 68°). Later work[343] showed that solutions after radiation contain from 15 to 40 per cent. of the *cis* form according to the solvent used. The two forms can also be separated chromatographically, the *cis* being much more strongly adsorbed by alumina.[344-5]

The physical properties of the new substance support the *cis* formula. The dipole moment is 3·0 D,[346] while that of the *trans* is zero. The crystal structure[347-8] shows that the molecule is *cis*; a more detailed study[349] showed that whereas *trans*-azobenzene is planar, in the *cis* the planes of the rings are inclined 15° to that of the  $\overset{C}{\diagdown}N{=}N\overset{C}{\diagup}$ group, which brings the nearest (*o*, *o*′) carbon atoms of the two rings 3·34 A apart. Hence there must be less resonance in the *cis* form than in the *trans*, and accordingly the C—N links are longer (*cis* 1·46, *trans* 1·41, theory C—N 1·47), though the N=N link is 1·23 in both (theory 1·20). The refractive powers also support this view, the differences corresponding to those observed between *cis* and *trans* stilbene.[350] The *cis* form is the less stable, owing, no doubt, to there being less resonance; heats of combustion[351] give the heats of formation H_f in the solid state as *cis* 75·65, *trans* 85·55 k.cals., so that the conversion of *cis* (solid) to *trans* (solid) evolves 9·9 k.cals. per mole. Accordingly it is found that the *cis* form slowly reverts in solution in the dark to the *trans*, and that the same occurs if it is kept above its melting-point (for the effect of solvents and catalysts on the rate of change, see ref. [343]).

The differences in solubility, especially in water, are very marked; the *cis* compound, with its high dipole moment, should be, and is, more soluble in water than the *trans*, the values being in mg. per litre at the ordinary temperature, *cis* 117·4, *trans* 4·37, ratio 26·9.

Diazo-compounds

The aliphatic diazo-compounds (which have but slight resemblances to the aromatic) were first made in 1883 by Curtius,[352] by the action of nitrous acid on certain amines, such as glycine ester:

$$HNO_2 + H_2N \cdot CH_2CO_2Et = N_2CH \cdot CO_2Et + 2\,H_2O.$$

The mother substance diazomethane H_2CN_2 was discovered by Pechmann in 1894[353]; it is a deep yellow gas, b.pt. −23°, m.pt. −145°[354]; it

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[343] G. S. Hartley, *J.C.S.* 1938, 633.

[344] L. Zechmeister, O. Frehden, and P. F. Jörgensen, *Naturwiss.* 1938, **26**, 495.

[345] H. Freundlich and W. Heller, *J.A.C.S.* 1939, **61**, 2228.

[346] G. S. Hartley and R. J. W. Le Févre, *J.C.S.* 1939, 531.

[347] J. M. Robertson, ib. 232.

[348] J. J. de Lange, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc.* 1939, **171**, 398.

[349] G. C. Hampson and J. M. Robertson, *J.C.S.* 1941, 409.

[350] K. v. Auwers, *Ber.* 1938, **71**, 611.

[351] R. J. Corruccini and E. C. Gilbert, *J.A.C.S.* 1939, **61**, 2925.

[352] T. Curtius, *Ber.* 1883, **16**, 754.

[353] H. v. Pechmann, ib. 1894, **27**, 1888; 1895, **28**, 855.

[354] H. Staudinger and O. Kupfer, ib. 1912, **45**, 507.

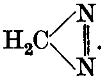
decomposes readily, and sometimes explosively, especially on heating, and in its reactions usually evolves nitrogen; thus it will methylate hydroxy-compounds:

$$R\cdot OH + N_2CH_2 = R\cdot O\cdot CH_3 + N_2.$$

So, too, it will take up iodine quantitatively:

$$I_2 + N_2CH_2 = I_2CH_2 + N_2.$$

There are three possible structures for H_2CN_2:

(I) 

(IIa) $H_2\overset{+}{C}{=}N{\overset{-}{\rightarrow}}N.$ (IIb) $H_2\overset{-}{C}{\leftarrow}N{\equiv}\overset{+}{N}.$

(I) was the type originally suggested by Curtius in 1883; the linear form was proposed by Angeli in 1907 and strongly supported by Thiele in 1911.

Electron diffraction has shown[355] that the C—N—N chain is linear, with the distances C—N 1·34, N—N 1·13 (both ± about 0·05 A); theory C—N 1·47. C=N 1·27: N—N 1·40, N=N 1·20, N≡N 1·09. This excludes structure (I). The dipole moment of the CN_2 group has been found[356] to be about 1·4 D (about that of the C—N link). The structures (II*a*) and (II*b*) must have very large moments in opposite directions, and the low moment observed can only be explained by resonance between these two structures. The whole of these conclusions are strongly supported by the properties of the azide group $-N_3$ (below, p. 716).

The aromatic diazo-compounds, discovered by Peter Griess in 1858,[357] have been of the utmost value to the development, both theoretical and practical, of organic chemistry. In synthetic work they enable the most various groups to be introduced into the benzene nucleus; they are of the highest technical importance as the basis of the vast class of azo-dyes, and their study has thrown great light on the phenomena of tautomeric change. They are normally made by the action of nitrous acid on primary aromatic amines; they all have one hydrogen atom on the benzene nucleus replaced by the group N_2X:

$$C_6H_5\cdot NH_2 + O{=}N{-}OH = C_6H_5\cdot N_2OH + H_2O.$$

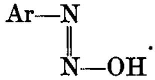
In many of their very numerous reactions the two nitrogen atoms are eliminated as nitrogen gas.

It has been shown, mainly by Hantzsch,[358] that the compounds exhibit a very remarkable example of double tautomerism, essentially between two types, the diazonium (I) and the diazo-, the latter occurring in *cis* (II*a*) and *trans* (II*b*) forms:

(I) $[Ar{-}N{\equiv}N][OH].$

(II*a*) 

$$\begin{matrix} Ar{-}N \\ \| \\ HO{-}N \end{matrix}.$$

(II*b*) 

$$\begin{matrix} Ar{-}N \\ \| \\ N{-}OH \end{matrix}.$$

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[355] H. Boersch, *Mon.* 1935, **65**, 331.

[356] N. V. Sidgwick, L. E. Sutton, and W. Thomas, *J.C.S.* 1933, 406.

[357] P. Griess, *Ann.* 1858, **106**, 123.

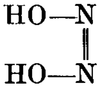
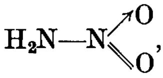
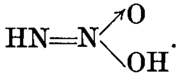
[358] See A. Hantzsch, 'Die Diazoverbindungen', *Sammlung Ahrens*, Bd. viii (Enke, Stuttgart, 1903).

The first are strong bases, like the tetra-alkyl ammonium salts, and the latter weakly basic and weakly acidic, like the hydroxylamines.

Nitramide, $H_2N \cdot NO_2$

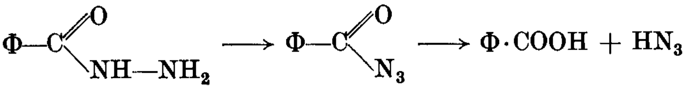
This was first made by Thiele and Lachman[359]; they converted nitrourethane $O_2N \cdot NH \cdot CO \cdot OEt$ with concentrated alkali into potassium nitrocarbamate $O_2N \cdot NK \cdot CO \cdot OK$ (or an isomeric form); they treated this with sulphuric acid at 0° and extracted with ether; this is still the best method of preparation, though a lower temperature gives a larger yield.[360]

Nitramide forms colourless crystals which melt with decomposition at 72–75°[361]; it is somewhat volatile even at the ordinary temperature.[362] The solid decomposes slowly on keeping, and suddenly with flame and explosion if a drop of concentrated alkali falls upon it[361]; on heating it readily changes to nitrous oxide and water. The dipole moment in dioxane is 3·75 D.[363] It is very easily soluble in water and in ether, but less so in benzene.[361] In water it is monomeric by the freezing-point.[364] It has an acid reaction, the dissociation constant being $2 \cdot 55 \times 10^{-7}$.[362] The aqueous solution soon decomposes: for the kinetics of this see references [365-9]. Its alkaline salts cannot be isolated, as they decompose at once on formation.

The suggestion that this is the *cis* form of hyponitrous acid  $\begin{array}{c}HO—N\\ \|\\ HO—N\end{array}$ has been disproved; it is no doubt the simple nitro-compound  $H_2N—N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$, having in water probably some of the tautomeric aci-form  $HN{=}N\begin{smallmatrix}\nearrow O\\ \diagdown OH\end{smallmatrix}$.

Hydrazoic Acid, HN_3

Hydrazoic acid can be obtained by the hydrolysis of organic acid azides, such as benzazide, which may be made by the action of nitrous acid on the hydrazide



$$\Phi—C\begin{smallmatrix}\nearrow\!\!\!\!/ O\\ \diagdown NH—NH_2\end{smallmatrix} \longrightarrow \Phi—C\begin{smallmatrix}\nearrow\!\!\!\!/ O\\ \diagdown N_3\end{smallmatrix} \longrightarrow \Phi \cdot COOH + HN_3$$

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[359] J. Thiele and A. Lachman, *Ber.* 1894, **27**, 1909.

[360] C. A. Marlies and V. K. LaMer, *J.A.C.S.* 1935, **57**, 2008.

[361] J. Thiele and A. Lachman, *Ann.* 1895, **288**, 297.

[362] J. N. Brönsted and C. V. King, *J.A.C.S.* 1927, **49**, 200.

[363] E. C. E. Hunter and J. R. Partington, *J.C.S.* 1933, 312.

[364] A. Hantzsch and L. Kaufmann, *Ann.* 1896, **292**, 339.

[365] E. C. Baughan and R. P. Bell, *Proc. Roy. Soc.* 1937, **158**, 464.

[366] C. V. King, *J.A.C.S.* 1938, **60**, 144.

[367] V. K. LaMer and J. Greenspan, *Trans. Far. Soc.* 1937, **33**, 1266.

[368] S. Liotta and V. K. LaMer, *J.A.C.S.* 1938, **60**, 1967.

[369] V. K. LaMer and J. Hochberg, ib. 1939, **61**, 2552.

and by other organic reactions. It can also be made by the action of nitrous oxide on sodamide at 190°[370-1]:

$$\mathrm{NaNH_2 + O{=}N\overset{\rightarrow}{=}N = NaN{\cdot}N_2 + H_2O}$$

and further by the action of sodium nitrite, ethyl nitrite, or nitrogen chloride, on hydrazine.

Hydrazoic acid is a liquid boiling at +37° and melting at −80°. It is enormously explosive; in one case 0·05 g. destroyed the glass apparatus containing it and spread mercury dust all over the room: in another, the explosion of 0·7 g. destroyed all the glass apparatus in the neighbourhood. It is also poisonous, attacking the mucous membrane.

As an acid it is a little stronger than acetic, $K_{25} = 2{\cdot}8\times 10^{-5}$.[372] In solution it is fairly stable, but in presence of platinum black it is decomposed in water to hydroxylamine and nitrogen, and light has the same effect:

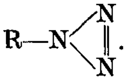
$$\mathrm{HN_3 + H_2O = H_2N{\cdot}OH + N_2}.$$

In presence of palladium it is reduced by hydrogen to ammonia and hydrazine.

Its salts, the metallic azides, resemble the halides in their solubilities in water. Most of them are soluble, but the silver, lead, and mercurous salts are very insoluble. The salts of the alkalies and the alkaline earths melt without decomposition, and decompose only on strong heating, and then as a rule quietly[373]; barium azide is used in spectroscopic work as a source of pure nitrogen. On the other hand, the salts of the heavy metals, especially silver and lead, explode violently when struck, sometimes at a touch, and (as usual) the more readily the larger the crystals.

There are two structural problems here, that of the azide ion $[\mathrm{N_3}]^-$ and that of the covalent molecules $\mathrm{R{-}N_3}$. The $\mathrm{N_3}$ ions are shown by X-ray measurements to be linear, and so must be $[\mathrm{N\overset{\leftarrow}{=}N\overset{\rightarrow}{=}N}]^-$. This follows from the crystal structures[374]; those of sodium, potassium,[375] and ammonium[376] azide are all similar; the same linear anion is found in the silver,[377] cadmium,[378] and strontium[379] salts. The N—N distances found are $\mathrm{NaN_3}$ 1·15; $\mathrm{KN_3}$ 1·16; $\mathrm{NH_4N_3}$ 1·17 (all ±0·02 A); $\mathrm{AgN_3}$ 1·18±0·04; $\mathrm{Sr(N_3)_2}$ 1·12 (theory for N=N 1·20, N≡N 1·09).

For the covalent azides (including the undissociated acid) there are three possibilities (as with diazomethane above):

(I) 

(IIa) $\mathrm{R{-}N{=}N\overset{\rightarrow}{=}N}$.   (IIb) $\mathrm{R{-}N{\leftarrow}N{\equiv}N}$.

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[370] J. Wislicenus, *Ber.* 1892, **25**, 2084.

[371] L. M. Dennis and A. W. Browne, *J.A.C.S.* 1904, **26**, 594.

[372] M. Quintin, *C.R.* 1940, **210**, 625

[373] For the kinetics see A. Wischin, *Proc. Roy. Soc.* 1939, 172, 314; N. F. Mott, ib. 325.

[374] S. B. Hendricks and L. Pauling, *J.A.C.S.* 1925, **47**, 2904.

[375] L. K. Frevel, ib. 1936, **58**, 779.

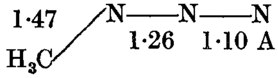
[376] Id., *Z. Krist.* 1936, **94**, 197.

[377] M. Bassière, *C.R.* 1935, **201**, 735.

[378] Id., ib. 1937, **204**, 1573.

[379] F. J. Llewellyn and F. E. Whitmore, *J.C.S.* 1947, 881.

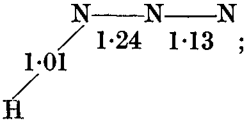
From the electron diffraction of methyl azide Pauling and Brockway[379a] have shown that the three N atoms form a straight chain, the dimensions being:



; angle 135±15°.

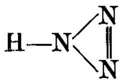
The examination of the crystal structure of cyanuric azide $C_3N_3(N_3)_3$ (above, p. 679) has led to a similar conclusion.

For hydrazoic acid itself Herzberg[380] deduced from the infra-red spectrum that the three nitrogen atoms lay in one straight line, and the hydrogen outside it; Eyster,[381-2] from a more detailed analysis of the infra-red bands, obtained the values



; angle 111°.

The two open-chain structures (II*a*) and (II*b*) have a high polarity in opposite directions. It has, however, been shown[356,383-4] that phenyl azide has a moment of only 1·55 D, about that to be expected from the C—N link, the N—N—N group apparently contributing nothing. This can only be explained by resonance between the two forms (II*a*) and (II*b*). In view of these facts the heat of formation of the azide group is of considerable interest.[384] The heats of combustion of phenyl azide and of ethyl azidoacetate have been determined by Roth,[385] and the heat of decomposition of the acid HN_3 into hydrogen and nitrogen gases by Günther and Meyer[386-7]; we may take the latter results as the simplest. They show that the heat of decomposition of hydrazoic acid HN_3 into hydrogen and nitrogen gases is −70·9 k.cals. per mole., whence H_a, its heat of formation from the atoms, is 318·6 k.cals. With the values H—N 92·9, N—N 38·4, N═N 97·6, and N≡N 225·0 (this last from molecular nitrogen) we can calculate the heats of formation from the atoms as:

(I)  267·3. (II*a*) H—N═N═N 288·1.

(II*b*) H—N—N≡N 356·3. Observed 318·6 k.cals.

This result is plainly impossible; if there is resonance between (II*a*) and (II*b*) their heats of formation must not be very different, and that observed for the actual acid must be greater than either by the amount of the

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[379a] L. Pauling and L. O. Brockway, *J.A.C.S.* 1937, **59**, 13.

[380] G. Herzberg, F. Patat, and H. Verleger, *Z. Elektrochem* 1935, **41**, 522.

[381] E. H. Eyster, *J. Chem. Phys.* 1940, **8**, 135.

[382] E. H. Eyster and R. H. Gillette, ib. 369.

[383] E. Bergmann and W. Schütz, *Nature*, 1931, **128**, 1077.

[384] N. V. Sidgwick, *Trans. Far. Soc.* 1934, **30**, 801.

[385] W. A. Roth and F. Müller, *Ber.* 1929, **62**, 1188.

[386] P. Günther and R. Meyer, *Z. Elektrochem.* 1935, **41**, 541.

[387] P. Günther, R. Meyer, and F. Müller-Skjold, *Z. physikal. Chem.* 1935, **175**, 154.

resonance energy. The error is in the value taken for the triple N≡N link. If we were right in supposing (p. 657) that the high value of the ratio of the heats of formation N≡N/N—N = 225/38·4 = 5·86 as compared with —C≡N/C—N = 212/69·3 = 3·06 is due to the adaptability of the unshared pair of electrons on the two atoms in elementary nitrogen, then since in (II*b*) only one of the triply linked nitrogens has this unshared pair, the strain should be greater and the heat of formation smaller; a more accurate value would be three halves of the —N=N— value as with the C—N links, i.e. 3/2 × 97·6 or 146·4 k.cals., instead of 225. If we use this, we get for the heat of formation of (II*b*) 277·7 k.cals., which fits with (II*a*) 288·1 and the observed heat for the hybrid 318·6.

This is good evidence for the view that an unshared pair of electrons can relieve the strain of a multiple link.

A singular derivative of hydrazoic acid is the chloride $Cl \cdot N_3$ obtained by Browne *et al.*[388] by the action of chlorine on silver azide, or of hypochlorous acid on hydrazoic acid; it is an orange liquid freezing at $-100°$ to an explosive solid; it is slightly soluble in water, readily in hydrocarbons; it is decomposed by ammonia, and after standing at the room temperature for 2 hours in pentane solution it is converted into hydrazoic acid and amyl chloride $C_5H_{11} \cdot Cl$. In the absence of water it reacts[389] with silver azide to give a compound N_3AgCl, stable only below $-30°$, and very reactive. This compound dissolves in pentane to give a blue solution, fairly stable at low temperatures; from its colour this may be a covalent argentic compound N_3—Ag—Cl.

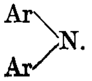
The fluoride $F \cdot N_3$ has recently been made by A. W. Browne and J. F. Haller by treating hydrazoic acid with fluorine in a stream of nitrogen. It is a greenish-yellow gas liquefying at $-82°$ and going to a greenish-yellow solid at $-154°$. It usually explodes on evaporating, and at the ordinary temperature decomposes to $N_2 + N_2F_2$ (see p. 705).[281a]

NITROGEN: FREE RADICALS

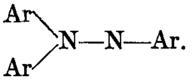
There are two classes of organic nitrogenous compounds in which the nitrogen atom, which is always attached to an aryl group, has—at least in one resonance form—only a septet of electrons, as it has in nitric oxide and nitrogen dioxide NO_2. In one class the covalency of the nitrogen is 2 (valency group $\underline{4}$, 3) and the nitrogen atom neutral: in the other it is 3 ($\underline{6}$, 1) so that the nitrogen has a positive charge, either as an ion or as a donor in co-ordination. The chief groups of compounds (which are all coloured and all paramagnetic) are these:

A. 2-covalent: valency group, $\underline{4}$, 3.

A. 1.



A. 2.



Diaryl nitrogens. Hydrazyls.

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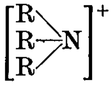
[388] W. J. Frierson, J. Kronrad, and A. W. Browne, *J.A.C.S.* 1943, 65, 1696.

[389] W. J. Frierson and A. W. Browne, ib. 1698.

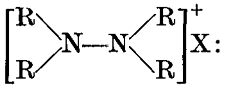
B. 3-covalent: valency group $\underline{6}$, 1.

B. 1.



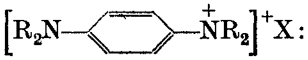
Aminium salts.

B. 2.



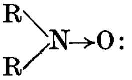
Hydrazinium salts.

B. 3.



Würster's salts.

B. 4.



Diaryl nitrogen oxides.

A. 2-COVALENT: NITROGEN ATOM NEUTRAL

A. 1.

Diaryl Nitrogens

By the oxidation of diarylamines Ar_2NH with lead dioxide in ether, or with permanganate in acetone,[390] and in other ways, Wieland obtained the tetra-aryl hydrazines $Ar_2N—NAr_2$, and showed that they dissociate in solution to a greater or less degree into the free radicals Ar_2N:

$$Ar_2N—NAr_2 \rightleftharpoons 2\,Ar_2N.$$

This is proved by their behaviour. The solids are colourless, being obviously associated; but on dissolving in chloroform or nitrobenzene they rapidly become yellow or green, through a dissociation which has a heat of activation; the colour deepens on warming and fades again on cooling; on dilution it does not obey Beer's law. The heat of dissociation appears[391] to be about 10·5 k.cals., instead of the normal N—N value of 38·4 k.cals.; for the heat of activation, which is much disputed, see references [392–3]. Further, they add on other free radicals, forming, for example, with nitric oxide a nitrosamine $Ar_2N—NO$; in this reaction the half-life of tetraphenyl hydrazine in *p*-dichlorobenzene at 100° is 3·1 minutes.[393] In the same way these radicals add on triphenyl methyl to give $Ar_2N—C\Phi_3$. Like other nitrogen radicals (but unlike the carbon radicals), they are not oxidized by oxygen.

The degree of dissociation of tetraphenyl hydrazine is less than that of hexaphenyl ethane, and the effect of substituents on it is, most remarkably, in the opposite direction in the two; with the hydrazines it is increased by positive substituents such as $O \cdot CH_3$ and $N(CH_3)_2$, whereas with the carbon compounds it is increased by negative groups like NO_2. Thus the dissocia-

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[390] H. Wieland and S. Gambarjan, *Ber.* 1906, 39, 1500.

[391] C. M. Anderson and E. C. Gilbert, *J.A.C.S.* 1942, 64, 2369.

[392] G. N. Lewis and D. Lipkin, ib. 1941, 63, 3232.

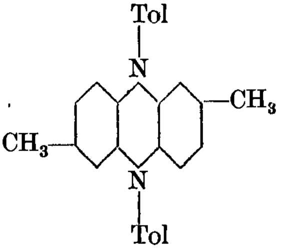
[393] C. K. Cain and F. Y. Wiselogle, ib. 1940, 62, 1163.

tion of the tetra-aryl hydrazines increases[394] in the following order of aryl groups ($P = C_6H_4$):

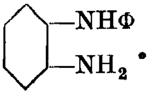
$$p\text{—}NO_2\cdot P < p\text{—}C_6H_5\cdot P < C_6H_5 < p\text{—}CH_3\cdot P < o\text{—}CH_3\cdot P < p\text{—}CH_3O\cdot P$$
$$< p\text{—}(CH_3)_2N\cdot P.$$

A 0·8 per cent. solution of p—$(Me_2N\cdot P)_2N$—$N(P\cdot NMe_2)_2$ is dissociated in the cold 10 per cent. in benzene and 21 per cent. in nitrobenzene.[395] The solutions are deeply coloured, the phenyl compound being emerald green and the others mostly yellow.

Chemically these diaryl nitrogen compounds are much less stable than the triaryl methyls. In light the dissociated free radicals rearrange themselves, mainly to 'perazines' (the p-tolyl compound giving I below) and to o-semidines (II below):

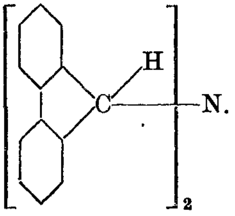


(I)



(II)

The formation of these free radicals is almost confined to the tetra-aryl hydrazines. Tetrabenzyl hydrazine does not dissociate, and can be distilled unchanged at 260°/32 mm.; the symmetrical alkyl-aryl hydrazines ArAlkN—NArAlk also are found not to dissociate,[396] though if heated with nitric oxide they form nitrosamines AlkArN—NO, which presumably indicates that there is some dissociation. The tetrafluorenyl compound is green in solution, and so is dissociated to some extent into the free radicals given here. The tetra-alkyl hydrazines are found to dissociate into free radicals at 100–200°.[397]



The determining effect of the aryl groups on the formation of the free radicals is no doubt due as with the triaryl methyls to the possibilities of resonance which they present.

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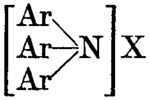
[394] Richter-Anschütz, 1935, ii. 2, p. 817.
[395] H. Wieland, *Ber.* 1915, 48, 1091.
[396] H. Wieland und H. Fressel, *Ann.* 1912, 392, 135.
[397] O. Westphal und M. Eucken, *Ber.* 1943, 76, 1137.

A. 2. $Ar_2N—N—Ar$: *Hydrazyls*

Similar di-covalent radicals are formed by the dissociation of the tetrazanes $Ar_2N—NAr—NAr—NAr_2$ that are obtained by the oxidation of the triaryl hydrazines $Ar_2N—NArH$ (St. Goldschmidt[398-401]); these are the hydrazyls $Ar_2N—N—Ar$. They correspond to the penta-aryl ethyls $Ar_3C—CAr_2$, and like these are less readily formed than the simple radicals; in their general behaviour they resemble the simple radicals closely. The dipole moments are very large (α, α-diphenyl-β-picryl hydrazyl 4·92D),[402] indicating resonance with more highly polar forms.

B. 3-COVALENT GROUP ($\underline{6}$, 1)

B. 1. *Aminium Salts*

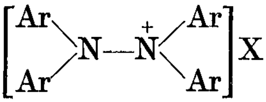


$[Ar_3N]X$

Triaryl amines can form salts of the type of $[Ar_3N]X$ by the direct addition of anions. For example, with bromine[403-5] they form $[Ar_3N]Br_3$: such amines as tri-*p*-tolylamine will dissolve in acids like picric in presence of an oxidizing agent to form these salts (triphenylamine cannot be used here because the para-hydrogen would be oxidized); the free radical ClO_4* will also combine directly with it to give the deep blue salt $[Ar_3N]ClO_4$. The existence of these salts is the more remarkable since triarylamines will not form ammonium salts of the ordinary kind with acids, except a very easily hydrolysed perchlorate.[406] The solutions of these salts are blue, and Beer's law holds up to high dilutions, so that a dimeric 'even' molecule is impossible. It has also been shown[407] that $[Tol_3N]ClO_4$ has a paramagnetic susceptibility of $1{,}247 \times 10^{-6}$, the value calculated by van Vleck's method for one free electron being $1{,}297 \times 10^{-6}$.

These salts are hydrolysed by water, but the free base, which is presumably $[Ar_3N]OH$, cannot be isolated. They are readily reduced, for example, by acidified potassium iodide solution, to the amine.

B. 2. *Hydrazinium Salts*



$[Ar_2N—\overset{+}{N}Ar_2]X$

Here again the nitrogen with the septet may be joined to a second and normal nitrogen atom. The tetra-aryl hydrazines, in addition to their dissociation to diaryl nitrogens, can add on anions when treated with an

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* This oxide has not been isolated, and its existence has been disputed (see under Chlorine, p. 1207); but it is evidently present either as monomer or as polymer in the solution formed by treating an ethereal solution of iodine with silver perchlorate; this solution reacts with the tertiary amine to give the aminium salt.

[398] St. Goldschmidt, ib. 1920, **53**, 44.

[399] St. Goldschmidt and K. Euler, ib. 1922, **55**, 616.

[400] St. Goldschmidt, *Ann.* 1942, **437**, 194.

[401] Id., ib. 1929, **473**, 137.

[402] J. Turkevitch, P. F. Oesper, and C. P. Smyth, *J.A.C.S.* 1942, **64**, 1179.

[403] E. Weitz, *Angew. Chem.* 1922, **39**, 1193.

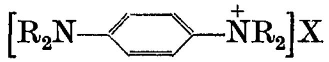
acid and an oxidizing agent, or with a free radical like ClO_4. As Weitz and Schwechten have shown,[408] the resulting salts must have one 'tetravalent' nitrogen atom; like the salts of a metal such as copper they are formed by strong acids only in the presence of an oxidizing agent, but if no other such agent is present the tetra-aryl hydrazine takes its place, removing the hydrogen from the acid to form diarylamine. With lead dioxide coloured N^{iv} salts are formed at once even with weak acids like picric or acetic. In the same way ClO_4 adds on to $Tol_2N—NTol_2$ to form $[Tol_2N—NTol_2]ClO_4$, dark violet crystals which have been shown to be paramagnetic[409]; like the diaryl nitrogens these radicals are not oxidized by oxygen.

These hydrazinium salts are formed by the action of aminium salts on tetra-aryl hydrazines:

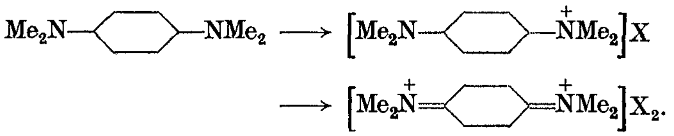
$$Ar_2N—NAr_2 + [Ar_3N]X = [Ar_2N—NAr_2]X + Ar_3N,$$

showing that the $N—\overset{+}{N}$ group is more stable than the $\overset{+}{N}$. They are easily reduced, for example, by potassium iodide.

B. 3. *Würster's Salts*



These resemble the hydrazinium salts in having two nitrogen atoms (not, however, directly united) of which only one has the septet. They were discovered by C. Würster in 1879[410]; they are intermediate products in the oxidation of a para-diamine to a quinonimonium salt:



They cannot be addition compounds of the first and last of these three stages, since they retain their intense colour in solution.[411] The potentiometric titration of the diamine with an oxidizing agent shows (Michaelis[412]) that the removal of the two electrons which is necessary to form the final product takes place in two distinct stages. Thus the intermediate compound must have an odd molecule with a deficiency of one electron, which may be on one of the carbon atoms or on one of the nitrogens, according as we

[404] E. Weitz and H. W. Schwechten, *Ber.* 1926, **59**, 2307.

[405] Id., ib. 1927, **60**, 545.

[406] K. A. Hofmann, A. Metzler, and K. Höbold, ib. 1910, **43**, 1080.

[407] P. Rumpf and F. Trombe, *C.R.* 1938, **206**, 671.

[408] E. Weitz and H. W. Schwechten, *Ber.* 1927, **60**, 1203.

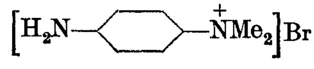
[409] E. Müller and W. Wiesemann, ib. 1936, **69**, 2157.

[410] See also R. Willstätter and J. Piccard, ib. 1908, **41**, 1462.

[411] J. Piccard, *Ann.* 1911, **381**, 357.

[412] L. Michaelis, *J.A.C.S.* 1931, **53**, 2953; L. Michaelis and E. S. Hill, ib. 1933, **55**, 1481.

suppose the ring to be quinonoid or not. This conclusion is supported by the observation of Rumpf and Trombe[413] that



is paramagnetic in methyl alcohol.

The intense colour of these salts is clearly due not so much to the presence of the septet as to the possibility of the positive charge being on either of the two nitrogen atoms, as in the triphenyl methane dyes. The absorption bands of the Würster salts got by the oxidation of *p*-phenylene diamines have been calculated by orbital methods,[414] and the results agree well with observation. The influence of substituents on the stability of these salts has been discussed by Michaelis[415]; they are much less stable when the ring has one and still less so when it has two ortho-methyl groups. This is presumably because the ortho-methyls interfere sterically with the planar structure which is essential to the resonance.

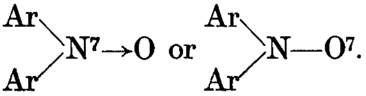
Similar salts are formed by the dipyridyl derivatives (Weitz).[416]

The compound which gives the well-known deep blue colour when diphenylamine is treated with nitric acid in concentrated sulphuric acid, and which is an oxidation product of diphenyl benzidine

$$\Phi\cdot NH—C_6H_4—C_6H_4—NH\Phi,$$

may be a similar odd molecule.

B. 4. *Diaryl Nitrogen Oxides*



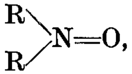
$$\begin{matrix}Ar\\Ar\end{matrix}\!\!>N^7\rightarrow O \text{ or } \begin{matrix}Ar\\Ar\end{matrix}\!\!>N—O^7.$$

This was the first group of nitrogen radicals to be recognized (Wieland[417]); they can obviously be regarded as substitution products of nitrogen dioxide $O{=}N—O$; like the dioxide they are bright red, but unlike it they show no sign of polymerization at low temperatures. Wieland made them[417-18] by the oxidation of N,N-diaryl hydroxylamines:

$$Ar\cdot N{=}O + Ar\cdot MgBr \longrightarrow Ar_2N\cdot O\cdot MgBr \longrightarrow Ar_2N\cdot OH$$

$$2\,Ar_2N\cdot OH + Ag_2O = 2\,Ar_2N—O + H_2O + 2\,Ag.$$

They can also be made by the reduction of certain nitric acid derivatives (K. H. Meyer).[419-20]

In these compounds the oxygen atom must be attached to the nitrogen by a single link as in $R_2N^7\rightarrow O^8$ or $R_2N^8—O^7$, since otherwise in  $\begin{matrix}R\\R\end{matrix}\!\!>N{=}O$,

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[413] P. Rumpf and F. Trombe, *J. Chim. Phys.* 1938, **35**, 110.

[414] M. G. Mayer and K. J. McCallum, *Rev. Mod. Phys.* 1942, **14**, 248.

[415] L. Michaelis, M. P. Schubert, and S. Granicke, *J.A.C.S.* 1939, **61**, 1981.

[416] E. Weitz, *Z. Elektrochem.* 1928, **34**, 538.

[417] H. Wieland and M. Offenbacher, *Ber.* 1914, **47**, 2111.

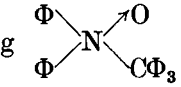
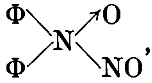
[418] H. Wieland and A. Roseeu, ib. 1915, **48**, 1117.

[419] K. H. Meyer and H. Gottlieb-Billroth, ib. 1919, **52**, 1476.

[420] K. H. Meyer and W. Reppe, ib. 1921, **54**, 327.

the nitrogen atom would have 9 electrons ($\underline{8}$, 1) which is impossible. The diaryl nitrogen oxides have the same relation to the diaryl nitrogens as the tertiary amine oxides to the tertiary amines.

Diphenyl nitrogen oxide $\Phi_2N—O$ looks like chromium trioxide, and gives solutions of a brilliant deep red; the absorption spectrum is very like that of nitrogen dioxide. Compounds of this type have been shown to be paramagnetic,[421-2] as the formula requires. The nature of the aryl groups has an enormous influence on the stability of the radicals (Wieland and Roth[423]); thus (*p*-tolyl)$_2$NO will keep at the ordinary temperature about 3 hours; $(C_6H_5)_2NO$ 24 hours; para-$(NO_2 \cdot C_6H_4)_2NO$ some months, and (*p*-$CH_3 \cdot O \cdot C_6H_4)_2NO$ for years. The melting-points of the above compounds are respectively 60°, 64°, 109°, and 150°; all of them melt only with decomposition.

Chemically all these compounds are very reactive; they readily add on other radicals, triphenyl methyl giving  (a tertiary amine-oxide); nitric oxide presumably first forms , but this goes to the nitramine $\Phi_2N—NO_2$, and ultimately to *p*-nitro-diphenylamine $NO_2 \cdot C_6H_4—NH\Phi$. They are quantitatively reduced by acid potassium iodide solution to diphenylamine.

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[421] L. Cambi, *Gaz.* 1933, **63**, 579.

[422] J. Katz, *Z. Phys.* 1933, **87**, 238.

[423] H. Wieland and K. Roth, *Ber.* 1920. **53**, 210.

PHOSPHORUS

The most fundamental difference between nitrogen and phosphorus is that the covalency of nitrogen is limited to 4, whilst that of phosphorus can extend to 6; at the same time a covalency of 4 is a very stable state for phosphorus, as it is for most of the heavier elements, especially for those which are only just heavy enough to be outside the limit of 4.

Phosphorus is thus able, like nitrogen, to form trivalent compounds such as PH_3 and PCl_3, with a complete mixed octet 2, $\underline{6}$; and further, while retaining the octet, to increase the covalency from 3 to 4, either by adding a cation and forming the phosphonium ion $[PH_4]^+$ or $[PR_4]^+$ analogous to ammonium, or by co-ordinating as a donor with a neutral atom or molecule, as in the phosphine oxides $R_3P \rightarrow O$ (like the amine oxides $R_3N \rightarrow O$) and the 'phosphinates' such as $H_3P \rightarrow AlCl_3$, which are analogous to ammines like $H_3N \rightarrow AlCl_3$.

Phosphorus is, however, able, in virtue of its higher covalency limit, to form a series of compounds which are impossible for nitrogen. The most obvious are the 5-covalent compounds of the type of PF_5, in which each of the 5 valency electrons is used for forming a separate covalency, giving the valency group $\underline{10}$; the 5 covalencies are arranged in a trigonal bipyramid (3 equatorial and 2 polar: see Introd., p. xx). A covalency of 5 is more stable than usual among the elements of this Vth Group, since it can be formed without co-ordination.

Finally, phosphorus can acquire by co-ordination its full covalency of 6, as in the remarkably stable salts of hexafluorophosphoric acid $H[PF_6]$; compounds of this type have recently been found to be more numerous than had been supposed.

The higher covalency limit sometimes makes resonance forms possible for phosphorus which are impossible for nitrogen; thus the phosphine oxides may have the structure $R_3P{=}O$, while the amine oxides can only be $R_3N \rightarrow O$; this is, however, of less importance owing to the instability of double links with phosphorus.

The 'inert pair' effect, which is so marked with bismuth, and is perceptible even with arsenic, is not observed with phosphorus.

Elementary Phosphorus

An active isotope ^{32}P, with a half-life of 14·07 days,[423a] can be made by nuclear bombardment.

The elements of the series Nitrogen—Bismuth tend in general to occur in two markedly different forms (often accompanied by others), one of which is voluminous, transparent, and highly non-metallic, while the other is denser, coloured or opaque, and often more or less metallic in behaviour. The stability of the second form increases with the atomic weight. With nitrogen, only the first type is known, but with phosphorus we have both, in white and red phosphorus, and the same with arsenic and antimony;

[423a] D. Mulder, C. W. Hoeksema, and C. J. Sizoo, *Physica*, 1940, 7, 849.

but the first type, which is only metastable even in phosphorus, gets more and more unstable, and the second type more and more metallic, until in bismuth the first type is unknown, and the second definitely a metal.

The allotropic solid forms of phosphorus are of three kinds, white, red (or violet), and black.

Black phosphorus, which is very dense and only produced under pressure, was first made by Bridgman[424] from the white under 12,000 atm. at 200°, or[425] under 35,000 atm. at the ordinary temperature; he found that it has a lower vapour pressure than the red form (2·3 cm. against red 5·2 cm. at 357°), and so claimed that it is the most stable form. This form can also be made[426] by a sudden and very brief application of 100,000 atm. to the white; it is said to revert slowly (in 6 months) to the white form, but this is incompatible with the other evidence that the white is the least stable allotrope.

A second but amorphous black form is also said to be formed under 12,000 atm. at 200°[427]; the densities of these forms and their heats of solution per g.-atom in bromine (giving the differences in energy content) are[427]:

	Density	*Ht. of soln.*
Black crystalline .	2·69	38·30 k.cals.
,, amorphous .	2·25	36·60 ,,
Red . . .	2·34	42·50 ,,
White . . .	1·83	59·48 ,,

These heats support Bridgman's view that the stable form at the ordinary temperature is the black; Jacobs[427] does not consider the small heat difference between the two black forms to be significant.

White phosphorus is a colourless transparent crystalline solid; it is often tinged with yellow, but if it is redistilled in complete absence of air and light it is quite colourless, and remains so as long as it is kept in nitrogen in the dark.[428] It melts at 44·1°, where its vapour pressure is 0·181 mm., and boils at 280°; it is very soluble in benzene and still more in carbon disulphide (solubilities at 10°: benzene 2·4, CS_2 900); it catches fire at 50° in air, and the lethal dose for a man is 0·1 g.

Red (or violet) phosphorus varies in colour from red to violet according to the method of preparation; according to Smits[429] the pure form is violet, and the red a mixture of this with a little of some other form; see further, reference [429a]. It sublimes with a vapour pressure of 1 atmosphere at 416°; melting-point (triple pt.) is 589·5°, where its vapour pressure is 43·1

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[424] P. W. Bridgman, *J.A.C.S.* 1914, **36**, 1344.

[425] Id., *Phys. Rev.* 1934, ii. **45**, 844.

[426] P. L. Günther, P. Geselle, and W. Rebentisch, *Z. anorg. Chem.* 1943, **250**, 373.

[427] R. B. Jacobs, *J. Chem. Phys.* 1937, **5**, 945.

[428] L. Wolf and K. Ristau, *Z. anorg. Chem.* 1925, **149**, 403.

[429] A. Smits and S. C. Bokhorst, *Z. physikal. Chem.* 1916, **91**, 249.

[429a] W. L. Roth, T. W. De Witt, and A. J. Smith, *J.A.C.S.* 1947, **69**, 2881.

atmospheres. The liquid formed by fusing red phosphorus is colourless, and so is presumably the same as that formed on melting the white. When pure, red phosphorus is practically insoluble in all solvents, and it only reacts at high temperatures; it is non-poisonous. The enormous differences between the vapour pressures of the two forms are shown by the following values (in atms., white referring to the liquid and red to the solid form):

Temp.	*V.p. white*	*V.p. red*	*Ratio*
308·5° C.	1·70 atm.	0·07	24
409·5° C.	7·36	0·81	9·1

The red is of course the stable form of the two. Phosphorus vapour on cooling normally condenses in the white form, but this goes over to the red on heating above 260°, and even in the cold in presence of light, and of certain catalysts such as iodine. For the kinetics of this see references [432-3]. Melville has, however, shown[430-1] that while white phosphorus gives off P_4 molecules, the red gives off—and is in equilibrium with—P_2 molecules; measurements of the concentration of P_2 over red phosphorus by means of its rate of evaporation show that this is only about 10^{-7} of the total pressure (given above), the vapour being mainly P_4; this makes the vapour pressure difference of the two forms far greater even than was supposed.

The enormous difference in stability of the two solid forms obviously implies a difference of molecular structure, and this is supported by Melville's results; but both give at equilibrium the same vapour and the same liquid, which have almost wholly the molecular form of white phosphorus. We have good evidence of the structure of white phosphorus and its vapour. White phosphorus, though its crystal structure has not been determined, is clearly made up of the P_4 tetrahedra which constitute the vapour at all but very high temperatures; they also compose the liquid, to judge from its Raman spectrum[436] and its X-ray diagram[437]; but the structures of the red and black forms are still not very certain[434] (see, however, for the black form, Wells[435]).

The vapour of phosphorus has the molecular weight of P_4 up to about 800°, and above that begins to dissociate into P_2 molecules, but only gradually, the density even at 1,700° indicating a mixture of about equal numbers of P_4 and P_2 molecules; the molecule in solution has been shown to be P_4 in benzene by the freezing-point and in carbon disulphide by the boiling-point. In the P_4 molecules of the vapour it has recently been shown by electron diffraction[438] that the 4 phosphorus atoms occupy the

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[430] H. W. Melville and S. C. Gray, *Trans. Far. Soc.* 1936, **32**, 271.

[431] Id., ib. 1026. [432] T. W. DeWitt and S. Skolnik, *J.A.C.S.* 1946, **68**, 2305.

[433] S. Skolnik, G. Tarbutton, and W. E. Bergman, ib. 2310.

[434] R. Hultgren, N. S. Gingrich, and B. E. Warren, *J. Chem. Phys.* 1935, **3**, 351.

[435] A. F. Wells, *S.I.C.*, p. 399.

[436] C. S. Venkateswaran, *Proc. Ind. Acad. Sci.* 1936, **4**, A, 345.

[437] C. D. Thomas and N. S. Gingrich, *J. Chem. Phys.* 1938, **6**, 659.

[438] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, ib. 1935, **3**, 699.

angular points of a tetrahedron, with valency angles of only 60°; the distance between two atoms was found to be 2·21±0·02 A (theory P—P 2·20).[439] This type of structure is otherwise known only in arsenic and perhaps antimony.

The formation of molecules of this peculiar kind, with the valency angles reduced to 60°, instead of P≡P molecules like the very stable N≡N, can only be due to a reluctance to form multiple links which phosphorus shares with other elements after the first short period (compare CO_2, SiO_2 and O_2, S_8), and which is supported by its whole behaviour (e.g. in the oxides). With the P—P links the heats of formation are known. Preuner and Brockmöller[440] have found from the change of vapour density with temperature the heat values:

$$P_4 = 2P_2 - 31{\cdot}5 \text{ k.cals. at } 800°$$
$$P_2 = 2P - 45{\cdot}45 \text{ ,, at } 1{,}400°.$$

From these Bichowsky and Rossini[441] calculate at 18° −30·0 and −42·2 k.cals. Hence the values for the heats of linkage are P—P 47·5, P≡P 117·0, ratio 2·46[442] (compare N≡N/N—N 8·50 and C≡C/C—C 2·10). Thus the strain in the triple link is of nearly the same relative value with phosphorus as with carbon.

Phosphorus occurs in nature (786 g./ton in the earth's crust) almost exclusively as phosphate. The most important minerals are phosphorite $Ca_3(PO_4)_2$ and apatite $3\,Ca_3(PO_4)_2$, $Ca(F,Cl)_2$. It also occurs to a considerable extent in guano.

Commercially it is practically always made by heating calcium phosphate with silica and carbon in the electric furnace to 1,300°, when calcium silicate $CaSiO_3$ is formed, and carbon monoxide and phosphorus vapour come over.[443]

HYDRIDES OF PHOSPHORUS

Phosphorus forms two volatile hydrides, PH_3 and P_2H_4, and a solid of doubtful character with a composition approaching P_2H. Physical constants are:

	B. pt.	*M. pt.*	*Trouton*	(*For N analogue*)
PH_3[a]	−87·7°	−133°	18·8	(−33·5°, −77°, 23·4)
P_2H_4[b]	+51·7°	−99°	24·2	(+113·5°, +1·8°, 25·8)

a = [446]; *b* = [447].

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[439] For a theoretical discussion of the P_4 molecule see J. R. Arnold, *J. Chem. Phys.* 1946, **14**, 351.

[440] G. Preuner and J. Brockmoller, *Z. physikal. Chem.* 1912, **81**, 129.

[441] *Thermochemistry*, p. 219.

[442] F. S. Dainton, *Trans. Far. Soc.* 1947, **43**, 244.

[443] For the mechanism of this reaction see H. H. Franck and H. Füldner, *Z. anorg. Chem.* 1932, **204**, 97.

[444] R. Höltje, ib. 1930, **190**, 241.

[445] R. Höltje and F. Meyer, ib. 1931, **197**, 93.

[446] C. C. Stephenson and W. F. Giauque, *J. Chem. Phys.* 1937, **5**, 149.

[447] P. Royen and K. Hill, *Z. anorg. Chem.* 1936, **229**, 97.

PH_3 is basic, but much weaker than ammonia; P_2H_4 is neutral (N_2H_4 is much weaker than NH_3).

Phosphine, PH_3

This is commonly made (along with a hypophosphite) by boiling phosphorus with an alkaline hydroxide solution:

$$4\,P + 3\,NaOH + 3\,H_2O = PH_3 + 3\,NaH_2PO_2.$$

It is also formed by disproportionation from lower oxidation products of phosphorus (thus dry phosphorous acid H_3PO_3 on heating gives phosphoric acid and phosphine), and by the action of acids or water on metallic phosphides; it is best made from aluminium phosphide AlP and sulphuric acid.[448] It usually contains traces of P_2H_4, and is then spontaneously inflammable in air; if the P_2H_4 is removed by passing the gas through concentrated sulphuric acid, it does not catch fire in air below 150°, though even pure PH_3 if it is thoroughly dried will catch fire in air in the cold.[449]

The structure of the PH_3 molecule has been determined from the spectra; the P—H distance is 1·45 A (theory 1·40), and the H—P—H angle $98 \pm 5°$[446] or $93 \pm 2°$.[450] The barrier to inversion

is about the same (2,000 cm.$^{-1}$) as in ammonia, but the frequency of inversion only about 1/1,000, so that optically active P*abc* molecules might be separated if the groups were large.[451] Solid phosphine occurs in four forms, owing apparently to the restricted rotation of the molecules.[450,452]

Phosphine is less associated than ammonia, as is shown by the low boiling-point (−87·4°; −33·5°);* it is also a much weaker base. The phosphonium salts $[PH_4]X$ even of strong acids are largely dissociated into $PH_3 + HX$; the dissociation tension of $[PH_4]Cl$ reaches 1 atmosphere below 0°, and that of $[NH_4]Cl$ only at 340°; also the phosphonium salts are decomposed into PH_3+acid by water. The small solubility of phosphine in water (0·26 vol. at 20°, 1/2,600 of that of NH_3) indicates that it has a much smaller tendency to hydration. It is also a much weaker donor than ammonia; see references [444-5]. In the vapour the phosphonium like the ammonium salts are completely dissociated into the hydride and the acid.

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* For the entropy and other thermodynamic properties see references [452-3].

[448] L. Moser and A. Brukl, *Z. anorg. Chem.* 1922, **121**, 73.
[449] M. Trautz and W. Gabler, ib. 1929, **180**, 321.
[450] D. P. Stevenson, *J. Chem. Phys.* 1940, **8**, 285.
[451] G. B. B. M. Sutherland, E. Lee, and C. K. Wu, *Trans. Far. Soc.* 1939, **35**, 1378.
[452] K. Clusius and A. Frank, *Z. physikal. Chem.* 1936, **B 34**, 405.
[453] D. P. Stevenson and D. M. Yost, *J. Chem. Phys.* 1941, **9**, 403.

Attempts to obtain a higher hydride such as PH_5 have failed, even with atomic hydrogen.[454]

The well-known explosion of mixtures of phosphine and oxygen when the pressure is reduced has been examined by Hinshelwood and Dalton[455-6] and by Trautz[449]; the explosion has both a lower and an upper pressure limit.

Phosphine will reduce nickel salts in aqueous solution, forming usually alloy-like P—Ni compounds with 0·4 to 0·1 P to 1 Ni; under special conditions definite phosphides Ni_3P, Ni_2P, and NiP are obtained.[457]

P_2H_4, '*Diphosphine*'

This is a by-product in the preparation of phosphine, and can be separated by freezing it out. It has recently been re-examined by Royen and Hill.[447] It is a colourless liquid (b.pt. 51·7°, m.pt. −99°) which is spontaneously inflammable in air. Further fractionation of the product gave no sign of the formation of a higher homologue such as P_3H_5. P_2H_4 is the phosphorus analogue of hydrazine, and is one of the very few compounds with two linked phosphorus atoms. It is unstable, and on keeping, especially in the light, changes into phosphine and the so-called solid hydride (see below); the same change is brought about by hydrogen chloride even at −125°, so that P_2H_4 has no basic properties, as we should expect, since PH_3 is so weak a base, and hydrazine is much weaker than NH_3.

'*Solid Phosphorus Hydride* $(P_2H)_n$'

This is a yellow insoluble powder which is formed when diphosphine decomposes, and as a by-product in many reactions in which the other hydrides are produced. According to Schenk[458] it has the composition P_2H and is soluble in white phosphorus, in which the freezing-point indicates the molecular weight of $P_{12}H_6$. The recent work of Royen[459] makes the existence of this compound very doubtful. He argues that it is really PH_3 adsorbed on amorphous phosphorus. He finds that the hydrogen content is variable: the solid gives no Debye X-ray pattern; and amorphous yellow phosphorus made by exposing a solution in CS_2 to light will absorb phosphine under pressure to give a solid of composition $P_{12}H_{4\cdot12}$ closely resembling the 'solid hydride'.

ALKYL AND ARYL PHOSPHINES[460]

The mono-, di-, and trialkyl phosphines are all known, especially the last[461]; they can be made by treating phosphonium iodide $[PH_4]I$ with

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[454] K. G. Denbigh, *Trans. Far. Soc.* 1939, **35**, 1432.

[455] R. H. Dalton and C. N. Hinshelwood, *Proc. Roy. Soc.* 1929, **125**, 294.

[456] R. H. Dalton, ib. 1930, **128**, 263.

[457] R. Scholder, A. Apel, and H. L. Haken, *Z. anorg. Chem.* 1937, **232**, 1.

[458] R. Schenk, *Ber.* 1903, **36**, 991, 4202.

[459] P. Royen, *Z. anorg. Chem.* 1936, **229**, 369.

[460] See Krause and v. Grosse, 1937, p. 444.

[461] A. W. Hofmann, *Ber.* 1871, **4**, 605; 1873, **6**, 302.

alcohols,[461] or better from the trihalides and the Grignard reagents (see especially refs. [462-4]).

The difference in boiling-point between PH_3 and NH_3 soon vanishes as the hydrogen atoms are replaced by the larger alkyls, as is shown by the following table (in which the boiling-points of the corresponding amines follow in brackets):

Boiling-points (PH_3 −87·7°, NH_3 −33·5°)

	PH_2R		PHR_2		PR_3	
R = CH_3	+14°[b]	(−6°)	+21·1°[a]	(+7·2°)	+37·8°[c]	(+3·5°)
C_2H_5	+25°	(+18·6°)	+56°	(+56°)	128°	(89°)
n-Pr	41°	(50°)	118°	(110°)	..	(156·5°)
n-Bu	62°	(77°)	153°	(159°)	215°	(216°)

a = [465]; *b* = [447]; *c* = [466].

The pyramidal form of $P(CH_3)_3$ is shown by the Raman spectra[467] and by the infra-red spectra.[468]

Like phosphine, many of the alkyl derivatives catch fire in air, and all are readily oxidized. The phosphorus takes up an oxygen atom, and at the same time any hydrogen attached to it is replaced by hydroxyl, thus:

$$\begin{array}{lllll} PH_3 & PH_2R & PHR_2 & PR_3 & \text{give respectively} \\ H_3PO_4 & H_2PRO_3 & HPR_2O_2 & R_3P{\rightarrow}O & \end{array}$$

This characteristic difference from nitrogen is due to the greater affinity of phosphorus for oxygen as compared with hydrogen; of the heats of linkage that of N—H is 34 k.cals. greater than that of N—O, while P—H is 16·5 k.cals. less than P—O; a similar difference was noted between carbon and silicon. The ease of oxidation of the tertiary phosphines first falls and then rises as the alkyls grow larger.[462-4]

As with ammonia, the substitution of alkyls for hydrogen increases the basicity; the monalkyl phosphonium halides are decomposed by water, but the secondary and tertiary are not more highly hydrolysed than ammonium salts.

The quaternary bases R_4POH have been shown by their conductivities[469] to be as strong as tetramethyl ammonium hydroxide or an alkali. The reaction

$$PR_3 + R{\cdot}hal = [PR_4]hal$$

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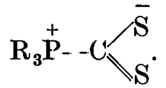
[462] W. C. Davies and W. J. Jones, *J.C.S.* 1929, 33.
[463] W. C. Davies, P. L. Pearse, and W. J. Jones, ib., 1262.
[464] I. K. Jackson, W. C. Davies, and W. J. Jones, ib. 1931, 2109.
[465] N. Davidson and H. C. Brown, *J.A.C.S.* 1942, **64**, 718.
[466] E. J. Rosenbaum and C. R. Sandberg, ib. 1940, **62**, 1622.
[467] E. J. Rosenbaum, D. J. Rubin, and C. R. Sandberg, *J. Chem. Phys.* 1940, **8**, 366.
[468] F. J. Wagstaffe and H. W. Thompson, *Trans. Far. Soc.* 1944, **40**, 41.
[469] G. Bredig, *Z. physikal. Chem.* 1894, **13**, 301.

is quicker than the corresponding nitrogen reaction, but it goes less quickly the heavier the alkyls.[470]

It was supposed that the quaternary chlorides Alk_4PCl broke up on heating into Alk_3PHCl and alkylene, but Ingold[471] finds that this is not so; the products (at about 350°) are $Alk_3P + Alk \cdot Cl$; the hydroxides Alk_4POH always give $Alk_3PO + Alk \cdot H$.

The ready formation of a 1:1 addition product with carbon disulphide (looking like chromium trioxide) is characteristic of tertiary phosphines[472] but the structure of the product is not clear[462,473-6]; perhaps the most probable view is Jensen's,[476] that it is of the betaine type  $R_3\overset{+}{P}\text{- -}C\genfrac{}{}{0pt}{}{\diagup \bar{S}}{\diagdown S}$.

All attempts to prepare compounds with 5 alkyl (or alkyl and aryl) groups attached to the phosphorus, which are not incompatible with the covalency rules, have failed,[477] even the treatment of the quaternary iodide Alk_4PI with lithium alkyl[478]; the supposed preparation of $\Phi_3P(Alk)_2$[479] was shown[480] to be incorrect. The nearest approach is the bright red compound $\Phi_3P{=}C\Phi_2$, made[477] by heating the azine

$$\Phi_3P{=}N{-}N{=}C\Phi_2;$$

this was confirmed by Marvel[478]; it may of course have the structure $\Phi_3P{\rightarrow}C\Phi_2$.

The aryl phosphines are in general similar to the alkyl.[481-4] Triphenyl phosphine $P\Phi_3$ (b.pt. over 360°, m.pt. 79·5°) decomposes with separation of phosphorus at 350° under 60 atm. of hydrogen.[483] On nitration with nitric acid of density 1·5[485] it gives only para-nitro-derivatives. It will react with bromobenzene in presence of aluminium chloride in 3 hours at 230° to 280° to give tetraphenyl phosphonium bromide $[\Phi_4P]Br$, m.pt. 282°[484,486]; the fact that this salt exists, while tetraphenyl ammonium bromide $[\Phi_4N]Br$ cannot be made, is presumably due to the larger radius of the phosphorus. Silver oxide converts the salt into the strongly alkaline

[470] W. C. Davies and S. U. Evans, *J.C.S.* 1934, 244.

[471] G. F. Fenton, L. Hey, and C. K. Ingold, ib. 1933, 989.

[472] A. W. Hofmann, *Proc. Roy. Soc.* 1860, **10**, 189, 616; 1862, **11**, 291; *Ann. Splbd.* 1861/2, **1**, 36.

[473] W. C. Davies, *J.C.S.* 1935, 462.

[474] V. Meyer and P. Jacobson, *Lehrb.*, ed. 2, Bd. I, p. 427.

[475] A. Hantzsch and H. Hibbert, *Ber.* 1907, **40**, 1508.

[476] K. A. Jensen, *J. prakt. Chem.* 1937, [ii] 148, 101.

[477] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635.

[478] D. D. Coffman and C. S. Marvel, *J.A.C.S.* 1929, **51**, 3496.

[479] V. Grignard and J. Savard, *C.R.* 1931, **192**, 592.

[480] B. K. Blount, *J.C.S.* 1931, 1891.

[481] I. K. Jackson, W. C. Davies, and W. J. Jones, ib. 1930, 2298.

[482] I. K. Jackson and W. J. Jones, ib. 1931, 575.

[483] V. Ipatiev and G. Razubaiev, *Ber.* 1930, **63**, 1110.

[484] H. Gilman and G. E. Brown, *J.A.C.S.* 1945, **67**, 824.

[485] F. Challenger and A. T. Peters, *J.C.S.* 1929, 2610.

[486] J. Chatt and F. G. Mann, ib., 1940, 1192.

hydroxide $[\Phi_4P]OH$, which, however, readily changes, even in the cold, into benzene and the oxide $\Phi_3P{\rightarrow}O$.

Phosphine Oxides, $R_3P{\rightarrow}O$ or $R_3P{=}O$

These are the products of the oxidation of the tertiary phosphines. Thus triethyl phosphine oxide Et_3PO is made by oxidizing Et_3P with mercuric oxide or nitric acid: m.pt. 52·9°, b.pt. 243°/760 mm. Triphenyl phosphine oxide Φ_3PO (m.pt. 153·5°, b.pt. over 360°/760 mm., v.d. normal) is made in the same way. It forms a hydrate Φ_3PO,H_2O, only slightly soluble in water but readily in benzene, from which it can be recrystallized.[487] The phosphine oxides are sharply distinguished from the amine oxides in having no oxidizing power.[488]

These compounds (unlike the amine oxides) can obviously have either the co-ordinate or the doubly linked formula, and presumably are resonance hybrids. The solubility of the hydrate suggests that this is the wholly covalent $\Phi_3P(OH)_2$. The absence of oxidizing power is obviously due to the great affinity of phosphorus for oxygen (compare nitric and phosphoric acids).

PHOSPHORUS-NITROGEN COMPOUNDS

Phosphorus forms a number of compounds with nitrogen, either alone, or along with hydrogen, oxygen, or the halogens. Of the binary nitrides three have been described, of the compositions P_3N_5, P_2N_3 (or P_4N_6), and PN. They are all no doubt polymerized, but their molecular weights are not known.

P_3N_5 was made by Stock[489] by heating the addition compound P_2S_5, $6\,NH_3$ to redness in a stream of ammonia. It is a white solid without taste or smell; in a vacuum or in nitrogen it decomposes at a red heat to give phosphorus and nitrogen, and in hydrogen to give ammonia as well (PN is also formed); it reacts with water, slowly at 100° and rapidly in a sealed tube at 180°, to give ammonia and phosphoric acid. These conclusions of Stock were confirmed by V. F. Postnikov and L. L. Kusmin,[490] who further showed that in air at 800° it is converted into nitrogen and phosphorus pentoxide, and that it is scarcely acted on by nitric sulphuric or aqueous hydrochloric acid at their boiling-points.

P_2N_3 (or P_4N_6) is formed along with hydrogen by heating the imide $P_2(NH)_3$[491]; it is stable up to 750°, where it changes into nitrogen and PN; if it is heated in a sealed tube with water it gives a mixture of ammonium phosphate and phosphite.

The nitride of composition *PN* was made by H. Moureu and P. Rocquet[492]

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[487] A. Michaelis and H. v. Soden, *Ann.* 1885, **229**, 306.

[488] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 612.

[489] A. Stock and B. Hoffmann, *Ber.* 1903, **36**, 314.

[490] *J. Appl. Chem. Russ.* 1935, **8**, 429.

[491] H. Moureu and G. Wetroff, *Bull. Soc. Chim.* 1937, [v], **4**, 918, 1839, 1850.

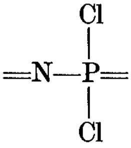
[492] Ib. 1936, [v] **3**, 1801.

by heating P_3N_5 to 750° *in vacuo*, when nitrogen is given off, and the PN sublimes. It occurs in two forms: α, red, stable, not acted on by cold sulphuric acid but oxidized by hot; and β, yellow, reacting with strong sulphuric acid in the cold; neither of these would give an X-ray pattern, so they both must be amorphous. PN begins to dissociate at 750°; nitrogen has no action on it at any temperature, but ammonia converts it into P_3N_5 at 800°. It can also be made[493-4] by the combination of phosphorus vapour and nitrogen on tungsten filament at 1,500-1,800°, its presence can be detected spectroscopically in the vapour at 450°, but it soon polymerizes on the walls. On heating with water in a sealed tube it is converted into ammonium phosphite with some phosphate and hydrogen.

As none of these phosphorus nitrides have had their X-ray patterns determined, it is useless to speculate on their (obviously polymerized) structures.

Hydrides. Phosphorus can replace successively all the hydrogen atoms of ammonia, giving $P(NH_2)_3$, $P_2(NH)_3$, and finally PN. For the preparation and properties of these compounds see references[495-7].

Various obscure *oxygen* derivatives have been made by heating PN with water[498] (PNO_2H_2 ?) and by heating phosphorus oxychloride with ammonia (PNO).[499]

More is known of the PN compounds of *chlorine* and *fluorine*. There are several polymers of the composition $(PNCl_2)_n$; they include a trimeric and a tetrameric form, both crystalline and of known molecular weight, and a remarkable high polymer with many of the properties of rubber. They all seem to be made up of  $=\!N\!-\!\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{P}}\!=$ groups variously arranged.

By treating the nitride P_2N_3 or P_3N_5 with chlorine at 700°, and in other ways,[501] a substance $(PNCl_2)_n$ can be made.[500] This on heating gives a series of polymers of which at least the trimer and the tetramer can be isolated. The tetramer can be made from the trimer by heating to 600°, various liquid and solid polymers being formed at the same time. Audrieth *et al.*[502] make use of the reaction

$$PCl_5 + NH_4Cl = PNCl_2 + 4\,HCl;$$

[493] H. Moureu and G. Wetroff, *C.R.* 1938, **207**, 915.

[494] H. Moureu, B. Rosen, and G. Wetroff, ib. 1939, **209**, 207.

[495] H. Moureu and P. Rocquet, ib. 1933, **197**, 1643.

[496] Id., ib. 1935, **200**, 1407.

[497] H. Moureu and G. Wetroff, *Bull. Soc. Chim.* 1937, [v], **4**, 918.

[498] P. Renaud, *C.R.* 1934, **198**, 1159.

[499] G. Wetroff, ib. 1937, **205**, 668.

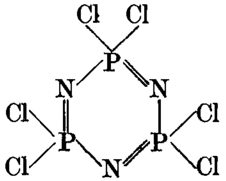
[500] Id., ib. 1939, **208**, 580.

[501] See H. N. Stokes, *Amer. Chem. J.* 1897, **19**, 782.

[502] R. Steinman, F. B. Schirmer, and L. F. Audrieth, *J.A.C.S.* 1942, **64**, 2377.

the trimer and the tetramer (about 40 per cent. of the product) are dissolved out with ligroin, and the trimer separated by distillation at 140°/12–14 mm.

The trimer $P_3N_3Cl_6$ (m. pt. 114·9°, b. pt. extrapolated 252·7°, Trouton constant 25·1)[502] has been examined by electron diffraction[503]; it has a fully planar ring with the distances P—N 1·65, P—Cl 1·97 (theory P—N 1·80, P=N 1·60; P—Cl 2·09, P=Cl 1·89), angle Cl—P—Cl 109±2°; it is obviously stabilized by a Kekule resonance.



The tetramer $P_4N_4Cl_8$ (b. pt. extrapd. 325·5°[504] was found[505] to have a puckered 8-ring of alternate P and N atoms, with 2 Cl on each P; P—N was 1·67 A, indicating aromatic resonance here too.

The vapour pressures of these compounds have been measured by Moureu,[504] who finds the heats of evaporation to be trimer 13, tetramer 15·5, high polymer ('mineral rubber') 15·5 k.cals. per $PNCl_2$, indicating a very small heat of polymerization. When the trimer is treated with benzene and aluminium chloride it has 2 but only 2 of the 6 Cl atoms replaced by phenyls,[506] and the product gives with water $(C_6H_5)_2PO \cdot OH$, confirming the view that the trimer has 2 Cl on 1 P.

The higher polymers of $PNCl_2$ are difficult to characterize; they are largely gums or rubber-like substances, and (as with polymerized formaldehydes) it is very difficult to know how many there are.[507-8] The rubber-like product which presumably is or contains the highest of the polymers has been examined by K. H. Meyer.[509] He calls this form of $PNCl_2$ an 'inorganic rubber', and shows how closely it resembles real rubber in its physical state; X-ray diagrams show that it is amorphous when it is not stretched, but when it is, it gives a crystalline pattern, which is such as to indicate that the molecule must be made up of zigzag chains formed of PCl_2 groups with nitrogen atoms between them.

An interesting development of this subject is due to Schmitz-Dumont and his colleagues,[510-11] who investigated the replacement of the chlorine in these compounds by fluorine. They found that the trimer $(PNCl_2)_3$

[503] L. O. Brockway and W. M. Bright, ib. 1943, **65**, 1551.

[504] H. Moureu and A. M. de Fiquelmont, *C.R.* 1941, **213**, 306.

[505] J. A. A. Ketelaar and T. A. de Vries, *Rec. Trav.* 1939, **58**, 1081.

[506] H. Bode and H. Bach, *Ber.* 1942, **75**, 215.

[507] P. Renaud, *Ann. Chim.* 1935, [xi] **3**, 443.

[508] A. M. de Fiquelmont, ib. **12**, 169.

[509] K. H. Meyer, W. Lotmar, and G. W. Pankow, *Helv. Chem. Acta*, 1936, **19**, 930.

[510] O. Schmitz-Dumont and H. Külkens, *Z. anorg. Chem.* 1938, **236**, 189.

[511] O. Schmitz-Dumont and A. Brasches, ib. 1939, **243**, 113.

on heating with lead fluoride PbF_2 for some hours at temperatures rising from 130° to 340° reacts to give a volatile liquid from which the compound $P_4N_4Cl_2F_6$ was isolated by distillation: b.pt. 105·8°, Trouton 23·1; monomeric by vapour density at 140° and by f.pt. in benzene; but at 300° the vapour density is little above that required for $P_2N_2ClF_3$. If this is heated at the ordinary pressure it remains a vapour and does not polymerize, but at 300° in a bomb tube under pressure it goes to a rubber-like substance, which, however, is much less stable than the pure chloride rubber, and readily depolymerizes to volatile forms. It is also possible to get from $PNCl_2$ and PbF_2 a less fluorinated compound $P_4N_4Cl_4F_4[= (PNClF)_4]$; this melts at −25°, boils at 130·5°, and has a Trouton constant of 21·7; at 200–300° its vapour is less dissociated than that of $P_4N_4Cl_2F_6$, but more than that of $P_4N_4Cl_8$. It also gives a rubber when heated under pressure to 300°. A similar and isomorphous compound $P_4N_4Br_8$ can also be made.[512]

On the other hand, if the $PNCl_2$ is heated with excess of lead fluoride the chlorine is completely replaced, presumably with the formation of $P_3N_3F_6$; this compound, however, could not be isolated as such, but separated out (when the materials were damp) as colourless crystals of the composition $P_3N_3F_6$, 2 HF, 2 H_2O, which melted at 32·5°. A series of phenyl derivatives such as $P_4N_4Cl_4(C_6H_5)_4$ can be made by treating $P_4N_4Cl_8$ with benzene in the presence of aluminium chloride.[513-14]

OXIDES OF PHOSPHORUS

Several oxides have been described, but only three are certain, P_4O_6, P_4O_{10}, and P_2O_4 (probably P_4O_8). The peroxide PO_3 or P_2O_6 also probably exists.

The supposed suboxide P_2O has been shown[515] to be a mixture of finely divided red phosphorus and adsorbed H_3PO_3.

Phosphorous Oxide, P_4O_6

This is formed by the combustion of phosphorus in a limited supply of oxygen or air. It contains traces of free phosphorus, which can be removed by dissolving it in carbon disulphide and exposing the solution to the light (when the free phosphorus goes over into the insoluble red form), filtering, and recrystallizing.[516] It then melts at 23·8°, and boils at 173°[516-17]; the liquid is a non-conductor of electricity. In solution, and in the vapour at lower temperatures, its molecular weight corresponds to P_4O_6. It is somewhat unstable; the vapour above 210° decomposes into the tetroxide P_2O_4 and free phosphorus; unless it is quite pure[516] it takes up oxygen slowly in air at the ordinary temperature, and the luminescence of phos-

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[512] H. Bode, *Z. anorg. Chem.* 1943, **252**, 113.

[513] H. Bode and H. Bach, *Ber.* 1942, **75**, 215.

[514] H. Bode and H. Thamer, ib. 1943, **76**, 121.

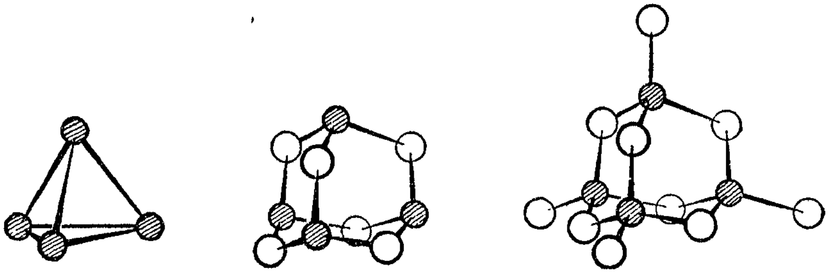
[515] L. J. Chalk and J. R. Partington, *J.C.S.* 1927, 1930.

[516] C. C. Miller, ib. 1928, 1847.

[517] P. M. van Doormaal and F. E. C. Scheffer, *Rec. Trav.* 1931, **50**, 1100.

phorus in air has been ascribed to this reaction. P_4O_6 is slowly converted by cold water into phosphorous acid H_3PO_3, but with hot water it reacts violently, forming in addition a certain amount of phosphine and phosphoric acid. It reacts with chlorine and bromine, with sulphur above 150°, and is converted by gaseous hydrogen chloride into phosphorus trichloride and phosphorous acid.

The structure of P_4O_6 has been examined by electron diffraction by Hendricks *et al.*[518] and by Hampson and Stosick[519] with concordant results. They find that the 4 phosphorus atoms occupy the points of a tetrahedron, with the 6 oxygen atoms on, or rather just outside, the middles of the six edges. The values are (those of Hampson and Stosick are in brackets): P—O 1·67 (1·65); angle P—O—P 128·5±0·5° (127·5±1°), O—P—O 98±2° (99±1°); theory for P—O 1·76; Hampson and Stosick point out that the small value of the phosphorus angle in X—P—X is common in PX_3 compounds: PF_3 99°, PCl_3 100°, PBr_3 100°, PI_3 98°, $(P(CH_3)_3$ 100° (all ±2-4°): for references see original.[519]


(*a*) (*b*) (*c*)

The structures of the molecules (*a*) P_4, (*b*) P_4O_6, and (*c*) P_4O_{10} in the vapour state (diagrammatic). Shaded circles represent P atoms (from Wells: *Structural Inorganic Chemistry*, Clarendon Press, Oxford)

Phosphorus Tetroxide, P_2O_4 *or* P_4O_8

This substance is formed, together with free phosphorus, by heating the vapour of P_4O_6 above 210°. It is a solid subliming at 180°; its molecular weight is unknown. It has the composition of an anhydride of hypophosphoric acid $H_4P_2O_6$, but it can neither be formed from nor converted into that acid, which almost certainly contains a P—P link (see p. 743). It dissolves in water with considerable evolution of heat to give equivalent quantities of phosphorous and phosphoric acids: it is clearly a mixed anhydride of these two acids.

Its molecular weight has not been determined, but the small volatility suggests polymerization, and it is almost certainly P_4O_8, with a tetrahedral structure derived from that of P_4O_6 by converting 2 of the phosphorus atoms into P→O or P═O (as in P_4O_{10}).

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[518] L. R. Maxwell, S. B. Hendricks, and L. S. Deming, *J. Chem. Phys.* 1937, 5, 626.

[519] G. C. Hampson and A. J. Stosick, *J.A.C.S.* 1938, 60, 1814.

Phosphorus Pentoxide, Phosphoric Oxide, P_4O_{10}

This is made by burning phosphorus in excess of air or oxygen. The molecular weight is given by the vapour density, which is approximately 150 at 670-1100°[520] (theory for P_4O_{10} 142). The structure of the gaseous molecule was determined by electron diffraction by Hampson and Stosick,[519] who found it to be that of P_4O_6, with an extra oxygen on each phosphorus at a distance of $1{\cdot}39 \pm 0{\cdot}02$ A, abnormally short even for pure P=O (theory P—O 1·76, P=O 1·55, P≡O 1·43); this is not satisfactorily explained.

The solid has long been known to be polymorphic. The form first produced by the combustion of phosphorus has vapour pressure of 1 atmosphere at 359°, but if it is heated to 400° or so it soon changes into another form with a far smaller vapour pressure. The relations of the various forms have been examined by several workers[521-4]; their work has recently been confirmed and extended by Hill, Faust, and Hendricks.[525] It is shown that there are three solid forms: (I) hexagonal, the volatile form first produced, (II) orthorhombic, got from this on heating, (III) tetragonal, got by further heating; this last is at all temperatures the stable modification. The constants are[525]:

	Triple pt.	*Density*	*Heat of volatilization*
I. Hexagonal	420°/360 cm.	2·30	22·7 k.cals./P_4O_{10}
II. Orthorhombic	562°/43·7 cm.	2·72	36·4 ,,
III. Tetragonal	580°/55·5 cm.	2·89	33·9 ,,

The heat of volatilization of the metastable fused hexagonal form is 16·2, and that of the stable liquid (above 580° C.) 18·7 k.cals./P_4O_{10}.

The solid hexagonal form is built of tetrahedral molecules of the vapour type. Solid orthorhombic[526] is made of sheets of interlocking rings of the same type, the phosphorus atoms being surrounded by shared tetrahedra of oxygens. The structure of the tetragonal modification is unknown. It is remarkable that this last can be heated above its melting-point without melting, even up to 700°.[527] This, which has also been observed with some felspars,[528] may be due to the fact that the melting involves a chemical change.

Phosphorus pentoxide absorbs moisture, going first to metaphosphoric

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[520] E. V. Britzka and E. Hoffmann, *Mon.* 1938, **71**, 317.

[521] A. N. and A. J. R. Campbell, *Trans. Far. Soc.* 1935, **31**, 1567.

[522] J. C. Southard and R. A. Nelson, *J.A.C.S.*, 1937, **59**, 911.

[523] S. Glixelli and K. Boratynski, *Z. anorg. Chem.* 1938, **235**, 225.

[524] A. Smits, E. P. S. Parve, P. G. Meerman, and H. C. J. de Decker, *Z. physikal. Chem.* 1940, B **46**, 43.

[525] W. L. Hill, G. T. Faust, and S. B. Hendricks, *J.A.C.S.* 1943, **65**, 794.

[526] H. C. J. de Decker, *Rec. Trav.* 1941, **60**, 413.

[527] A. Smits and H. W. Deinum. *Z. physikal. Chem.* 1930, **149**, 337.

[528] A. L. Day and E. T. Allen, *Carnegie Inst. Wash.* 1905, Pubn. 31, 45.

acid HPO_3 and then to the pyro- and ortho-acids. It is the most efficient drying agent known (magnesium perchlorate is nearly as good), and no traces of moisture can be detected in a gas which has stood in contact with it. It is practically always the first (hexagonal) form that is used for drying because this naturally has the largest surface. It has been shown, however,[525] that for equal surfaces all three modifications absorb moisture from the air at about the same rate; but on addition to liquid water the hexagonal reacts violently, the orthorhombic reacts very slowly even at 100°, and the tetragonal at once forms a jelly, which then slowly liquefies. Phosphorus pentoxide is as efficient a drying agent at 90° as it is at 0°.[529]

Phosphorus Peroxide, PO_3 or P_2O_6

Schenk has shown[530–1] that if a mixture of phosphorus pentoxide vapour and oxygen is sparked, a deep violet solid of high oxidizing power is formed. Analysis shows that this is pentoxide containing up to 5 per cent. of a higher oxide PO_3 or P_2O_6. On heating, it begins at 130° to lose colour, oxygen, and oxidizing power. The aqueous solution will oxidize potassium iodide to iodine, aniline to nitroso and nitrobenzene, and manganous sulphate to permanganate; it behaves in fact as a solution of peroxyphosphoric acid $H_4P_2O_8$, of which no doubt this oxide is the anhydride; if so it should have the double formula and the structure $O_2P—O—O—PO_2$, which would account for its reactions, but not for its colour.

OXY-ACIDS OF PHOSPHORUS

PHOSPHORUS forms a series of oxy-acids, some of which can exist in more than one form; they are, in order of increasing oxidation:

1. Hypophosphorous acid H_3PO_2.
2. Phosphorous acid H_3PO_3. The pyro- $H_4P_2O_5$ and meta-form HPO_2 are known, but are much less stable than the corresponding phosphoric acids.
3. Hypophosphoric acid $H_4P_2O_6$.
4. Phosphoric acid H_3PO_4, with pyro- $H_4P_2O_7$ and meta- HPO_3.

5 and 6. Peroxy-diphosphoric $H_4P_2O_8$ and peroxy-monophosphoric acid H_3PO_5, derivatives of pyro- and orthophosphoric acids with a peroxide —O—O— group.

1. *Hypophosphorous Acid,* H_3PO_2

This is formed together with phosphine by heating phosphorus with sodium or barium hydroxide, or by the oxidation of phosphine by iodine in water.[534] The free acid (from the barium salt) melts at 26·5°; it can be

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[529] D. A. Lacoss and A. W. C. Menzies, *J.A.C.S.* 1937, **59**, 2471.

[530] P. W. Schenk and H. Platz, *Naturwiss*, 1936, **24**, 651.

[531] P. W. Schenk and H. Rohaag, *Z. anorg. Chem.* 1937, **233**, 403.

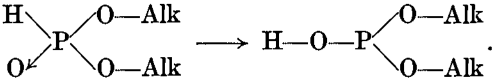
[532] L. Hackspill and J. Weiss, *C.R.* 1931, **192**, 425.

[533] R. O. Griffith, A. McKeown, and R. P. Taylor, *Trans. Far. Soc.* 1940, **36**, 752.

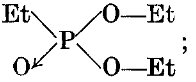
[534] R. Paris and P. Tardy, *C.R.* 1946, **223**, 242.

This second ester boils 40° higher than its isomer (198° : 156°), an indication of the effect of the co-ordinate link through the dipole moment, as in the nitrites and nitro-compounds, and in the trialkyl-hydroxylamines and amine oxides.

The dialkyl esters of phosphorous acid (from PCl_3 and alcohol) are themselves tautomeric. The rate of oxidation of dialkyl phosphites $HPO(OAlk)_2$ by excess of iodine in water[543] is independent of the concentration of the iodine, and it is the same for bromine as for iodine; the oxidation must therefore depend on an isomeric change, and this is no doubt



This is supported by the effect of various catalysts on the oxidation, and by the fact that trialkyl esters $P(OAlk)_3$ are much more easily oxidized than the dialkyl, which thus must be in the 4-covalent form. The isomeric triesters are themselves interconvertible. $P(OEt)_3$ will change[544] in presence of ethyl iodide into



and the normal butyl ester $P(O—Bu)_3$ (b. pt. 120°/8 mm.) if heated with butyl iodide at 150° goes[545] into its isomer (b. pt. 150°/10 mm.). See further, Kosolapoff.[546-7]

A pyrophosphite ester $(Et—O)_2P—O—P(O—Et)_2$, of b. pt. 83°/2 mm., has been made[548-9] by the action of bromine on sodium diethyl phosphite $NaO \cdot P(O \cdot Et)_2$.

3. *Hypophosphoric Acid*, $H_4P_2O_6$

This acid has many peculiarities, and does not seem to fall into line with the others. It is formed (I) along with phosphorous and phosphoric, when phosphorus is oxidized by moist air. It is made by leaving sticks of white phosphorus exposed to air, and adding sodium acetate to the liquid which forms, when the rather slightly soluble sodium hypophosphate

$$Na_2H_2P_2O_6, 6\,H_2O$$

separates. It can also be made by treating red phosphorus with concentrated sodium hydroxide and hydrogen peroxide, and also (II) by the action of alkaline hydrogen peroxide on P_2I_4,[550] or (III) by the hydrolysis

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[543] P. Nylén, *Z. anorg. Chem.* 1938, **235**, 161.

[544] W. Staronka, *Rocz. Chem.* 1927, **7**, 42.

[545] A. Arbusov and J. Arbusov, *J. Russ. Phys. Chem. Soc.* 1930, **62**, 1533.

[546] G. M. Kosolapoff, *J.A.C.S.* 1945, **67**, 1180. [547] Id., ib. 2259.

[548] A. E. Arbusov and B. A. Arbusov, *J. prakt. Chem.* 1931, ii. **131**, 337.

[549] Id., *Ber.* 1932, **65**, 195.

[550] J. H. Kolitowska, *Rocz. Chem.* 1935, **15**, 29.

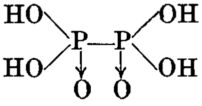
of phosphorus trichloride or better tribromide[551] in presence of iodine. It is to be noticed that methods I and II start with a material containing P—P links. Hypophosphoric acid is not formed by the hydration of P_4O_8, which only yields phosphorous and phosphoric acids.

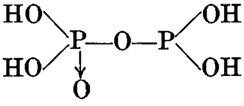
Lead and barium hypophosphates are insoluble, and the free acid can be obtained from them by means of hydrogen sulphide or sulphuric acid. It forms a hydrate $H_4P_2O_6$, 2 H_2O, m.pt. 70°, from which the anhydrous acid is formed on standing *in vacuo* over phosphorous pentoxide.

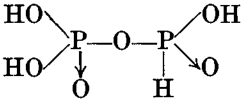
Hypophosphoric acid has far less reducing power than phosphorous, but it is hydrolysed in strongly acid solution to phosphorous and phosphoric acids.

The double formula $H_4P_2O_6$ is established by molecular weight determinations by the freezing-point of solutions in water of the free acid and of the salt $Na_2H_2P_2O_6$.[552] Further, Sugden has shown[553] that the sodium salts $Na_2H_2P_2O_6$, 0 and 6 H_2O, and the silver and guanidine salts are diamagnetic; an acid H_2PO_3 and its salts, being odd molecules, must be paramagnetic. Also the rate of hydrolysis of the acid by hydrogen ion to $H_3PO_3+H_3PO_4$ is strictly monomolecular for $H_4P_2O_6$.[554-6] The supposed ester which was said to be monomeric was found by Sugden to be a mixture of other substances; another ester made[557] by treating sodium diethyl phosphite with bromine was found[552] to have the composition and molecular weight of $Et_4P_2O_6$, but its genetic relation to hypophosphoric acid is obscure.

It is thus clear that the acid is $H_4P_2O_6$, and possible structures for this are:


(I)


(II)


(III)

The evidence points to (I) for these reasons: (1) the acid is made almost only from compounds that already have P—P links; (2) its resistance to oxidation, as compared with trivalent phosphorus compounds such as phosphorous acid: neither halogens nor salts of noble metals, nor even nitric acid have any effect, but only permanganate and dichromate, and these probably only as the acid is hydrolysed to phosphoric and phosphorous acids. Further evidence is given by the X-ray absorption edges[552]; these are for pentavalent phosphorus in [PO_4] at 5,750·7 X units, for trivalent in $P(OR)_3$ at 5,759·9 X; for $O_3P—PO_3$ we should expect about

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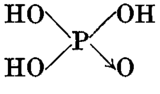
[551] Id., *Z. anorg. Chem.* 1937, **230**, 310.
[552] P. Nylen and O. Stelling, ib. 1933, **212**, 169.
[553] F. Bell and S. Sugden, *J.C.S.* 1933, 48.
[554] R. G. van Name and W. J. Huff, *Amer. J. Sci.* 1918, [4] **45**, 103.
[555] A. Rosenheim and H. Zilg, *Z. physikal. Chem.* 1928, **139**, 12.
[556] B. Blaser, ib. 1933, **166**, 59.
[557] A. E. Arbusov and B. A. Arbusov, *J. prakt. Chem.* 1931, [ii] **130**, 103.

5,756. The observed value agrees with this, and is at 5,755·9; for structures (II) and (III) there should be two edges, one for PO_3 and the other for PO_4.

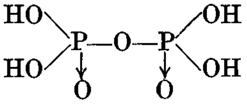
4. *Phosphoric Acid*

This is the most stable oxy-acid of phosphorus, and it is as phosphates that the element occurs in nature. The acid has three forms, about whose structure there is no doubt apart from the resonance between P→O and P=O; this is of less importance owing to the instability of the double link to phosphorus, but it will increase the stability of the molecule.

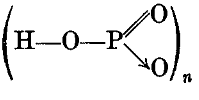
The three forms are:



H_3PO_4: ortho



$H_4P_2O_7$: pyro



HPO_3: meta.

Orthosphoric acid H_3PO_4 melts at 41·5°[558] and is very soluble in water (670/25°)[559]; its dissociation constants are K_1 $1{\cdot}1\times10^{-2}$; K_2 $5{\cdot}6\times10^{-8}$; K_3 $1{\cdot}2\times10^{-12}$; hence the tertiary salts when they are soluble in water are very highly hydrolysed. H_3PO_4 combines with ether to form solids of the compositions $6\,H_3PO_4, Et_2O$, m.pt. 28·2°, and $4\,H_3PO_4, Et_2O$, m.pt. 30·0°.[560]

Orthophosphoric acid is stable as a solid, but the pyro-acid $H_4P_2O_7$ soon separates out from it above its melting-point,[558] and on further heating it loses water, giving first (at 200-300°) the pyro- and then the meta-acid, which loses no more water but volatilizes at a red heat. In solution the three acids and their ions change into one another only slowly, the rate being increased by heating or by the addition of hydrogen ion. Hence the acids and their salts have distinctive reactions; for example, with silver nitrate the ortho gives a yellow and the meta and pyro white precipitates, and a solution of the meta, but not of the pyro, will coagulate albumen. It is singular that it was found by Hull[561] that there is no exchange of radioactive phosphorus between ortho, pyro, and meta ions in solution at 20° or at 100°. The hydration of the meta to the pyro is monomolecular.[562] The hydrolysis of pyro to ortho is monomolecular, and proportional to the concentration of hydrogen ion.[563]

Pure metaphosphoric acid can be made[564-6] by treating the pentoxide with water and ice, and not letting the temperature rise above 0° during the hydration. When freshly dissolved in water it is a better conductor of electricity (at the same phosphorus concentration) than the pyro, and

[558] A. Simon and G. Schulze, *Z. anorg. Chem.* 1939, **242**, 313.

[559] W. H. Ross and R. M. Jones, *J.A.C.S.* 1925, **47**, 2165.

[560] M. Rabinovitsch and S. Jakubsohn, *Z. anorg. Chem.* 1923, **129**, 55.

[561] D. E. Hull, *J.A.C.S.* 1941, **63**, 1269.

[562] A. Travers and Y. K. Chu, *C.R.* 1934, **198**, 2100.

[563] J. Muus, *Z. physikal. Chem.* 1932, **159**, 268.

[564] S. Glixelli, R. Chrzanowska, and K. Boratynski, *Z. anorg. Chem.* 1936, **227**, 402.

[565] S. Glixelli and K. Boratynski, ib. 1938, **235**, 225.

[566] S. Glixelli and S. Jaroszowna, *Rocz. Chem.* 1938, **18**, 515.

much better (2 to 3 times) than the ortho, into which it changes on standing with a fall of conductivity; when made from amorphous pentoxide the solution contains a gel, which soon dissolves.

Salts: orthophosphates. The PO_4 ion has been shown by X-ray analysis to be tetrahedral; the P—O distances found were 1·56 A in KH_2PO_4,[568] 1·54 in BPO_4,[569] and 1·61 in Ag_3PO_4[567]: theory P—O 1·70, P=O 1·55. The salts are converted into pyro[573] and metaphosphates on heating so far as they contain hydrogen or volatile bases like ammonia, just like the acids. Thus Na_2HPO_4 at 211° goes to $Na_4P_2O_7$ (m.pt. 980°).[571]

$$\left.\begin{matrix} NaH_2PO_4 \\ Na(NH_4)HPO_4 \end{matrix}\right\} \longrightarrow Na_2H_2P_2O_7 \longrightarrow NaPO_3.^{572}$$

For the system Na_2O, P_2O_5, H_2O see reference [570].

All primary orthophosphates MH_2PO_4 are soluble in water, but of the secondary M_2HPO_4 and the tertiary M_3PO_4 only those of the alkalies. Apatite, essentially $Ca_3(PO_4)_2$, is treated on the large scale with concentrated sulphuric acid and is thereby converted into the more soluble acid salt $Ca(H_2PO_4)_2$, which is the fertilizer 'superphosphate'.

The *pyrophosphates* occur only in two series, $M'_2H_2P_2O_7$ and $M'_4P_2O_7$; of the latter only the alkaline salts are soluble in water, and they have an alkaline reaction. For the crystal structures of the salts

$$M^{iv}P_2O_7 \ (M^{iv} = Si, Ti, Sn, Zr, Hf)$$

see reference [573]. When the anhydrous metaphosphate and pyrophosphate of sodium are heated together there is no sign up to 700° of the formation of any higher polyphosphate than $Na_5P_3O_{10}$.[574]

The *metaphosphates*, such as $NaPO_3$, in the fused state will dissolve metallic oxides, forming, for example, $NaCuPO_4$ with copper oxides, and these are often coloured ('phosphate bead' test, by fusion with microcosmic salt $Na(NH_4)HPO_4$).

Esters of all three types of phosphoric acid are known. Ortho-esters are best made[575] from phosphorus oxychloride and alcohol, in presence of pyridine; the boiling-points are[576] Me_3PO_4 196°; ethyl 215°; *n*-propyl 252°; *n*-butyl 289°. Methyl orthophosphate $(CH_3)_3PO_4$ is dimorphic, with the melting-points α- (stable) −46·7°, β- −62·5°[577]; it is unusually soluble in water, with a cryohydric point at −77·0° and 52 per cent. ester.[578] For

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[567] L. Helmholz, *J. Chem. Phys.* 1936, **4**, 316.

[568] J. West, *Z. Krist.* 1930, **74**, 306.

[569] G. E. R. Schulze, *Z. physikal Chem.* 1934, B **24**, 215.

[570] H. Menzel and E. v. Sahr, *Z. Elektrochem.* 1937, **43**, 104.

[571] H. Menzel and L. Sieg, ib. 1932, **38**, 283.

[572] D. Balarew, *Z. anorg. Chem.* 1921, **118**, 123.

[573] G. R. Levi and G. Peyronel, *Z. Krist.* 1935, **92**, 190.

[574] E. P. Partridge, V. Hicks, and G. W. Smith, *J.A.C.S.* 1941, **63**, 454.

[575] C. R. Noller and G. R. Dutton, ib. 1933, **55**, 424.

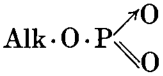
[576] D. P. Evans, W. C. Davies, and W. J. Jones, *J.C.S.* 1930, 1310.

[577] H. A. Pagel and W. A. Schroeder, *J.A.C.S.* 1940, **62**, 1837.

[578] H. A. Pagel and F. S. Maxey, ib. 1941, **63**, 2499.

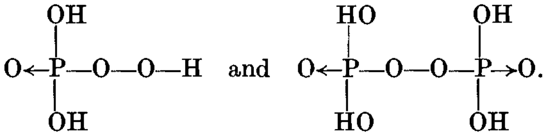
its hydrolysis see Blumenthal[579]; by the use of heavy oxygen he showed that the link in P—O—Me that breaks is in alkaline solution the P—O, but in neutral or acid solution the O—C.

Ethyl pyrophosphate $Et_4P_2O_7$ can be made[580] from the silver salt and ethyl iodide, and also by the action of iodine on sodium diethyl phosphite $NaO \cdot P(OEt)_2$; its supposed[572] formation by the combination of the ortho- and meta-esters is not confirmed.[580]

The meta-esters  $Alk \cdot O \cdot P\begin{smallmatrix}\nearrow O \\ \searrow O\end{smallmatrix}$ can be made from the pentoxide and a dialkyl ether,[581-2] or from the alcohol and phosphorus oxychloride[583]; they are oils or semi-crystalline masses which on heating decompose without vaporizing, and are hard to purify.

5. *Perphosphoric Acids*[584]

Two of these acids have been prepared,[585-7] a peroxymonophosphoric acid H_3PO_5 and a 'peroxydiphosphoric' acid $H_4P_2O_8$; their structures presumably are:



$$O \leftarrow \overset{\displaystyle OH}{\underset{\displaystyle OH}{P}} - O - O - H \quad \text{and} \quad O \leftarrow \overset{\displaystyle HO}{\underset{\displaystyle HO}{P}} - O - O - \overset{\displaystyle OH}{\underset{\displaystyle OH}{P}} \rightarrow O.$$

Both are formed with 30 per cent. hydrogen peroxide, the first with phosphorus pentoxide:

$$P_2O_5 + 2\,H_2O_2 + H_2O = 2\,H_3PO_5;$$

the reaction is very violent, but it can be moderated by using acetonitrile as a solvent.[588] This is a stronger oxidizing agent than peroxymonosulphuric acid; with silver salts it gives oxygen and silver phosphate Ag_3PO_4; it converts aniline into nitroso- and nitrobenzene, and manganous salts quickly in the cold into permanganates. If pyrophosphoric acid is treated with hydrogen peroxide the peroxy-acid $H_4P_2O_8$ is formed along with the mono-acid. The two behave differently with potassium iodide: the mono-acid separates iodine at once, and the other acid only slowly. In water the two acids go over into one another, the mono- predominating in acid and the di- (peroxy-) in alkaline solution.

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[579] E. Blumenthal and J. B. M. Herbert, *Trans. Far. Soc.* 1945, **41**, 611.

[580] P. Nylen, *Z. anorg. Chem.* 1933, **212**, 182.

[581] K. Langheld, *Ber.* 1910, **43**, 1858.

[582] Id., ib. 1911, **44**, 2080.

[583] D. Balarew, *Z. anorg. Chem.* 1917, **99**, 188.

[584] For a general account see P. W. Schenk and H. Rehaag, *Z. anorg. Chem.* 1937, **233**, 408.

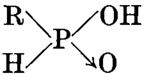
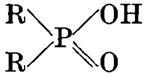
[585] J. Schmidlin and P. Massini, *Ber.* 1910, **43**, 1162.

[586] J. d'Ans and W. Friederich, ib., 1880.

[587] F. Fichter and J. Müller, *Helv. Chim. Acta*, 1918, **1**, 297.

[588] G. Toennies, *J.A.C.S.* 1937, **59**, 555.

Organo-acids of Phosphorus

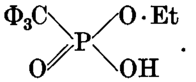
These are oxy-acids with alkyl or (more often) aryl groups attached to the phosphorus. Their terminology is very confused. According to Beilstein[590] ‘in the literature compounds $R\cdot P(OH)_2$ or  $R(H)P(OH)O$ are called “alkylphosphinigsäuren” but  $R_2P(OH)O$ “dialkylphosphinsäuren”, though they should be named after the mono-acids -inig-’. This makes no distinction between phosphorous and phosphoric compounds. The rational method is to call $R\cdot P(OH)_2$ and (if they exist) $R_2P\cdot OH$ mono- and di-phosphinic, and $R\cdot PO(OH)_2$ and $R_2PO\cdot OH$ mono- and di-phosphonic, on the analogy of the sulphinic $R\cdot SO_2H$ and sulphonic $R\cdot SO_3H$ compounds.

These acids can be made by oxidation (by air or otherwise) of the mono- and di-substituted phosphines (see above, p. 731). Of the phosphorous derivatives only the mono are known,[591] and these almost only in the aryl series; they can be made by the oxidation of primary phosphines, or by hydrolysis of their chlorides $R\cdot PCl_2$[589]; an example is $\Phi\cdot P(OH)_2$, m.pt. 70°, very soluble in hot water. They give monobasic salts, and mono- and di-esters. Chlorine oxidizes the acid to the phosphonic acid $R\cdot PO(OH)_2$.

The monophosphonic acids $R\cdot PO(OH)_2$ are made by oxidizing the phosphinic acids or by hydrolysing the chlorides $R\cdot PCl_4$: e.g. $CH_3PO(OH)_2$ m.pt. 105°, sol^y in water 23·5/15°.

Of the di-phosphonic acids, $(CH_3)_2PO\cdot OH$, made by oxidizing dimethyl phosphine with nitric acid, melts at 76°, and is easily soluble in water and ether. $\Phi_2PO\cdot OH$, m.pt. 190°, is insoluble in water.

The triphenyl-methyl derivatives were examined by Hatt.[593-4] Triphenyl carbinol and phosphorus trichloride give $\Phi_3C—O—PCl_2$,[592] which when hydrolysed by sodium ethylate in alcohol undergoes an isomeric change[593] to



$$\Phi_3C\cdot PO(O\cdot Et)(OH).$$

Other derivatives were made later[594]; the triphenyl-methyl group is remarkably mobile, either going, as above, from oxygen to phosphorus or breaking right off.

Fluorophosphoric Acids

One and two of the hydroxyl groups of phosphoric acid can be replaced by fluorine. There is some indication that chlorine can behave in the same

[589] See Krause and v. Grosse, p. 448.

[590] Beilstein, vol. xvi, p. 790 (1933).

[591] A. E. Arbusov, *J. Gen. Chem. Russ.* 1934, 4, 898, claims to have made $\Phi_2P\cdot O\cdot CH_3$ from $\Phi\cdot PCl_2$ and sodium methylate; but this surprising result has not been confirmed.

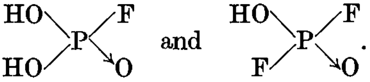
[592] D. R. Boyd and G. Chignell, *J.C.S.* 1923, **123**, 813.

[593] H. H. Hatt, *J.C.S.* 1929, 2412.

[594] Id., ib., 1933, 776.

way,[595-6] but the salts in this case are very unstable and have not been isolated.

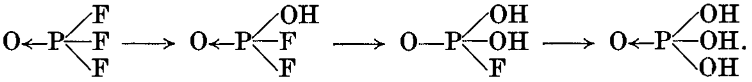
The fluorophosphoric acids are of two types:



They are formed by the hydrolysis of phosphorus oxyfluoride; by fusion of the pentoxide with ammonium fluoride; and the monofluoro acid by the action of concentrated hydrogen fluoride on phosphoric acid.

Difluorophosphoric Acid, HPO_2F_2

The hydrolysis of POF_3 takes place in three stages:[597]



The first stage is rapid, but the others are slow. In the presence of alkali the reaction practically stops at the first stage, the $[PO_2F_2]^-$ ions formed being (apparently owing to their charge) only very slowly hydrolysed further. A better way is to fuse P_2O_5 with three molecular proportions of ammonium fluoride: the product contains much $NH_4PO_2F_2$, which can be extracted with alcohol and recrystallized from hot water.

Free difluorophosphoric acid HPO_2F_2 cannot be isolated. It is only slowly hydrolysed by water, but rapidly by heating with concentrated alkali or acid.

Most of the salts are excessively soluble in water, but those of potassium and caesium, and of certain organic bases such as strychnine, brucine, and nitron, only moderately. They resemble the perchlorates very closely (and hence also the fluoroborates MBF_4 and the fluorosulphates MSO_3F): the less soluble salts of both acids contain the same bases. The alkaline salts are isomorphous with the perchlorates, fluoroborates, and fluorosulphates.

This resemblance is obviously due to these being all strong monobasic acids, with anions of the same tetrahedral structure, and nearly the same size. The observed distances X—A are[598] P—O 1·55; B—F 1·43[599]; S—O 1·51; Cl—O 1·48 A.

Monofluorophosphoric Acid, H_2PO_3F

Concentrated alkali ultimately hydrolyses the difluoro-acid completely, but with dilute alkali under proper conditions the only product is the monofluoro-compound.[600] This can also be made by dissolving phosphoric acid or P_2O_5 in concentrated hydrofluoric acid:

$$H_3PO_4 + HF = H_2PO_3F + H_2O.$$

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[595] H. Meerwein and K. Bodendorf, *Ber.* 1929, **62**, 1952.

[596] H. C. Goswami, *J. Ind. Chem. Soc.* 1937, **14**, 660.

[597] W. Lange, *Ber.* 1929, **62**, 786.

[598] L. Pauling, *Chem. Bond*, p. 240.

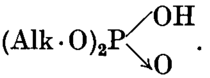
[599] Theoretical value: J. L. Hoard and V. Blair, *J.A.C.S.* 1935, **57**, 1985.

[600] W. Lange, *Ber.* 1929, **62**, 793.

The equilibrium is only slowly established, but is more favourable to the fluoro-acid than with sulphuric acid and fluorosulphuric.[601-3] Anhydrous hydrogen fluoride acts on H_3PO_4 to give a mixture of H_2PO_3F and HPO_2F_2; with HPO_3 it gives only H_2PO_3F.[605] It can also be made by fusing the pentoxide with a smaller excess of ammonium fluoride than is required for making $NH_4PO_2F_2$. The acid is separated as its silver salt Ag_2PO_3F, from which other salts can be obtained. The free acid is an oily liquid, which begins to decompose without distillation at 185°, and solidifies to a glass by $-78°$. It is slowly and reversibly hydrolysed by water to H_3PO_4.[605] The $[PO_3F]''$ ion resembles $[SO_4]''$ even more closely than $[PO_2F_2]'$ does $[SO_3F]'$, and for the same reasons. The solubilities of the fluorophosphates and the sulphates, in moles per litre at 20°, are:

	Ca, 2 H_2O	Sr, H_2O	Ba	Ag	Pb	Hg′
PO_3F	$6{\cdot}3\times10^{-2}$	$5{\cdot}5\times10^{-2}$	6×10^{-4}	6×10^{-2}	$3{\cdot}2\times10^{-4}$	5×10^{-4}
SO_4	$1{\cdot}5\times10^{-2}$	6×10^{-4}	1×10^{-5}	$2{\cdot}5\times10^{-2}$	$1{\cdot}3\times10^{-4}$	8×10^{-4}

The esters of H_2PO_3F can be made from the silver salt with alkyl halides.[604,604a] They are volatile liquids (b.pt. CH_3 150°, C_2H_5 171°) with a pleasant aromatic smell, but a very poisonous action on the brain and lungs.[604a] The methyl ester dissolves readily in water and is at once hydrolysed by it; the others are relatively insoluble, and (perhaps for this reason) are only hydrolysed slowly. In the hydrolysis it is not the alkyl group which separates, but the fluorine, the product being the dialkyl phosphate



$(Alk\cdot O)_2P\begin{matrix}\nearrow OH\\ \searrow O\end{matrix}$.

PHOSPHORUS SULPHIDES

The history of these compounds is, as Stock[606] says, a real comedy of errors. At least twelve have been described, but it is now clear that not more than four have been obtained.

P_4S_3, P_4S_7, and P_4S_{10} (the last is generally known as the pentasulphide) can be got from their components with evolution of heat, by heating them alone (to 300°), or in carbon disulphide solution,[607-8] or in naphthalene or xylene,[609] especially in presence of traces of iodine. Their melting-points

[601] Id., ib. 1084.

[602] W. Lange and G. Stein, ib. 1931, **64**, 2772.

[603] W. Lange, *Z. anorg. Chem.* 1933, **214**, 44.

[604] W. Lange and G. v. Krueger, *Ber.* 1932, **65**, 1598.

[604a] B. C. Saunders and G. J. Stacey, *J.C.S.* 1948, 695; id. and F. Wild and I. G. E. Wilding, ib. 699.

[605] W. Lange and R. Livingston, *J.A.C.S.* 1947, **69**, 1073.

[606] A. Stock, *Ber.* 1909, **42**, 2062.

[607] W. D. Treadwell and C. Beeli, *Helv. Chim. Acta*, 1935, **18**, 1161.

[608] C. Beeli, ib. 1172.

[609] J. Mai, *Ber.* 1911, **44**, 1229, 1725.

and solubilities in carbon disulphide (in g. to 100 g. solvent at the ordinary temperature) are:

Compound	*M. pt.*	*Solubility*
P_4S_3	172°	76·9
P_4S_7	305°	0·029
P_4S_{10}	290°	0·22

There is also a sulphide P_4S_5. They are all hydrolysed by water to hydrogen sulphide and phosphorous or phosphoric acid, the ease of hydrolysis being in the increasing order[608] $P_4S_3 < P_4S_{10} < P_4S_7$.

Stock[611] examined the melting-points and freezing-points of the P—S system from P_4S_3 to P_4S_{10}; this is difficult because the liquids are very viscous and only crystallize slowly, and the solids sinter and melt over about 5° even when pure (hence the confusion in the earlier work on the subject). But Stock found the melting-point curve to be quite definite; it showed only the two eutectics with a maximum between them at 305° and at the composition P_4S_7. Mai[609] confirms these conclusions, and agrees that the supposed P_3S_6 does not exist. The only other sulphide is P_4S_5, made[610] by exposing a carbon disulphide solution of P_4S_3 and sulphur to light in presence of a little iodine; this is confirmed by Treadwell and Beeli,[607] who add that it is monomeric in carbon disulphide by the boiling-point.

These four compounds are all yellow and crystalline; the molecular weights of the first two have been determined in the vapour, and those of the last two in CS_2 solution; they all have four atoms of phosphorus in the molecule.

P_4S_3 boils at about 230° under 10 mm. pressure; at 40-60° (not in the cold) it glows with oxidation in the air, but like yellow phosphorus only if the oxygen pressure is not too high.

P_4S_{10}[611] forms yellow crystals which boil without decomposition at 530°, and so the vapour can be used for high-temperature thermostats. With water it gives hydrogen sulphide and phosphoric acid.

The sulphides of phosphorus, and especially the pentasulphide, will often replace an oxygen atom in an organic compound by sulphur; in this way alcohols can be converted into mercaptans, acids amides and ketones into their thio-analogues, succinic acid into thiophene, etc.

We have no X-ray or electron diffraction data, but the structure of P_4S_{10} is presumably like that of P_4O_{10}; the presence of the P_4 group in P_4S_3 is remarkable.

A telluride P_2Te_3 can be made from the elements at 320°; it is black, insoluble in water and in carbon disulphide, and stable in dry air.[612]

[610] R. Boulouch, *C.R.* 1904, **138**, 363.

[611] A. Stock and K. Thiel, *Ber.* 1905, **38**, 2719.

[612] E. Montignie, *Bull. Soc.* 1942, [v] **9**, 658.

Oxyhalides of Phosphorus

Oxyhalides of the type of nitrosyl chloride O═N—Cl, which would require a double link, are unknown, but the phosphoryl halides PO(hal)$_3$ have all been made (as well as some mixed halides) except the iodide POI_3. The boiling- and melting-points are:

Compound	*B. pt.*	*M. pt.*	*Compound*	*B. pt.*	*M. pt.*
POF_3	−39 8°	−39·4°	$POBrF$[d]	+30·5°	−84·8°
POF_2Cl[a]	+3·1°	−96·4°	$POBr_2F$[d]	110·1°	−117·2°
$POFCl_2$[a]	52·9°	−80·1°	$POBr_3$	189·5°	+56°
$POCl_3$	105·3°[b]	+1·2°[c]			

a = [613], *b* = [614], *c* = [615], *d* = [616].

The oxyfluoride is made by treating the oxychloride with zinc fluoride or antimony trifluoride. It fumes only slightly in air, and when dry does not attack glass; it is hydrolysed by water to hydrogen fluoride and phosphoric acid.

Phosphorus oxychloride $POCl_3$ is made by heating the pentachloride with the pentoxide, or by the partial hydrolysis of PCl_5, best by heating it with anhydrous oxalic acid, which supplies the water:

$$PCl_5 + (COOH)_2 = POCl_3 + 2\,HCl + CO + CO_2.$$

It is hydrolysed (rather slowly in the cold) to hydrochloric and phosphoric acids, and can be used as a mild reagent for replacing organic hydroxyl by chlorine.

Phosphorus oxybromide is made and behaves in the same way.

These are obviously non-associated (the Trouton constants average 22) covalent compounds, and must be resonance hybrids of $X_3P{\rightarrow}O$ and $X_3P{=}O$.[620] The parachors were supposed to favour the first formula, but they do not really help, as the change from P—O to P═O is just balanced by that from P^{iii} to P^{v}.[617–19] It has been shown[621] by electron diffraction that in POF_3, POF_2Cl, $POFCl_2$, and $POCl_3$[622] the hal-P-hal angles are reduced from 109·5° to 106°, suggesting that the P—O bond has some double-link character. The P—O distance in all of them is 1·55 A, as it is in the PO_4 ion (theory P—O 1·76, P═O 1·55); P—F is 1·51 and P—Cl 2·02, practically the same as in PF_3 and PCl_3 (see below) (theory P—F 1·74, P—Cl 2·09).

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[613] H. S. Booth and F. B. Dutton, *J.A.C.S.* 1939, **61**, 2937.

[614] K. Aru, *Inst. Phys.-Chem. Tokyo*, 1929, **8**, 545.

[615] A. P. Rollet and W. Graff, *C.R.* 1933, **197**, 555.

[616] H. S. Booth and C. G. Seegmiller, *J.A.C.S.* 1939, **61**, 3120.

[617] S. Sugden, J. B. Reed, and H. Wilkins, *J.C.S.* 1925, **127**, 1525.

[618] J. L. R. Morgan and G. K. Daghlian, *J.A.C.S.* 1911, **33**, 672.

[619] S. Sugden, *J.C.S.* 1927, 1173.

[620] See L. Pauling, *Chem. Bond*, 83, 248.

[621] L. O. Brookway and J. Y. Beach, *J.A.C.S.* 1938, **60**, 1836.

[622] For the results with phosphoryl and thiophosphoryl bromide see J. H. Secrist and L. O. Brookway, ib. 1944, **66**, 1941.

Thiophosphoryl Halides

The boiling- and melting-points of these compounds are:

	PSF_3	PSF_2Cl	$PSFCl_2$	$PSCl_3$	PSF_2Br	$PSFBr_2$	$PSBr_3$
B. pt.	−52·9°	+6·3°	64·7°	125°	35·5°	125·3°	decp. 175°
M. pt.	−148·8°	−155·2°	−96·0°	−36·2°	−136·9°	−75·2°	+38°

The fluoride PSF_3[623] is made from the chloride and arsenic trifluoride, or by heating P_2S_5 with lead fluoride.[624·5] It is a monomeric gas; it does not attack glass, but is spontaneously inflammable in air, owing apparently to the loose attachment of the sulphur, which separates irreversibly on strong heating.[625] It is very slowly hydrolysed by water, the first product being the acid $H[PSOF_2]$.

The chloride $PSCl_3$ is made from the pentasulphide and the trichloride, and is dimorphic in the solid state. With water it first gives H_3PSO_3. The bromide $PSBr_3$ is best made by the action of bromine on a mixture of phosphorus and sulphur in carbon disulphide (for details see *Inorganic Syntheses*, vol. ii); it is similar to the others. The chloride[626] and bromide[627] can have the halogens replaced by fluorine on treatment with arsenic or antimony fluorides.

Electron diffraction shows that in $PSCl_3$[628] the distances are P—Cl 2·02 (as in $POCl_3$) and P—S 1·94 (theory P—Cl 2·09, P—S 2·14, P=S 1·94). In PSF_3[629] P—S is only 1·85 A; 'the additional shortening of the bond relative to that in $PSCl_3$ is presumably the result of triple-bond character made possible by the large amount of ionic character of the P—F bonds'.[630]

PHOSPHORUS HALIDES

These are nearly all tri- or pentahalides, but a chloride P_2Cl_4 and an iodide P_2I_4 are known, presumably derived from P_2H_4.

Trihalides

Boiling- and Melting-points

	PF_3[a]	PF_2Cl[a]	$PFCl_2$[a]	PCl_3[b]	PF_2Br[c]	$PFBr_2$[c]	PBr_3	PI_3
B. pt.	−101·1°	−47·3°	−13·85°	74·7°	−16·1°	78·4°	175·3°	Decp.
M. pt.	−151·5°	−164·8°	−144·1°	−93·6°	−133·8°	−115·0°	−40°	61·0°

a = [631], *b* = [632], *c* = [633].

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[623] T. E. Thorpe and J. W. Rodger, *J.C.S.* 1889, **55**, 306.

[624] S. A. Vossnesenski and L. M. Dubnikov, *J. Gen. Chem. Russ.* 1941, **11**, 507.

[625] W. Lange and K. Askitopoulos, *Ber.* 1938, **71**, 801.

[626] H. S. Booth and M. C. Cassidy, *J.A.C.S.* 1940, **62**, 2369.

[627] H. S. Booth and C. A. Seabright, ib. 1943, **65**, 1834.

[628] J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.* 1938, **6**, 75.

[629] D. P. Stevenson and H. Russell, *J.A.C.S.* 1939, **61**, 3264.

[630] L. Pauling, *Chem. Bond*, p. 244.

[631] H. S. Booth and A. R. Bozarth, *J.A.C.S.* 1939, **61**, 2927.

[632] K. Arii and M. Kawabata, *Bull. Inst. Phys.-Chem. Res. Japan*, 1938, **17**, 299.

[633] H. S. Booth and S. G. Frary, *J.A.C.S.* 1939, **61**, 2934.

The trifluoride PF_3 is best prepared by the action of arsenic trifluoride (itself made from arsenic trioxide and calcium fluoride) on phosphorus trichloride. It is a fairly stable gas, only slowly decomposed by water (to phosphorous acid and hydrogen fluoride), and it does not attack glass except at a high temperature.

Phosphorus trichloride is made from the elements; it has a definitely unsaturated behaviour; it takes up oxygen from the air in the cold to give the oxy-chloride $POCl_3$, sulphur to give $PSCl_3$, and chlorine to give PCl_5. For its thermodynamic properties see Yost.[634-5] The chlorine atoms can be successively replaced by fluorine[631] either with antimony trifluoride and pentachloride, or by passing the vapour over heated calcium fluoride. The structures have been examined by electron diffraction. The X—P—X angles[636] are F—P—F 104°, Cl—P—Cl 102°, Br—P—Br 100°, I—P—I 98°. The distances, with the theoretical values and the differences, are[637-8]:

	P—F	P—Cl	P—Br	P—I
Obs.	1·52	2·00	2·23	2·47 A
Theoret.	1·74	2·09	2·24	2·43
Diff.	−0·22	−0·09	−0·01	+0·04

The last two are within the limits of experimental error. The differences with fluorine and chlorine are not fully understood.

Pentahalides

Boiling- and Melting-points

	PF_5	PF_3Cl_2	PCl_5[a]	PF_3Br_2[b]	PBr_5
B. pt.	−75°	+10°	159° sbl.	*ca.* 106°	Decpse.
M. pt.	−83°	−8°	160°	−20°	Below 100°

a = [639], *b* = [640].

The pentafluoride PF_5 can be made by treating the trifluoride with bromine, PF_3Br_2 being first formed, which then goes over to PF_5+PBr_5; also by heating the pentoxide P_2O_5 with calcium fluoride,[641-2] or from the pentachloride and arsenic trifluoride. It can also be made by heating the pentachloride with the fluoride of a divalent metal (such as Ca, Ba, Zn, or Pb), but if ammonium or an alkaline fluoride is used it does not form PF_5 but the complex fluoride $M[PF_6]$.[643] PF_5 is a colourless gas, fuming in

[634] T. F. Anderson and D. M. Yost, *J. Chem. Phys.* 1936, **4**, 529.

[635] D. P. Stevenson and D. M. Yost, ib. 1941, **9**, 403.

[636] For references see L. O. Brockway, *Rev. Mod. Phys.* 1936, **8**, 231.

[637] A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Far. Soc.* 1937, **33**, 852.

[638] O. Hassel and A. Sandbo, *Z. physikal. Chem.* 1938, B **41**, 75.

[639] E. B. R. Prideaux, *J.C.S.* 1909, **95**, 445.

[640] W. Fischer and O. Jübermann, *Z. anorg. Chem.* 1938, **235**, 337.

[641] H. J. Lucas and F. J. Ewing, *J.A.C.S.* 1927, **49**, 1270.

[642] H. S. Booth and A. R. Bozarth, ib. 1933, **55**, 3890.

[643] W. Lange and G. v. Krueger, *Ber.* 1932, **65**, 1253.

air (unlike PF_3) and attacking the skin. It does not affect glass, but is decomposed by water.

Phosphorus pentachloride, made from the elements, dissociates in the vapour 13·5 per cent. at 160° and 1 atm.,[640] and wholly above 300°, into chlorine and trichloride. The pentabromide forms yellow crystals melting to a partly dissociated liquid. The pentaiodide is unknown.

The molecules in the vapour of the pentafluoride and chlorofluoride PF_3Cl_2, and in that of the pentachloride so far as it is not dissociated, are shown by electron diffraction to form trigonal bipyramids (2 polar and 3 equatorial positions; PF_5[644-5], PF_3Cl_2[645], PCl_5[646]) like most if not all other 5-covalent molecules. The distances are P—F 1·57 A in PF_5 and 1·59 in PF_3Cl_2 (theory 1·74; obs. in PF_3 1·52); P—Cl 2·05 in PF_3Cl_2, 2·04 equatorial and 2·11 polar in PCl_5 (the only 5-covalent molecule where such a difference has been found); theory for P—Cl is 2·09, obs. in PCl_3 2·00. In PF_3Cl_2 the chlorine atoms are polar and the fluorines equatorial. In liquid PCl_5 the Raman spectrum indicates that the trigonal bipyramid persists.[647]

In the solid state it has been shown by X-ray analysis[648] that PCl_5 is a salt $[PCl_4]^+[PCl_6]^-$, the cation being tetrahedral with P—Cl 1·98 A, and the anion octahedral with P—Cl 2·06; the salt character is supported by the high dielectric constant (Lowry), and by the conductivity of solutions in nitrobenzene[649] and in bromine.[650] A different salt structure is found in the solid pentabromide,[651] which is $[PBr_4]Br$; we should expect the larger size of the bromine atom to affect the stability more in the anion, with valency angles of 90°, than in the cation, with angles of 109·5°.

Di- or Tetrahalides

The tetrachloride P_2Cl_4 (presumably) was made by the action of an electric discharge on a mixture of PCl_3 vapour and hydrogen.[652] It is a colourless fuming liquid, oxidized by air, sometimes with inflammation. It decomposes on standing to trichloride and phosphorus. It melts at −28° and boils at 180°. The iodide P_2I_4, made directly from the elements,[653-4] melts at 110° and decomposes before it boils. It is hydrolysed by water at 0° to hypophosphorous, phosphorous, and phosphoric acids, phosphine, etc.; with aqueous sodium hydroxide and hydrogen peroxide it gives a yield of hypophosphoric acid,[654] almost the only way of making

[644] H. Braune and P. Pinnow, *Z. physikal. Chem.* 1937, B **35**, 239.

[645] L. O. Brockway and J. Y. Beach, *J.A.C.S.* 1938, **60**, 1836.

[646] M. Rouault, *C.R.* 1938, **207**, 620.

[647] H. Moureu, M. Magat, and G. Wetroff, ib. 1937, **205**, 276.

[648] D. Clark, H. M. Powell, and A. F. Wells, *J.C.S.* 1942, 642.

[649] G. W. F. Holroyd, H. Chadwick, and J. E. H. Mitchell, ib. 1925, **127**, 2492.

[650] W. A. Plotnikov and S. Jakubson, *Z. physikal. Chem.* 1928, **138**, 235.

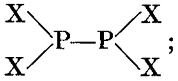
[651] H. M. Powell and D. Clark, *Nature*, 1940, **145**, 971.

[652] A. Besson and L. Fournier, *C.R.* 1910, **150**, 102.

[653] J. H. Kolitowska, *Rocz. Chem.* 1935, **15**, 29.

[654] F. E. E. Germann and R. N. Traxler, *J.A.C.S.* 1927, **49**, 307.

this acid that does not start from elementary phosphorus. These two halides obviously have the structure



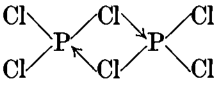
the formation of hypophosphoric acid confirms the presence of the P—P link.

COMPLEX PHOSPHORUS COMPOUNDS

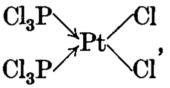
The compounds of trivalent phosphorus, such as phosphine and the trichloride, can act as donors. Phosphine forms analogues of ammines, though its power of co-ordination is much less than that of ammonia, and the number of known products is small, because they are easily oxidized.

Höltje[655] finds that at −110° phosphine will form compounds 2 X, 3 PH_3 with stannic chloride (m.pt. −33°) and bromide (+29°), and compounds X, PH_3, and X, 2 PH_3 with titanium tetrachloride and tetrabromide; but it does not combine with the tetraiodides of tin or titanium, or with any halides of silicon and germanium. Aluminium halides[656] react with phosphine only on heating to 70–110°, and always give X, PH_3; the dissociation pressures of phosphine are 10 mm. for $AlCl_3$, PH_3 at +10°, for $AlBr_3$, PH_3 at 85°, and for AlI_3, PH_3 at 93°.

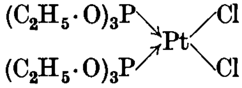
The trihalides behave in a similar way. They do not polymerize, as do those of aluminium and iron, because they cannot act as acceptors. In a molecule



the phosphorus atom would have a valency group of 2, $\underline{8}$ which is impossible unless the first pair of electrons can be inert. But they can and do act as donors. Thus we have a platinous chloride compound



which, as Werner found, occurs in a *cis* and a *trans* form, showing that the four valencies of the platinum lie in a plane. The stability of the co-ordination is shown by the fact that alcohol replaces the chlorine atoms by alkyloxy-groups without removing the phosphorus, the ester



being formed. Similar addition compounds are formed by phosphorus trialkyls and by alkyl phosphites with cuprous and aurous halides, as well as with palladous and platinous chloride; the trialkyl derivatives are[657]

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[655] R. Höltje, *Z. anorg. Chem.* 1930, 190, 241.

[656] R. Höltje and F. Meyer, ib. 1931, 197, 93.

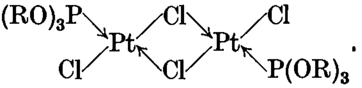
[657] See Beilstein, iv. 563.

mostly of the type AX, 2 $PAlk_3$, while the phosphorous ester complexes are nearly all[658-9] AX, $P(O \cdot Alk)_3$; for example $(C_2H_5 \cdot O)_3P \rightarrow Au—Cl$ m.pt. $-10°$, miscible with ether and benzene.

The platinous chloride complexes occur in two other types as well as the $PtCl_2$, 2 PR_3 mentioned above. Tetra-complexes $PtCl_2$, 4 PR_3 are known, which are clearly ionized, and should be written $[Pt(PR_3)_4]Cl_2$; two of the PR_3 molecules can be replaced by ammonia, giving the salt

$$[Pt(PR_3)_2(NH_3)_2]Cl_2,$$

which has been shown to occur in *cis* and *trans* forms. There is further a series of 1:1 platinous complexes of the composition $PtCl_2$, $P(OR)_3$; Rosenheim[660] showed that these are dimeric in benzene, and Pfeiffer[661] points out that they must have the structure



In agreement with this they readily co-ordinate further, taking up for every Pt atom 2 NH_3, 1 CO, 1 PCl_3, or 1/2 C_2H_4.

Compounds of pentavalent phosphorus like the pentafluoride should be able to attain their maximum covalency of 6 by acting as acceptors. This does not occur often, probably owing to the great stability both of the phosphorus octet and of the 5-covalent phosphorus compounds, which are formed directly, and need no co-ordinate links. We only know the hexafluorides $M[PF_6]$, and one hexachloride $[PCl_4](PCl_6)$.

Our knowledge of the hexafluorophosphates $M[PF_6]$ is due to Lange.[662-5] A small amount (less than 1 per cent.) is formed along with difluorophosphoric acid HPO_2F_2 when the pentoxide dissolves in concentrated hydrofluoric acid. A better way is to heat the pentachloride with excess of ammonium or potassium fluoride, when a 70-80 per cent. yield of the salt is obtained. The reaction is exothermic; if the mass is strongly heated at one point the change proceeds through the whole. The salt formed can be purified by recrystallization. If the fluoride of a divalent metal is used, no hexafluorophosphate is formed, and the whole of the phosphorus is evolved as the pentafluoride.

$H[PF_6]$ is a strong acid, and the alkaline salts have a neutral reaction; this is to be expected, since the phosphorus is covalently saturated. For the same reason the salts are remarkably stable, especially to alkalies.

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[658] A. Arbusov, *Ber.* 1905, **38**, 1172.

[659] L. Lindet, *Ann. Chim.* 1887, [6] **11**, 185, 190.

[660] A. Rosenheim and W. Löwenstamm, *Z. anorg. Chem.* 1903, **37**, 394.

[661] *Org. Mol.-verbindungen*, ed. 2, 1927, 201.

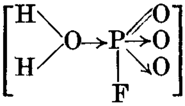
[662] W. Lange, *Ber.* 1928, **61**, 799.

[663] W. Lange and E. Müller, ib., 1930, **63**, 1058.

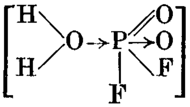
[664] W. Lange and G. v. Krueger, ib., 1932, **65**, 1253.

[665] W. Lange, *Z. anorg. Chem.* 1932, **208**, 387.

The P in $[PF_6]$, like the S in SF_6, cannot act as donor or acceptor, whereas it can be an acceptor in the ions $[PO_3F]''$ and $[PO_2F_2]'$, forming



and



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The $M[PF_6]$ salts are not hydrolysed by heating with aqueous alkali for days to 100°, which completely destroys the mono- and di-fluorophosphates. To decompose them for analysis they must be fused with solid potash, and even then they first dissolve quietly, and then react violently. But they are hydrolysed, though slowly, when heated with strong acids.

The salts have a remarkable resemblance in properties to the perchlorates and their allies with the ions BF_4, SO_3F, PO_2F_2. The crystalline form is quite different from that of the perchlorates, and the molecular volume about 14 c.c. greater; but the two series have this in common, that they are the salts of a strong monobasic acid, with almost spherical anions of about the same size,* having on the outside very slightly deformable atoms. The resemblance is shown by the solubilities, and also by the fact that the diazonium salts $Ar\cdot N_2[PF_6]$ are quite stable when they are dry, and on heating do not explode, but decompose quietly to $ArF+N_2+PF_5$. The diazonium fluoroborates behave in exactly the same way, to give BF_3; the fluorosulphates $Ar\cdot N_2[SO_3F]$ also decompose quietly, though in a different way. The solubilities in moles per litre at 20° are:

	K	Rb	Cs	$Ni(NH_3)_6$	Me_4N	Et_4N	ΦN_2, (0°)	$TolN_2$, (0°)
PF_6	0·432	0·076	0·030	0·0018	0·0077	0·0294	0·036	0·013
ClO_4	0·120	0·071	0·084	0·0069	0·0632	0·1056	0·070	0·038

	Pyr.	*Strychn.*	*Nitron.*
PF_6	0·180	0·0032	0·0002
ClO_4	0·530	0·0054	0·00005

The conductivities, and their changes with dilution, are practically the same for KPF_6 and $KClO_4$. Another remarkable property, which is proof of their great stability, is that in spite of their high fluorine content they are very slightly poisonous. An injection of 0·5 g. per kg. is not fatal to a frog, and 0·02 g. per kg. has no action on a rabbit.

The corresponding salts $M[XF_6]_x$ are known for arsenic, antimony, and tantalum, but not for vandalium or niobium. The arsenic salts $[MAsF_6]_3$ for some reason have a much smaller resemblance to the perchlorates, and have quite a different crystalline form from the fluorophosphates.

The hexachlorophosphates $M[PCl_6]$ are known only in solid phosphorus pentachloride, which has been shown (see above, p. 754) to be

$$[PCl_4]\cdot[PCl_6];$$

the pentabromide is not $[PBr_4]\cdot[PBr_6]$ but $[PBr_4]Br$.

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* P—F 1·70; for other distances see p. 748.

ARSENIC, ANTIMONY, AND BISMUTH

These three elements form with phosphorus a regular series, the most marked changed being the appearance of the 'inert pair', just perceptible in arsenic, well marked in antimony, and dominant in bismuth, where it is accompanied by the almost complete disappearance of the pentavalent form. This also makes the trivalent cation M^{+++} possible, with the structure —(18), 2, these last 2 being inert. The ion occurs to some extent with antimony (not with arsenic) and is well defined with bismuth, which in many compounds resembles a trivalent metal of Group III, such as lanthanum.

ELEMENTS

Arsenic

Elementary arsenic occurs in three solid modifications. They differ enormously in density, and it is interesting to compare the densities of this series of elements in their various forms:

Phosphorus	*Dens.*	*At. vol.*	*Ratio*	*Arsenic*	*Dens.*[a]	*At. vol.*	*Ratio*
White	1·83	17·0 c.c.	1·43	Yellow	1·97	38·1	2·91
Violet	2·35	13·2	1·15	Black	4·73	16·1	1·23
Black	2·69	11·5	1	*Grey*	5·73	13·1	1

Antimony	*Dens.*	*At. vol.*	*Ratio*	*Bismuth*	*Dens.*	*At. vol.*
Yellow	..	Large	Large			
Black	5·3	23·0	1·26			
Grey	6·67	18·3	1	Metal	9·80	21·3

a = [686]

1. Yellow arsenic, obtained by the sudden cooling of the heated vapour, is the least stable. It is very like white phosphorus in its general character. It is soluble in carbon disulphide (100 g. dissolve 11 g. at the b. pt. of 47° and 4 g. at 0°), and its molecular weight in this solvent corresponds to As_4. It has no doubt a lattice of As_4 tetrahedra. It has more than twice the atomic volume of either of the other two forms. It changes into the stable grey form on heating (like white phosphorus, but more readily), the change being catalysed by light, by iodine, and (unlike that of phosphorus) by bromine.

2. Black arsenic, density 4·7, has been described: it is said to be more stable than (1), but less than (3), into which it changes on heating. Its individuality is not certain. It may be a finely divided form of (3).

3. Grey arsenic, the ordinary stable form. This is definitely metallic, having a specific conductivity of $2{\cdot}56 \times 10^4$ at 0°, nearly half as great as that of lead, or 4·2 per cent. of that of silver. The vapour pressure of the solid is 1 atm. at 633°, and it melts at 817°, where its vapour pressure is 36 atm. (compare red phosphorus).

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[686] H. Stöhr, *Z. anorg. Chem.* 1939, **242**, 138.

Arsenic vapour, which is the same whichever form it comes from, consists of As_4 molecules up to 800°: it then begins to break up to As_2, but the change is not complete below 1,700°. The structure of the As_4 vapour molecules was shown[667] by electron diffraction to be the same as that of P_4: tetrahedral, with a distance As—As of $2{\cdot}44+0{\cdot}03$ A, agreeing well with Pauling's value of 1·21 for the radius. The heats of linkage (see above, p. 728) are As—As 34 and As=As 91·3 k.cals., ratio 2·69.[442]

Elementary Antimony

This seems to occur in four solid forms.

1. Yellow antimony. This corresponds to white phosphorus and yellow arsenic: it is transparent and soluble in carbon disulphide, and is evidently covalent. It was prepared by Stock[668] by the action of oxygen on liquid stibine SbH_3 at −90°. It is very unstable. It changes in light at −180°, and even in the dark at −90°, into the second form:

2. Black antimony. This is formed from the yellow form, or by the action of oxygen on stibine at low temperatures but above −80°, or by the rapid cooling of antimony vapour. It is much more active chemically than the ordinary form (3): it is oxidized by cold air, and is sometimes pyrophoric. On heating it goes to (3).

3. Metallic (ordinary) antimony. This is definitely metallic, with a specific conductivity of $2{\cdot}71 \times 10^4$ at 0° (4·4 per cent. of that of silver); it melts at 630° to give an opaque and conducting liquid (sp. cond. at 630°, solid 0·62, liquid $0{\cdot}88 \times 10^4$), and boils at 1,325.°

4. Explosive antimony. This peculiar form is produced by the electrolysis of antimony trichloride, tribromide, or tri-iodide, with a high current density. It changes explosively on heating to 200°, or sometimes on scratching, to the ordinary form (3), with an evolution of about 2·4 k.cals. of heat per g. atom. It always contains 10–15 per cent. of occluded or adsorbed halide,[669] and the X-ray diagram shows the antimony to be in the amorphous state.[670–1] According to Coffin[672–3] it is probably a gel-like structure of antimony and its trichloride; the explosion is due to the heat evolved when the former becomes crystalline; at lower temperatures this change occurs gradually and quietly.

The vapour density of antimony corresponds to $Sb_{2\cdot96}$ at 1,572° and $Sb_{2\cdot68}$ at 1,640°. Hence it is slightly less dissociated than arsenic (which is As_2 at 1,700°), but rather more than phosphorus, which has the value of $P_{3\cdot0}$ at 1,677°.

The structure of the molecule has not been determined, but there is no

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[667] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *J. Chem. Phys.* 1935, **3**, 699.

[668] A. Stock and O. Guttmann, *Ber.* 1904, **37**, 885.

[669] E. Cohen and C. C. Coffin, *Z. physikal. Chem.* 1930, **149**, 417.

[670] H. v. Steinwehr and A. Schulze, *Z. Phys.* 1930, **63**, 815.

[671] J. A. Prins, *Nature*, 1933, **131**, 760.

[672] C. C. Coffin and S. Johnston, *Proc. Roy. Soc.* 1934, **146**, 564.

[673] C. C. Coffin, ib., 1935, **152**, 47.

reason to doubt that like phosphorus and arsenic the Sb_4 molecules which occur at lower temperatures are tetrahedral.

Elementary Bismuth

This occurs only in the metallic state. It is dimorphic.[674-5] It melts at 273°, and expands about 4 per cent. on freezing: the liquid, like water, has a maximum density, which is 10·06 at 270° (super-cooled). Its specific conductivity $\times 10^4$ is: 0·93 at 0° (about 1·4 per cent. of that of silver), 0·63 at 100°, and at 271° liquid 0·78, solid 0·36. The whole behaviour indicates the existence of polyatomic molecules in the liquid and probably in the solid. Bismuth has a reddish-white colour, and crystallizes in large crystals.

It is diamagnetic, and its conductivity is greatly affected by the magnetic field, far more than with any other known metal, being doubled by a field of 20,000 gauss, and at −180° being increased more than 1,000 times by 250,000 gauss.[676] It boils about 1,560°, and its vapour at all temperatures examined is a mixture of Bi and Bi_2 molecules. The percentage of Bi is 40 at 850°,[677] about 50 at 1,650°, and about 90 at 2,070.° The melting-points and boiling-points of these elements in their stable forms (e.g. red phosphorus, etc.) are as follows:

	Phosphorus	*Arsenic*	*Antimony*	*Bismuth*
M. pt.	589° (43 atm.)	818° (36 atm.)	631°	273°
B. pt.	416° subl.	633° subl.	1,325°	1,560°

The elements are all rather less electropositive than hydrogen, and hence will only dissolve in oxidizing acids. The ease of oxidation falls off in the series (P) > As > Sb > Bi, as is shown by the temperatures at which they combine with oxygen, and the concentration of HNO_3 which oxidizes them.

HYDRIDES

	NH_3	PH_3	AsH_3	SbH_3	BiH_3
B. pt.	−33·5°	−87°	−54·8°	−18°	*ca.* +20°
M. pt.	−78°	−135·5°	−113·5°	−88°	..

All these elements form hydrides of the AH_3 type, but their stability and ease of formation fall off with rise of atomic number.

Arsine AsH_3 is the only known hydride of arsenic, although there are numerous organic derivatives of $H_2As—AsH_2$ (cacodyl compounds) and of $HAs{=}AsH$ (arseno-benzenes, salvarsan). Arsine is formed by the action of nascent hydrogen on arsenic compounds, most easily by treating metallic arsenides, such as Zn_3As_2, with sulphuric acid. It is endothermic and

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[674] E. Cohen and A. L. T. Moesveld, *Z. physikal. Chem.* 1913, **85**, 419.

[675] E. Jänecke, ib., 1915, **90**, 313.

[676] P. Kapitza, *Proc. Roy. Soc.* 1928, **119**, 401.

[677] Molecular beam, I. F. Zartman, *Phys. Rev.* 1931, ii. **37**, 383.

highly poisonous. At a red heat it decomposes, forming a metallic mirror of arsenic:

$$2\ AsH_3 = 2\ As + 3\ H_2 + 88{\cdot}4\ \text{k.cals.}$$

It is a strong reducing agent, and with silver nitrate gives metallic silver, As_2O_3, and HNO_3.

Stibine SbH_3 is best made by dissolving the Sb—Mg alloy in hydrochloric acid and freezing it out from the gas evolved. The yield is not nearly so good as that of arsine. It is almost as poisonous as arsine.

Bismuthine BiH_3 is the most difficult to prepare of the whole series. It was discovered by Paneth in 1918.[678–81] He first obtained it by using the isotope thorium C, which was deposited on a magnesium plate, and this dissolved in acid: the gas had the activity of thorium C, and hence contained a volatile hydrogen compound of ThC or bismuth. Later he made it from ordinary bismuth by dissolving the alloy Bi_2Mg_3, or even a mixture of bismuth and magnesium in acid and freezing out. The yield is very small, about 1/20,000 of the bismuth dissolved. The gas is formed by the action of the nascent hydrogen on the surface of the metal, on the bismuth salt in the solution. Enough was obtained to give a weighable bismuth mirror, but not enough to determine its physical properties: the boiling-point of +20° is obtained by extrapolation from those of the hydrides of the other elements. It is not acted on by light; it is decomposed by heat, but not extraordinarily easily, 35 per cent. remaining unchanged after passing through a glass tube at 160°, and 9 per cent. at 250°. Like AsH_3 it is not affected by H_2S solution, but it is removed by silver nitrate.

The properties of these hydrides all change regularly as we descend the series. Their stability and readiness of formation decrease in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. The basicity, that is, the tendency to go over into AH_4^+ ions, falls off in the same way. As we saw, phosphine is a much weaker base than ammonia, arsine is weaker still, stibine weaker again, and bismuthine, so far as we know, has no basic properties at all.

ARSENIC ALKYL AND ARYL COMPOUNDS

THE organic derivatives of these three elements, and above all of arsenic, are numerous; Krause and v. Grosse[682] say that of the 12,000 or so metal-carbon compounds known in 1937, about 8,000 were compounds of arsenic. This is of course on account of their therapeutic value, and it is a testimony to the energy of modern pharmacologists.

The following account of these compounds is largely based on that given by Krause and v. Grosse.[683]

[678] F. Paneth, *Ber.* 1918, **51**, 1704.

[679] F. Paneth and E. Winternitz, ib. 1728.

[680] F. Paneth, A. Johannsen, and M. Matthies, ib. 1922, **55**, 769.

[681] F. Paneth and E. Rabinovitsch, ib. 1925, **58**, 1150.

[682] *Metallorganische Verbindungen*, 1937, p. 2.

[683] Loc. cit.: As pp. 450–592; Sb 593–640; Bi 641–53.

The alkyl compounds of arsenic were the earliest 'organometallic' compounds to be made, 'Cadet's fuming liquid'[684] having been discovered by L. C. Cadet de Gassicourt in 1760. The first real investigation of the subject (and of this liquid) was begun in 1837 by Bunsen, who isolated free cacodyl from it in 1842. This work led to Frankland's search for free radicals, and to the use of organometallic compounds for the determination of atomic weights and valencies.

Ehrlich's work on the aryl arsenic oxides as trypanocides began in 1905, and these investigations were the chief cause of the modern development of the subject. A general account of the therapeutic action of arsenic compounds is given by H. Schlossberger.[685]

The primary alkyl arsines are formed by the reduction of primary arsonic acids $Alk\cdot AsO(OH)_2$, made by the action of alkyl iodides on sodium arsenite[686] with zinc and hydrochloric acid in the absence of oxygen. Unlike arsine itself they are oxidized by air, but less energetically than the secondary or tertiary arsines, which catch fire; they have very weak basic properties, and hence are only slightly soluble in water. Thus methyl arsine $CH_3\cdot AsH_2$[687-9] boils at $+2°$, and fumes in the air but does not catch fire; 0·1 g. dissolves in 1 litre of water at 25° and 1 atm.; dry oxygen converts it into the oxide $CH_3\cdot As{=}O$, which in presence of water takes up more oxygen to give the arsonic acid $CH_3\cdot AsO(OH)_2$. The weakness of attachment of the hydrogen atoms in methyl arsine is shown by their reacting with iodine to give $CH_3\cdot AsI_2 + 2\,HI$. By itself methyl arsine is very stable, but 3 days' heating at 300° converts it into arsenic, hydrogen, and methane.

The dialkyl arsines Alk_2AsH can be made by reducing the secondary arsinic acids $R_2AsO\cdot OH$ with zinc and hydrochloric acid, or by the reduction of the dialkyl arsenic oxides and chlorides (cacodyl compounds). Diethyl arsine $Et_2As\cdot H$ is also formed by the action of moulds on inorganic arsenic compounds, such as paints in wall-papers.[690] They are more reactive than the monoalkyl compounds; they catch fire in air even at 0°, and form salts with acids. By itself dimethyl arsine $(CH_3)_2As\cdot H$ is stable below 330°, even in sunlight; it is a strong reducing agent, being oxidized first to cacodyl $(CH_3)_2As{-}As(CH_3)_2$ or its oxide or chloride, and finally, to the acid $(CH_3)_2AsO\cdot OH$.

The trialkyl arsines Alk_3As can be made from sodium arsenide and alkyl iodides (Landolt 1854) or by the action of arsenic trihalides on zinc alkyls (Hofmann, 1855) or on the Grignard reagent.[691] They are colourless liquids of repulsive smell, not miscible with water, which are readily

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[684] According to M. Valeur and P. Gailliot, *C.R.* 1927, **185**, 956, this contains on the average 56 per cent. of free cacodyl and 40 per cent. of cacodyl oxide.

[685] *Ber.* 1935, **68**, A 149.

[686] G. Meyer, ib. 1883, **16**, 1440.

[687] A. Palmer and W. M. Dehn, ib. 1901, **34**, 3594.

[688] W. M. Dehn, *Amer. Chem. J.* 1905, **33**, 120.

[689] Id., ib., 1908, **40**, 117.

[690] See F. Challenger and L. Ellis, *J.C.S.* 1935, 396.

[691] See W. Steinkopf and J. Müller, *Ber.* 1921, **54**, 841.

oxidized by air, especially tribenzyl arsine,[693] and so must be handled in carbon dioxide or nitrogen. By themselves they are fairly stable. They are feebly basic, and form salts with the halogen hydrides, which are unstable and decomposed by water. The Raman spectra indicate a pyramidal structure.[692]

Like the tertiary amines and phosphines they readily act as donors, giving co-ordination compounds such as $(R_3As)_2PdCl_2$ and $(R_3As)_2SnCl_4$.[694] These are some boiling-points:

	AsH_3	$R.AsH_2$	$R_2As.H$	R_3As
R = CH_3	−54·8°	+2°	+36°	+49·5°[a]
Et	..	+36°	105°	142°

a = [695]

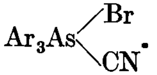
The aryl substitution products of arsine were first prepared by Michaelis in 1882, and are made like the alkyls. They are known in all three series, $Ar\cdot AsH_2$, Ar_2AsH, and Ar_3As. The mono-derivatives resemble the alkyl compounds in general, and have no basic properties. They are oxidized by air, and are in general very reactive; they attack the skin. $\Phi\cdot AsH_2$ gives $\Phi_2As{-}As\Phi_2$ when treated with $\Phi\cdot MgBr$ and iodine, and $\Phi\cdot As{=}As\cdot\Phi$ with $\Phi\cdot As(OH)Cl$.[696] They have a remarkable reaction with aldehydes (Krause and v. Grosse, p. 505):

$$Ar\cdot AsH_2 + 2\,R\cdot CHO = Ar\cdot As(CHOH\cdot R)_2.$$

They react with oxygen, sulphur, and the halogens to give the oxides, sulphides, and di-halogen derivatives.

Of the diaryl compounds Ar_2AsH only one, the phenyl compound $(C_6H_5)_2As\cdot H$, is known; it is very like the dimethyl analogue $(CH_3)_2AsH$.

The triaryl arsines Ar_3As are on the whole much more stable than the trialkyls. Thus triphenyl arsine distils unchanged above 360°, and these compounds can be nitrated and the products reduced to amines without splitting the link of arsenic to carbon; they have no basic properties. They will add on alkyl halides, but not aryl halides (though Ar_4As salts exist), to form quaternary salts; with halogens they give dihalides Ar_3AsX_2, and with cyanogen bromide



$Ar_3As\begin{smallmatrix}Br\\CN\end{smallmatrix}$.

Tetra-alkyl and -aryl Arsonium Salts

These compounds of the type $[R_4As]X$ are numerous, though attempts to prepare penta-alkyl compounds Alk_5As have not been successful.[697] The

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[692] E. J. Rosenbaum, D. J. Rubin, and C. R. Sandberg, *J. Chem. Phys.* 1940, **8**, 366.

[693] J. Dondonov and H. Medox, *Ber.* 1935, **68**, 1254.

[694] G. J. Burrows and E. E. Turner, *J.C.S.* 1921, **119**, 1448.

[695] E. J. Rosenbaum and C. R. Sandberg, *J.A.C.S.* 1940, **62**, 1622. The Trouton constant of $As(CH_3)_3$ is 20·6.

[696] F. F. Blicke and J. F. Oneto, ib. 1935, **57**, 749.

[697] M. E. P. Friedrich and C. S. Marvel, *J.A.C.S.* 1930, **52**, 376.

arsonium salts can be made from the tertiary arsines and alkyl iodide or even from arsenic and the alkyl iodides.[698] The salts, even of strong acids, are neutral in solution; the free bases $[R_4As]OH$, made from the chlorides with moist silver oxide, closely resemble the alkalies (and the quaternary ammonium bases), being deliquescent solids whose solutions absorb carbon dioxide from the air. The salts are very poisonous, and have a curare-like (not arsenic-like) action. Numerous mixed arsonium compounds are known.

As the triaryl arsines will not take up aryl iodides, the tetra-aryl bases must be made in other ways, as by the action of the Grignard reagent on the oxides Ar_3AsO.[699] The quaternary arsonium salts, both the mixed and the tetra-aryl, are very stable and are strong electrolytes; the tetraphenyl ion $[\Phi_4As]^+$ seems[700] to have the abnormally small mobility of 11 at 25°. It has been shown[701] by X-ray analysis that the cation of tetraphenyl arsonium iodide has a tetrahedral structure with the As—C distance 1·95 A (theory 1·96).

Examples are the phenyl salts $[\Phi_4As]Cl$, m.pt. 256–70; $[\Phi_4As]Br$ 273-5°; $[\Phi_4As]I$ 312-13°. On heating (above 300°) they break up into the triaryl arsines and aryl halides. The tetra-aryl compounds, though they are not so easy to make as the mixed compounds (doubtless for steric reasons), are especially stable.

Tetraphenyl arsonium chloride can be used for the quantitative estimation of zinc, cadmium, mercury, or tin, since the salts

$$(\Phi_4As)_2[MCl_4] \text{ (M } = \text{ Zn, Cd, or Hg)}$$

and $(\Phi_4As)_2[SnCl_6]$ are insoluble in 1*n* to 3·5*n* sodium chloride solution. Rhenium can also be determined, since the salt $(\Phi_4As)[ReO_4]$ is insoluble in water.[702]

OXY-DERIVATIVES OF THE ARSINES

These include (A) two trivalent types, (1) the ether-like $R_2As—O—AsR_2$ (cacodyl oxide type) and (2) the oxides $R\cdot As{=}O$; and (B) three pentavalent types, (1) the oxides $R_3As{=}O$, (2) the mono-R-arsonic acids $R\cdot AsO(OH)_2$, and (3) the di-R-arsinic acids $R_2AsO\cdot OH$.

A. 1. *Cacodyl Oxide Type*, $R_2As—O—AsR_2$

The methyl compound (cacodyl oxide itself) is contained to some 40 per cent. in Cadet's fuming liquid (made by distilling arsenious acid with potassium acetate); it is also easily formed by oxidizing cacodyl

$$(CH_3)_2As—As(CH_3)_2;$$

it is further oxidized in air to dimethyl arsinic acid $(CH_3)_2AsO\cdot OH$; it boils at 120°, and the phenyl compound $\Phi_2As—O—As\Phi_2$ melts at 92°.

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[698] W. Steinkopf and G. Schwen, *Ber.* 1921, **54**, 1451.

[699] F. F. Blicke and C. Marzano, *J.A.C.S.* 1933, **55**, 3056.

[700] F. F. Blicke and E. Monroe, ib. 1935, **57**, 720.

[701] R. C. L. Mooney, ib. 1940, **62**, 2995.

[702] H. H. Willard and G. M. Smith, *J. Ind. Eng. Chem.* 1939, *Anal.* **11**, 269, 305.

A. 2. *Trivalent Oxides,* R·As=O

These can be made from the dihalides $R \cdot AsCl_2$ with alkaline hydroxide or carbonate. They are low-melting ($CH_3 \cdot AsO$ 95°) solids or liquids of very unpleasant smell, which are somewhat volatile in steam. When distilled with potassium hydroxide they undergo a singular reaction

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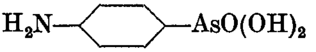
Aryl antimony oxides do the same.

The compound  was the starting-point of all Ehrlich's work on the therapeutic powers of these organic arsenic compounds; he found that this oxide kills the trypanosome of sleeping-sickness *in vitro*, and that its oxidation product



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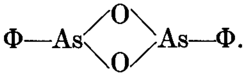
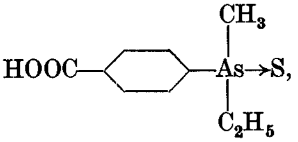
Phenyl arsenic oxide Φ·As=O, which is made in the same way from the chloride $\Phi \cdot AsCl_2$, melts at 142-5° and is easily soluble in benzene. If phenyl arsonic acid $\Phi \cdot AsO(OH)_2$ is reduced with sulphur dioxide, an isomer of this is produced, which melts at 210-20° and is insoluble in benzene; this may be the dimeric compound .[703]

The corresponding sulphides R·As=S can be made by treating the primary arsines $R \cdot AsH_2$ with sulphur (Baeyer, 1858).

B. 1. *Pentavalent Oxides,* $R_3As{=}O$ *or* $R_3As{\rightarrow}O$

These compounds are formed by the oxidation of the tertiary arsines with atmospheric air. They are very weak bases neutral to litmus, and the salts they form with acids are highly hydrolysed by water.[704] The methyl compound $(CH_3)_3AsO$ forms deliquescent crystals. The triaryl oxides are similar.

A similar series of sulphides $R_3As{=}S$ (or $R_3As{\rightarrow}S$) is known, one of which, *p*-carboxyphenyl methyl ethyl arsine sulphide



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[703] W. Steinkopf, S. Schmidt, and H. Penz, *J. prakt. Chem.* **1934, 141, 304.**

[704] P. Nylen, *Z. anorg. Chem.* **1941, 246, 227.**

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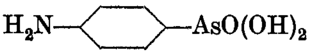

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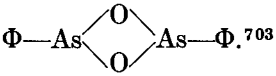
Phenyl arsenic oxide $\Phi \cdot As=O$, which is made in the same way from the chloride $\Phi \cdot AsCl_2$, melts at 142–5° and is easily soluble in benzene. If phenyl arsonic acid $\Phi \cdot AsO(OH)_2$ is reduced with sulphur dioxide, an isomer of this is produced, which melts at 210–20° and is insoluble in benzene; this may be the dimeric compound [703]

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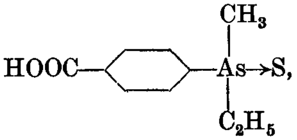

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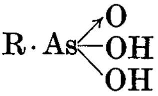
B. 2. *Mono-alkyl or -aryl Arsonic Acids*, R·As

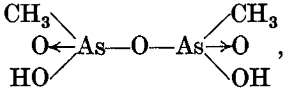


$$R\cdot As\begin{smallmatrix}\nearrow O\\ \leftarrow OH\\ \searrow OH\end{smallmatrix}$$

These can be made by the oxidation of the primary arsines or their oxides or dihalides, and most simply by G. Meyer's method from an arsenite and an alkyl halide. They are colourless crystalline solids, soluble in alcohol and water, but not in ether. They are relatively strong acids, as the following values at 25° of the Ostwald dissociation constants K_1 and K_2 show[706]:

	$K_1 \times 10^4$	$K_2 \times 10^9$
Methyl arsonic	2·46	5·69
Ethyl ,,	1·28	4·47
n-Propyl ,,	0·611	0·808
n-Hexyl ,,	0·693	0·642
[Acetic acid 0·18.]		

The methyl compound loses half a molecule of water at 130° to give the 'pyro' acid



which at 180° breaks up into methyl alcohol and arsenic trioxide. Benzyl arsonic acid $\Phi\cdot CH_2\cdot AsO(OH)_2$,[707-8] which forms colourless soluble crystals, illustrates the instability common in compounds with a benzyl group attached to a metal; it is broken up by concentrated hydrochloric acid into benzyl chloride + arsenic trioxide, and slowly even by water, giving benzyl alcohol. This acid irritates the skin and mucous membrane, while the alkyl-arsonic acids have no such action (there is a similar difference between benzyl halides and alkyl halides).

Aryl Arsonic Acids, $Ar\cdot AsO(OH)_2$

These acids can scarcely be made by G. Meyer's method from arsenic tri-oxide with an aryl halide, because the aryl holds the halogen too firmly, but they can be made by Barth's method[709] with the diazo-compound

$$Ar\cdot N_2\cdot Cl + As(OK)_3 = Ar\cdot AsO(OK)_2 + KCl + N_2.$$

They are crystalline, soluble in water and alcohol but not in ether (like the alkyl compounds). They are extremely stable; they can be nitrated and reduced, and the NH_2 group eliminated, without rupture of the As—C link; on heating they give anhydrides $Ar\cdot AsO_2$, which go back with water; negative substituents on the aryl make them lose water less easily.

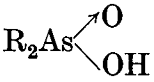
[706] J. H. Backer and C. C. Bolt, *Rec. Trav.* 1935, **54**, 186.

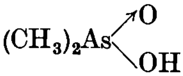
[707] W. Dehn and S. McGrath, *J.A.C.S.* 1906, **28**, 354.

[708] B. Englund, *Svensk. Kem. Tidskr.* 1933, **45**, 170 (*B.C.A.* 1933, 1061).

[709] D.R.P. 1910, **250**, 264.

The phenyl compound $\Phi\cdot AsO(OH)_2$ is colourless, and sinters at 158° with loss of water. It is extraordinarily stable; hot concentrated nitric or sulphuric acid has no action on the As—C link. Phosphorous acid reduces it to arsenobenzene $\Phi\cdot As{=}As\cdot\Phi$.

B. 3. *Di-alkyl or -aryl Arsinic Acids.*  $R_2As\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}$

These acids are formed by the action of water on the dialkyl trihalides $R_2As(hal)_3$, or (with some violence) by the oxidation of the oxides of the cacodyl oxide type $R_2As{-}O{-}AsR_2$, for example by mercuric oxide in presence of water. The best known is cacodylic acid  $(CH_3)_2As\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}$. This, which melts at 200°, is easily soluble in water, and is extremely stable; fuming nitric acid, aqua regia, or potassium permanganate have no action on it even on warming, nor have such reducing agents as nascent hydrogen, ferrous sulphate, or sulphur dioxide (but it can be reduced by hypophosphorous acid or stannous chloride). Hence it is less poisonous than most arsenic compounds, as much of it is eliminated from the body unchanged; it is used medically for malaria and anaemia.

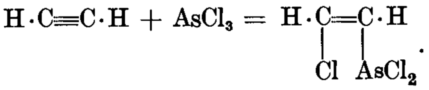
The presence of a second alkyl group greatly weakens the acidity. Cacodylic acid is amphoteric, the dissociation constants being[710-11] K_a $7{\cdot}5\times10^{-7}$, K_b $5{\cdot}6\times10^{-13}$. Many metallic salts are known,[712-15] but they are decomposed by carbon dioxide. The ethyl compound $Et_2AsO\cdot OH$ is similar, but the benzyl compound $(\Phi\cdot CH_2)_2AsO\cdot OH$, like so many of the benzyl compounds, is very unstable.[716]

HALOGEN DERIVATIVES OF THE ARSINES

These comprise (A) the trivalent compounds $R\cdot AsX_2$ and R_2AsX, and (B) the pentavalent types $R\cdot AsX_4$, R_2AsX_3, R_3AsX_2; and finally, $R_4As[X]$, which last has already been discussed among the arsonium salts.

A. 1. $R\cdot AsX_2$

They can be made by the action of the halogen hydrides on the oxides $R\cdot As{=}O$; or (as vinyl derivatives) by the addition of acetylene or its derivatives to arsenic trichloride:



$$H\cdot C{\equiv}C\cdot H + AsCl_3 = \underset{Cl}{H\cdot C}{=}\underset{AsCl_2}{C\cdot H}.$$

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[710] W. Fraenkel, *Z. physikal. Chem.* 1907, **60**, 202.

[711] B. Holmberg, ib., *Arrhenius Festband*, 1910, **70**, 153.

[712] R. Tiollais, *Bull. Soc. Chim.* 1936, [v] **3**, 70.

[713] R. Tiollais and L. Berthois, ib. 1938, [v] **5**, 73.

[714] R. Tiollais and H. Perdreau, ib. 1939, **6**, 631.

[715] R. Tiollais, H. Perdreau, and L. Berthois, ib. 638.

[716] A. Michaelis and U. Paetow, *Ber.* 1885, **18**, 42; *Ann.* 1886, **233**, 61.

The fluorides can be made[717] by treating the chlorides with ammonium fluoride at 80-100°; the alkyl compounds are colourless fuming liquids, whose vapour densities show slight association (20 per cent. with $CH_3 \cdot AsF_2$ at 100° and 420 mm.). They are hydrolysed completely by water (the chlorides only reversibly).[717] Some of their boiling-points and melting-points are:

$R \cdot AsF_2$	*M. pt.*	*B. pt.*	*Trouton*
$R = CH_3$	−29·7°	76·5°	24·3
C_2H_5	−38·7°	94·3°	22·1
C_6H_5	+42°	110°/48 mm.	. .

$R \cdot AsCl_2$	*M.pt.*	*B.pt./*760 *mm.*
$R = CH_3$ . . .	−42·5°	132·5°
C_2H_5 . . .	. .	155·3°
n-Pr . . .	−28·2°	175·3°
C_6H_5 . . .	+18°	253°
o-tolyl . .	. .	264°
m-tolyl . .	. .	270°
2,5-$(CH_3)_2C_6H_3$—	+63°	285°

The methyl compound $CH_3 \cdot AsCl_2$ is hydrolysed by water but does not fume in the air. It is extremely poisonous, attacking the lungs; the phenyl compound $\Phi \cdot AsCl_2$ makes extremely painful burns on the skin. The β-chlorovinyl compound $Cl \cdot CH{=}CH \cdot AsCl_2$ (which is readily made by passing acetylene into arsenic trichloride, and boils at 190° under 760 mm.) is the well-known poison gas Lewisite (named after W. Lee Lewis).

The benzyl compound $\Phi \cdot CH_2 \cdot AsCl_2$[718] is quite unusually unstable; it is decomposed even by atmospheric oxygen with the formation of benzyl chloride, and by water with the liberation of benzoic acid or benzaldehyde: and chlorine, instead of giving the tetrachloride, breaks it up to benzyl chloride and arsenic trichloride.

Numerous aryl derivatives of this type have been made, as intermediate products in the preparation of arsenical drugs.

A. 2. *Monohalides* $R_2As \cdot X$

These can be made by the action of hydrogen chloride on the secondary arsine R_2AsH,[719] an unusual 'back substitution' like that observed with boron or silicon:

$$R_2As \cdot H + HCl = R_2As \cdot Cl + H_2;$$

by the action of halogen on the As—As compounds such as cacodyl $(CH_3)_2As—As(CH_3)_2$; and by the reduction of arsinic acids such as cacodylic $(CH_3)_2AsO \cdot OH$ with sodium hypophosphite in presence of HCl.[720]

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[717] L. H. Long, H. J. Emeleus, and H. V. A. Briscoe, *J.C.S.* 1946, 1123.

[718] A. Michaelis and U. Paetow, *Ann.* 1886, **233**, 91.

[719] W. Dehn and B. Wilcox, *Am. Chem. J.* 1906, **35**, 28.

[720] W. Steinkopf and W. Mieg, *Ber.* 1920, **53**, 1016.

Dimethyl arsenic chloride $(CH_3)_3AsCl$ is colourless and boils at 107°; its vapour attacks the eyes and nose violently; the bromide, b. pt. 128–9°, and the iodide, b. pt. 154-7°, m. pt. −35°, are also known.

The phenyl compound Φ_2AsCl is the poison gas 'Blue Cross', and causes incredibly violent sneezing. The fluoride $\Phi_2As{\cdot}F$ has been made from the chloride by treatment with silver fluoride: m.pt. 17-19°: b.pt. 157-8°/8 mm.[721]

Pentavalent Halides: B. 1. $R{\cdot}AsX_4$

These are few in number, and in the alkyl series are very unstable. If chlorine is passed into CH_3AsCl_2 in CS_2 at −10°, the tetrachloride $CH_3{\cdot}AsCl_4$ separates, but even at 0° this decomposes into $AsCl_3$ and CH_3Cl. The iodide, got by reducing $CH_3{\cdot}AsO(ONa)_2$ with concentrated aqueous hydriodic acid, forms brown crystals, and seems to be more stable, but it may be the periodide $CH_3{\cdot}AsI(I_3)$.

The aromatic compounds, prepared in the same way from the $ArAs(hal)_2$ and halogen, are more stable. The phenyl compound $\Phi{\cdot}AsCl_4$ forms yellow needles, m.pt. 45°, which fume in air and are violently hydrolysed by water. It converts acetic acid into chloracetic, whereas $\Phi{\cdot}PCl_4$ converts it into acetyl chloride; this recalls the instability of the pentachloride of arsenic compared with that of phosphorus.

B. 2. R_2AsX_3

These are more stable than the last class. Thus $(CH_3)_2AsCl_3$ (from dimethyl arsenic monochloride and chlorine in carbon disulphide) is a crystalline substance which goes back to its components at 40-50°. Water hydrolyses it to the arsinic acid $(CH_3)_2AsO{\cdot}OH$.

The aryl compounds are again similar but more stable. Diphenyl arsenic trichloride Φ_2AsCl_3[722] melts at 191°; on warming it slowly breaks up again to $\Phi_2AsCl+Cl_2$, while if heated in a sealed tube to 200° it gives phenyl dichlorarsine and chlorobenzene

$$\Phi_2AsCl_3 = \Phi AsCl_2 + \Phi{\cdot}Cl.$$

B. 3. R_3AsX_2

These compounds are formed when a tertiary arsine is treated with halogen; the reaction is so violent that it must be moderated by the use of a solvent. They can also be got by the action of halogen hydrides on the oxides R_3AsO, or of an alkyl halide on the trivalent monohalide R_2AsX. Thus from dimethyl bromoarsine and methyl bromide we can get $(CH_3)_3AsBr_2$, which goes back to these components on heating. It is hydrolysed by water. The iodide $(CH_3)_3AsI_2$ is similar.

The aryl compounds as before are similar but more stable; for example, triphenyl arsine dichloride Φ_3AsCl_2 (made from triphenyl arsine and

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[721] M. Sartori and E. Recchi, *Ann. Chim. Appl.* 1939, 29, 128.

[722] W. Steinkopf and S. Schmidt, *Ber.* 1928, 61, 675.

chlorine) melts at 204-5°. These compounds are very readily hydrolysed by water, giving first the hydroxy-chloride $Ar_3As(OH)Cl$, and then the dihydroxide $Ar_3As(OH)_2$, which goes to the oxide $Ar_3As{=}O$. The greater stability of the aryl compounds is also shown by the fact that if a mixed compound $AlkAr_2AsX_2$ is heated, the aryl group remains on the arsenic, the products being $Ar_2AsX + Alk \cdot X$.

With all these arsenic compounds the general rule seems to be that the alkyl derivatives are less stable than the aryl, and the benzyl are the least stable of all.

B. 4. $[R_4As]X$

These have already been dealt with among the arsonium compounds (p. 763) above.

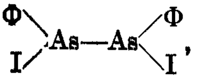
As—As COMPOUNDS: DIARSINES

These include the famous 'free cacodyl' $(CH_3)_2As{-}As(CH_3)_2$, which was isolated by Bunsen in 1842. The arsines of this 'hydrazine' type $R_2As{-}AsR_2$ can be made by the reduction of the dialkyl arsine monochlorides R_2AsCl with zinc, or of the arsinic acids $R_2AsO \cdot OH$ electrolytically or with hypophosphorous acid, or from $R_2AsCl + H \cdot AsR_2$. Cacodyl boils at 170°, and its ethyl homologue at 187°. They are spontaneously inflammable in air but stable alone up to 400°; on oxidation they give first the oxide $R_2As{-}O{-}AsR_2$ and then the acid $R_2AsO \cdot OH$. They are split by halogens to give the secondary halides $R_2As \cdot X$.

The corresponding aryl compounds are made in the same way, best by the reduction of the oxide or acid. They are remarkably insoluble; they are not spontaneously inflammable, though they are readily oxidized by air to the peroxide $Ar_2As{-}O{-}O{-}AsAr_2$ (not to the oxide $R_2As{-}O{-}AsR_2$ as happens to the alkyl diarsines). This is some indication (and there are others) that they are slightly dissociated in solution into the free radicals R_2As,[723] but the phenyl compound has a normal molecular weight in solution, and none of them have shown more than 10 per cent. dissociation.

Tetraphenyl diarsine $\Phi_2As{-}As\Phi_2$, which can be made by the reduction of the oxide $\Phi_2As{-}O{-}As\Phi_2$ with phosphorous acid, or by shaking diphenyl iododarsine Φ_2AsI with mercury,[724] forms white crystals melting at 135°, which are quickly oxidized in air.[725]

A remarkable compound is symmetrical diphenyl-di-iodo-diarsine



$(\Phi)(I)As{-}As(\Phi)(I)$, which can be made by the reduction of phenyl di-iodoarsine $\Phi \cdot AsI_2$ with phosphorous acid,[726] or by the addition of iodine to arsenobenzene $\Phi \cdot As{=}As \cdot \Phi$[727]; it forms yellow crystals melting at 176-7°;

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[723] F. F. Blicke, O. J. Weinkauff, and G. W. Hargreaves, *J.A.C.S.* 1930, **52**, 780.

[724] F. F. Blicke, R. A. Patelski, and L. D. Powers, ib. 1933, **55**, 1158.

[725] See further F. F. Blicke and C. L. Webster, ib. 1937, **59**, 534.

[726] A. Michaelis and C. Schulte, *Ber.* 1882, **15**, 1954.

[727] F. F. Blicke and F. D. Smith, *J.A.C.S.* 1930, **52**, 2937.

it has a normal molecular weight in benzene; it is very rapidly oxidized by air to phenyl arsonic acid $\Phi \cdot AsO \cdot (OH)_2$, and is converted by iodine into the di-iodide $\Phi \cdot AsI_2$.

Aryl Arseno-compounds $Ar \cdot As{=}As \cdot Ar$

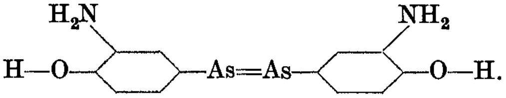
Alkyl compounds of this composition, such as $(CH_3 \cdot As)_n$, are evidently polymerized, and are dealt with later (p. 772).

The aromatic arseno-compounds, which include salvarsan, have been studied in great detail. They are formally analogous to the azo-compounds $Ar \cdot N{=}N \cdot Ar$, but they differ from them in colour, in solubility, in ease of oxidation and reduction, and in their reactions with sulphur, the halogens, etc. They are considerably (up to twice) associated in solution, which is natural in view of the instability of multiple links between arsenic atoms. The arseno-compounds can be made by reducing the aryl oxides $Ar \cdot As{=}O$ or the aryl arsonic acids $Ar \cdot AsO(OH)_2$ with phosphorous or hypophosphorous acid, with stannous chloride and hydrochloric acid, with sodium hydrosulphite, or with sodium amalgam in alcohol, and also by condensing the oxides $Ar \cdot As{=}O$ with the primary arsines $H_2As \cdot Ar$.

Unlike the azo-compounds they are colourless when pure and they then are not oxidized by air[728]; but in presence of traces of acid or of the chloride $Ar \cdot AsCl_2$ they readily go to the oxide $Ar \cdot As{=}O$. Those that have substituted aryls usually oxidize more easily.

Arsenobenzene $\Phi \cdot As{=}As \cdot \Phi$ is associated in most solvents; the association factor was found[729] to be in naphthalene by f. pt. 2·1; in benzene by b. pt. 1·5; in carbon disulphide by b. pt. 1·1. It is colourless and melts at 213°; at 255° it is converted into triphenyl arsine and arsenic.[736] Its dipole moment in benzene at 25° is practically zero (polarization difference 1·2 c.c.)[730]; so if in this solution it is largely monomeric, this must be the *trans* form, and any polymers present must have symmetrical structures.

A very large number of derivatives of arseno-benzene have been prepared, for therapeutic purposes. Salvarsan itself has the structure



It is got from $(NO_2)(OH)C_6H_3 \cdot AsO(OH)_2$, the corresponding arsonic acid, by first reducing the NO_2 to NH_2, and then reducing this product to salvarsan. It is a pale yellow powder which is insoluble in water, but dissolves in hydrochloric acid, taking up two molecules of the acid to form a salt, obviously through the two amino-groups. The normal dose for an adult is about 0·3 g. Many substitution products and modifications of this substance are now in use.

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[728] Id., ib. 2946.

[729] C. S. Palmer and A. B. Scott, ib. 1928, 50, 536.

[730] R. J. W. Le Fèvre and C. A. Parker, *J.C.S.* 1939, 677.

'*Arsenomethane*', $(CH_3\cdot As)_n$

This was first made by Auger in 1904[731] by treating sodium methylarsonate with hypophosphorous acid. It is a yellow oil, b. pt. 178°/15 mm.,[729] which forms yellow crystals melting at 12°[732]; it goes over readily at 100° and even more readily in the solid state into a brick-red or dark brown crystalline form, which can also be made[733] by the action of methyl arsenic oxide $CH_3\cdot AsO$ on methyl arsine $CH_3\cdot AsH_2$; this slowly melts at 180° or above to give the yellow liquid. The molecular weight is difficult to measure, as the work must be done in an indifferent gas, and the solubilities are small. The freezing-points and boiling-points in benzene and nitrobenzene[731,734] gave the association factor *n* as about 5. Vapour-density measurements (necessarily at low pressures) gave about 5 at 200° and 0·20 g./litre, and about 3 at 270° and 0·11 g./litre.[732] X-ray analysis of the yellow crystals showed a distance of 2·4 A, which must be that of the single As—As link (theory 2·42 A), but otherwise the results were obscure.[732] Electron diffraction measurements again showed the As—As distance of 2·42 A, but also one of 3·44 A, which suggests the grouping $\mathrm{As}\diagdown_{\mathrm{As}}\diagup\mathrm{As}$ with an angle of 90°.[732] Waser and Schomaker propose a 5-As ring, much crumpled (with angles of 90° instead of 108°); this agrees with all the observations, but some reason is needed to show why this 5-ring is more stable than a 4- or a 6-ring.

The corresponding propyl compound $(CH_3\cdot CH_2\cdot CH_2\cdot As)_n$ is also known[736]; it is a yellow oil, with b. pt. 177–9° at 1 mm.; the freezing-point in nitrobenzene indicates that $n = 5$.

Steinkopf *et al.*[734] also made the mixed ethyl phenyl compound of the composition $Et\Phi As_2$ by the action of ethyl arsenic oxide $Et\cdot As{=}O$ on phenyl arsine $\Phi\cdot AsH_2$. This compound (which is very easily oxidized) was found by measurement of the boiling-point in benzene to have the simple monomeric formula corresponding to $\Phi\cdot As{=}As\cdot C_2H_5$ (calcd. mol. wt. 256: found 259, 299·7).

ANTIMONY ALKYL AND ARYL COMPOUNDS

THE antimony alkyls were first made by Löwig and Schweizer in 1850, and the aryls by Michaelis in 1882. An important method of preparation of the aryls is from a diazo-salt and an antimonite.[737]

The antimony compounds in general resemble those of arsenic, and most of the same types are known, including the arseno-type in $Ar\cdot Sb{=}Sb\cdot Ar$, which have high trypanocidal properties. But compounds with hydrogen

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[731] V. Auger, *C.R.* 1904, 138, 1705.

[732] J. Waser and V. Schomaker, *J.A.C.S.* 1945, 67, 2014.

[733] W. Dehn, *Am. Chem. J.* 1905, 33, 120: 1908, 40, 108.

[734] W. Steinkopf, S. Schmidt, and P. Smie, *Ber.* 1926, 59, 1463.

[736] W. Steinkopf and H. Dudek, *Ber.* 1928, 61, 1906.

[737] H. Schmidt, *Ann.* 1920, 421, 174.

still attached to the antimony, such as $R \cdot SbH_2$ and R_2SbH_2 are unknown, and the cacodyl analogues cannot be made by the same reaction as with arsenic, but only by Paneth's method with free radicals.

The Sb—C link is somewhat weaker than As—C, as is shown in various ways. The antimony alkyls are harder to make; not only does the cacodyl reaction fail, but also in the aryl series the heating of the halides, etc., with antimonic acid. The aryl-antimony oxides $Ar \cdot SbO$ readily decompose on heating with separation of antimony trioxide, and finally, if triphenylstibine is heated with elementary arsenic, it gives antimony and triphenyl arsine.

The behaviour of the trialkyl stibines with acids is very peculiar. They do not take up the acid. as an amine does, but they behave like metals, forming the salt $Ar_3Sb[X]_2$ and evolving hydrogen, for example,

$$Et_3Sb + 2\,HCl = Et_3SbCl_2 + H_2.$$

(The bismuth alkyls do not react with acids in this way: see p. 781.)

The organic antimony compounds have the same violent action on the skin as those of arsenic.

Trialkyl Stibines

These were first prepared from the alkyl iodides and a potassium-antimony alloy; they can also be made by treating antimony trichloride with zinc alkyls or Grignard reagents. They can be purified by conversion into the dibromides Alk_3SbBr_2, which are then reduced by distillation with zinc.[738]

They are colourless liquids, stable to water and insoluble in it, but soluble in benzene. The lower members are volatile; trimethyl stibine boils at 78·5°, and has a Trouton constant of 22·1[739]; triethyl stibine boils at 158·5°. They are all very readily oxidized; the methyl and ethyl compounds are spontaneously inflammable in air, but the oxidation becomes less violent as the alkyl groups get larger. They add on halogens, sulphur, and selenium quantitatively.

Triaryl Stibines

These can be made with the Grignard reagents; from the aryl bromide, antimony trichloride, and sodium; by the reduction of their dihalide salts; or by heating the mono-aryl oxides:

$$3\,Ar \cdot SbO = Ar_3Sb + Sb_2O_3.$$

The triaryl stibines are stable substances by themselves. Triphenyl stibine melts at 48-50°, and the tri-*p*-tolyl at 127°. The mixed aryl-alkyl compounds are mostly liquid, such as $Et_2\Phi Sb$, b.pt. 128°/17 mm.

The aryl differ from the alkyl stibines (1) in being quite stable to air (but the mixed stibines are readily oxidizod by it); (2) in not reacting with hydrogen halide to form hydrogen and the dihalides (though the latter

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[738] G. T. Morgan and V. E. Yarsley, *J.C.S.* 1925, **127**, 184.

[739] E. J. Rosenbaum and C. R. Sandberg, *J.A.C.S.* 1940, **62**, 1622.

exist); (3) in not adding on alkyl halides: there are no $Ar_4Sb[X]$ compounds, though salts $Alk_3ArSb[X]$ exist. On the other hand, triaryl stibines will take up halogen and so reduce cupric, thallic, and ferric salts; they are oxidized by nitric acid to a nitrate or by sulphuric acid to a sulphate $Ar_3Sb[SO_4]$. Potassium permanganate oxidizes them in acid or alkaline solution and hydrogen peroxide in neutral solution. In hot alkaline solution hydrogen peroxide splits off one aryl group to give the stibinate $Ar_2SbO \cdot ONa$; mercuric chloride also splits off one aryl group, forming $Ar \cdot HgCl + Ar_2SbCl$.

Triaryl stibines will not combine with sulphur directly, any more than with oxygen, but the sulphides Ar_3SbS can be made in other ways.

The link of antimony to carbon in the aryl stibines is strong enough to allow of their being nitrated, and the nitro-compounds reduced, and sometimes even sulphonated, without decomposition.[740] Thus nitric acid at 40° not only oxidizes a triaryl stibine to the nitrate $Ar_3Sb(NO_3)_2$, but puts a *meta*-nitro group into each ring. The product can then be reduced to the triamine, diazotised, coupled to form azo-dyes, and so forth.

Though among the stibines the alkyl are less stable than the aryl, the *quaternary stibonium compounds* $R_4Sb[X]$ cannot carry more than one aryl group. This seems to be largely due to steric causes, for even among the purely aliphatic compounds the rate of conversion of the tertiary into the quaternary with alkyl iodides falls off rapidly as the molecular weight of the alkyl increases: thus methyl iodide combines with trimethyl stibine very rapidly; ethyl iodide with triethyl stibine very slowly in the cold, though rapidly at 100°; methyl iodide combines with triethyl stibine quicker than ethyl iodide; while amyl iodide has no action on triamyl stibine even in a sealed tube at 100°.

The tetra-alkyl hydroxides, which are formed from the halides with silver oxide, are bases as strong as their ammonium analogues.[741] They are easily soluble in water, but not soluble in ether (not even when they are oils, as all but the methyl compound are); tetramethyl stibonium hydroxide $[(CH_3)_4Sb]OH$ sublimes on heating with only partial decomposition.[742] They give a whole series of salts including halides (forming platini-halides), nitrates, sulphates, oxalates, and even bicarbonates.

The benzyl compounds are, as with arsenic, very unstable; tribenzyl stibine dichloride $(\Phi \cdot CH_2)_3SbCl_2$ and the oxide and sulphide are known, but all attempts to reduce them to the stibine $(\Phi \cdot CH_2)_3Sb$ only lead to the separation of metallic antimony.

The only known mixed quaternary compounds are those with only one aryl, which can be made by the action of alkyl iodide on the dialkyl-aryl stibine, a reaction which goes much quicker with methyl than with ethyl iodide.[743]

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[740] G. T. Morgan and F. M. G. Micklethwait, *J.C.S.* 1911, **99**, 2297.

[741] G. Bredig, *Z. physikal. Chem.* 1894, **13**, 301.

[742] H. Landolt, *J. prakt. Chem.* 1861, [i] **84**, 51.

[743] G. Grüttner and M. Wiernik, *Ber.* 1915, **48**, 1759.

Oxy-derivatives of Stibines

'Ethers', $R_2Sb—O—SbR_2$. The tetraphenyl compound can be made from the chloride Φ_2SbCl by treatment with sodium hydroxide: it melts at 78°.[744]

Oxides, $R\cdot Sb{=}O$. These are amorphous (no doubt polymerized) solids, which can be made by the reduction of stibonic acids $R\cdot SbO(OH)_2$.[745] They are usually insoluble in water; unlike antimony trioxide they are scarcely soluble in alkali, but they are far more basic than the trioxide, and readily form salts with all kinds of acids, even organic. Thus $\Phi\cdot SbO$ is a powder which sinters at 153-4° and is insoluble in water, alkalies, and most organic solvents. At 100° it begins to separate the trioxide, and forms the 'ether' $\Phi_2Sb—O—Sb\Phi_2$, which at 180-200° is converted into triphenyl stibine and more trioxide.

Stibonic acids, $R\cdot SbO(OH)_2$. These are formed by the oxidation of the oxides $Ar\cdot SbO$, for example by alkaline hydrogen peroxide; or much more easily by treating the diazonium salt with an antimonite[746]:

$$Ar\cdot N_2\cdot OH + NaH_2SbO_3 = Ar\cdot SbO(OH)(ONa) + N_2 + H_2O.$$

Copper can be used as a catalyst, but it is often unnecessary. These acids are usually amorphous, and do not melt without decomposition. It should be noticed how many of these compounds containing the $Sb{=}O$ or $Sb{\rightarrow}O$ group form amorphous, high-melting, or infusible solids; the group is presumably (except in the $R\cdot Sb{=}O$ compounds) a resonance hybrid of the two forms, but it evidently polymerizes very readily. The acids are insoluble in water, and are amphoteric like antimonic acid H_3SbO_4 itself; they dissolve in alkalies, and even in alkaline carbonates or ammonia, to give salts: those of the heavy metals are insoluble. The acids also dissolve in concentrated hydrochloric acid to form an acid with complex antimony anions, $H[Ar\cdot SbCl_5]$. They readily go into the colloidal state.

Di-alkyl or -aryl Stibinic Acids, $R_2SbO\cdot OH$

These can be made, for example, from the diaryl trichlorides Ar_2SbCl_3 by hydrolysis; by Schmidt's diazo-synthesis, starting with a mono-aryl oxide; or by splitting off an aryl group from a tertiary stibine with alkaline hydrogen peroxide.[747] They are highly polymerized and have a varying water content; they dissolve in alkalies, but though they will dissolve in hot dilute hydrochloric acid they are insoluble in the concentrated acid. The aryl groups can be nitrated (in the meta-position) by nitric acid without separation from the antimony.[748]

Pentavalent Oxides, $R_3Sb{=}O$

These compounds are peculiarly readily formed in the alkyl-antimony series; it is their formation which makes the trialkyl stibines spontaneously

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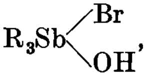
[744] H. Schmidt and F. Hoffmann, ib. 1926, **59**, 555.

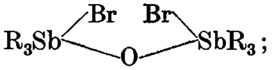
[745] H. Schmidt, *Ann.* 1920, **421**, 217.

[746] Id. ib. 174.

[747] Id., ib. 1922, **429**, 125.

[748] G. T. Morgan and F. M. G. Micklethwait, *J.C.S.* 1911, **99**, 2293.

inflammable; in the preparation of the oxides the reaction must be moderated by diluting either the oxygen or the stibine. The oxides are solids which are neutral to litmus,[749] they react with hydrogen bromide to give hydroxy-bromides  $R_3Sb\begin{smallmatrix}Br\\OH\end{smallmatrix}$, which lose water to form the derivatives



$$R_3Sb(Br)\text{—}O\text{—}(Br)SbR_3;$$

in water the hydroxy-halides are to some extent hydrolysed to $[R_3SbOH]OH$, which then loses water to give the oxide.[749]

Sulphides such as Et_3SbS, m. pt. 100°, are formed by the trialkyls (but not by the triaryls) by direct addition of sulphur. They are soluble in water, and seem to be ionized, as the solution precipitates metallic sulphides and gives hydrogen sulphide with acids (see p. 778).

Triaryl stibine oxides, $Ar_3Sb{=}O$. Unlike the trialkyl stibines, the triaryl are not oxidized by atmospheric oxygen, but are by alkaline hydrogen peroxide; the oxides can also be made by the action of alkali on the dichlorides Ar_3SbCl_2. In general behaviour they are similar to the trialkyl stibine oxides.

HALOGEN DERIVATIVES OF THE STIBINES

As with arsenic, there are two trivalent and four pentavalent types: (A) $R\cdot SbX_2$ and R_2SbX, and (B) $R\cdot SbX_4$, R_2SbX_3, R_3SbX_2, and finally, R_4SbX, the stibonium salts, which have already been discussed.

Trivalent. A. 1.. $R\cdot SbX_2$

These are easily made from the dialkyl trihalides:

$$R_2SbCl_3 = R\cdot SbCl_2 + R\cdot Cl,$$

a reaction which goes very readily, with the chloride on fusion, and with the iodide even at −15°. Examples of the products are $CH_3\cdot SbCl_2$, liquid, b. pt. 115-120°/60 mm.; $CH_3\cdot SbBr_2$, m. pt. 42°; $CH_3\cdot SbI_2$, m. pt. 110°. They are at once hydrolysed by water to the oxide $R\cdot SbO$.

The aryl compounds $Ar\cdot SbX_2$ are made in the same way, or by the reduction of stibonic acids. If a triaryl stibine is heated with antimony trichloride a mixture of the chlorides $Ar\cdot SbCl_2$ and Ar_2SbCl is obtained (Michaelis, 1882). In properties the aryl dichlorides resemble the alkyl compounds.

A. 2. $R_2Sb\cdot X$

These are easily made by heating the trialkyl dihalides in an atmosphere of carbon dioxide:

$$R_3SbCl_2 = R_2SbCl + R\cdot Cl.$$

They can also be got by treating the cacodyl compounds $R_2Sb—SbR_2$ with

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[749] A. Hantzsch and H. Hibbert, *Ber.* 1907, **40**, 1512.

halogen. $(CH_3)_2SbCl$ is a colourless oil, b.pt. 155-160°/760 mm., which catches fire in air at 40°; the bromide melts at 89° and boils at 175-80°. With potassium hydroxide they give the oxide $Alk_2Sb—O—SbAlk_2$, which is spontaneously inflammable in air even when cold. The aryl compounds are similar.

Pentavalent. B. 1. $R \cdot SbX_4$

The only known alkyl compound of this type is $CH_3 \cdot SbX_4$, which is presumably formed when halogen is added to $CH_3 \cdot SbCl_2$, but cannot be isolated.

The phenyl compound $\Phi \cdot SbCl_4$, obtained from phenyl antimony dichloride with chlorine, forms very hygroscopic crystals, m.pt. 60-5°, soluble in benzene, chloroform, and ether; it is hydrolysed by water. It is very unstable, and on keeping, changes slowly in the cold and quickly on heating, giving Φ_2SbCl and $SbCl_3$.

B. 2. R_2SbCl_3

In the alkyl series only the methyl compounds are known; they are made from the dimethyl halide and chlorine,[750] and, as we have seen, very easily lose methyl halide.

The aryl compounds seem to be more stable. Φ_2SbCl_3, H_2O crystallizes out from a solution of the stibinic acid in aqueous hydrochloric acid, or can be got in the anhydrous form by treating the monochloride with chlorine; it is crystalline, melts at 176°, and is soluble in alcohol and in dilute hydrochloric acid (probably forming complex ions), but insoluble in water.

B. 3. R_3SbCl_2

This group is exceptionally stable, and also appears to ionize to give the cations $[R_3Sb]^{++}$, or more probably $[R_3SbX]^+$. The compounds are formed with great readiness; the trialkyl stibines react violently with halogens, and the reaction must be modified by dilution. They can also be got directly from the Grignard reagents and antimony pentachloride; the strong tendency to form them is further shown by their production from the trialkyl (but not the triaryl) stibines and hydrogen chloride:

$$SbAlk_3 + 2\,HCl = Alk_3SbCl_2 + H_2.$$

In the same way the trialkyl stibines will reduce such salts as mercuric chloride, auric chloride, silver nitrate, etc., to the metals. The methyl compounds are crystalline; of the ethyl compounds the chloride and bromide are oils, but the nitrate is solid; the methyl chloride $(CH_3)_3SbCl_2$ is soluble in hot water, but as the alkyls become larger the solubility in water falls off. The methyl halides in the solid state are covalent. A. F. Wells[751] finds from X-ray analysis that all three halides $(CH_3)_3SbCl_2$,

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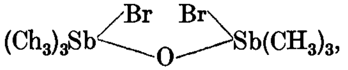
[750] G. T. Morgan and G. R. Davies, *Proc. R.S.* 1926, **110**, 523.

[751] A. F. Wells, *Z. Krist.* 1938, **99**, 367.

$(CH_3)_3SbBr_2$, and $(CH_3)_3SbI_2$ are isomorphous; they all have the structure of a trigonal bipyramid, the three methyl groups being symmetrically arranged round the equator, and the two halogen atoms being at the poles; the dipole moment of Φ_3SbCl_2 has been found to be zero.[752]

In water these halides are obviously ionized, but the indications are that the cation is not $[R_3Sb]^{++}$ but $[R_3SbX]^+$. This would be expected, since in the latter the antimony has an octet of valency electrons, but in the former only a sextet. The dibromide was shown by Hantzsch and Hibbert[749] to be very largely but not wholly hydrolysed in water, in concentrated solution less completely than its phosphorus and arsenic analogues. The oxide-bromide



which can be made from the dibromide and the oxide, shows by its conductivity that it is considerably but by no means completely hydrolysed in solution. In fact the dibromide behaves as the salt of a rather weak base $[Me_3SbBr]OH$, which is to some extent hydrolysed by water to $[Me_3SbOH]OH$.

The sulphide R_3SbS gives in water the reactions of the sulphide ion S^{--}, because it is hydrolysed through the intermediate product $[R_3SbSH]OH$ to $[R_3SbOH]OH$ and so to R_3SbO.

These bases form a series of other salts; thus we have Alk_3SbX_2 where $X_2 = Cl_2$, Br_2, I_2, (Br, OH), $(CNS)_2$, $(NO_3)_2$, SO_4, etc. The nitrate and sulphate in particular are very soluble in water, and much less in ether.

The aryl derivatives, mixed and pure, are similar; these are some melting-points:

Compound	X_2=Cl_2	Br_2	I_2
$(C_6H_5)_3SbX_2$	143°	216°	153°
(*o*-tolyl)$_3$SbX$_2$	178°	209°	174°
(*p*-tolyl)$_3$SbX$_2$	156°	233°	182°
(α-$C_{10}H_7)_3SbX_2$	260°	229°	. .
$(CH_3)_2C_6H_5SbX_2$	128°	112°	99°

B. 4. $[R_4Sb]X$

[These have already been discussed among the stibonium salts, p. 774.]

Sb—Sb COMPOUNDS

The alkyl distibines Alk_2Sb—$SbAlk_2$ are the analogues of the cacodyls; they cannot, however, be made in the same way, or by any of the usual methods, but it was shown by Paneth[753-4] that they can be made by the action of free methyl or ethyl groups (formed by heating lead tetra-alkyl)

[752] K. A. Jensen, *Z. anorg. Chem.* 1943, **250**, 257.

[753] F. Paneth, *Trans. Far. Soc.* 1934, **30**, 179.

[754] F. Paneth and H. Loleit, *J.C.S.* 1935, 366.

on a hot antimony mirror; if the mirror is cold, almost the only product is antimony trialkyl, since the distibine then remains on it exposed to the free alkyl, and is reduced. Paneth was thus able to make 20–30 mg. of the product per hour. Tetramethyl distibine or 'antimony cacodyl' $(CH_3)_2Sb—Sb(CH_3)_2$ is a bright red solid melting at 17·5° to a pale yellow liquid (a change of colour almost without parallel outside this group); the crystals become pale at −180° C., and their colour is darkest just before they melt; solutions in benzene or ether are also pale yellow; the extrapolated boiling-point is 190° C., and the heat of evaporation 12 k.cals. per mole., which for a b.pt. of 190° gives the high Trouton constant of 25·9. The ethyl compound is a pale yellow oil, which freezes at −61° to a pale orange solid. Both compounds are monomeric in benzene solution by the freezing-point, and both are easily oxidized, the methyl distibine being spontaneously inflammable. Bromine or chlorine convert them into the dialkyl antimony monohalides Alk_2SbX, and oxidation into the stibinic acids Alk·SbO·OH; in fact they behave like their arsenic analogues.

The aromatic distibines, $Ar_2Sb—SbAr_2$, can be made by a more ordinary method, by the reduction of the oxide, for example, $\Phi_2Sb—O—Sb\Phi_2$[755] or the iodide Φ_2SbI[756-7] with hypophosphorous acid: no corresponding bismuth compound could be made. $\Phi_2Sb—Sb\Phi_2$ forms pale yellow crystals, melting at 121-2°. It absorbs oxygen eagerly from the air, and like the arsenic compound forms the peroxide $\Phi_2Sb—O—O—Sb\Phi_2$; in the same way it at once reacts with iodine to give the iodide Φ_2SbI. These two reactions are strong evidence that there is some dissociation into free Φ_2Sb radicals.

'*Stibino-compounds*' Ar·Sb=Sb·Ar

No alkyl compounds of this type are known. The aryl compounds are made by reducing aryl stibonic acids or oxides with sodium hydrosulphite $Na_2S_2O_4$; they are dark brown powders insoluble in water, which oxidize in air so quickly that they sometimes catch fire; the diphenyl compound does this, and is oxidized explosively by nitric acid.[755] The solubilities of these compounds are little known, and their molecular weights have not been determined.

Mixed arseno-stibino-compounds of the type Ar·As=Sb·Ar can be made; they are similar to the stibino compounds, but rather more stable (see Krause and v. Grosse, p. 619).

BISMUTH ALKYL AND ARYL COMPOUNDS

THE bismuth alkyls resemble those of antimony in many ways; only the tertiary are known; they are usually spontaneously inflammable in air; they decompose above 150°, sometimes (like the lead and cadmium alkyls) with explosion. Water (in which they are insoluble) decomposes them only on long boiling, but they are soluble in all organic solvents.

[755] H. Schmidt, *Ann.* 1920, **421**, 235.

[756] F. F. Blicke, U. O. Oakdale, and F. D. Smith, *J.A.C.S.* 1931, **53**, 1025.

[757] F. F. Blicke and U. O. Oakdale, ib. 1933, **55**, 1198.

The bismuth aryls are solid, much more stable, and not oxidized by air.

Compounds of pentavalent bismuth are unknown in the alkyl series, where chlorine and bromine split the trialkyls to the dialkyl bismuth halides Alk_2BiX and alkyl halide. Methyl iodide has no action on bismuth trialkyls at 150°, while at 200° it splits off alkyls to form $Alk \cdot BiI_2 + 2\ Alk \cdot CH_3$.

The trialkyl bismuthines are best made by the action of the Grignard reagent on bismuth trihalides. A remarkable synthesis of trimethyl bismuthine is by the action of aluminium carbide Al_4C_3 on a hydrochloric acid solution of bismuth trichloride[758]:

$$BiCl_3 + Al_4C_3 + 9\ HCl = Bi(CH_3)_3 + 4\ AlCl_3.$$

The alkyl groups can be removed from these bismuthines in the following ways:

1. By hydrochloric acid, giving $BiCl_3 +$ paraffins $Alk \cdot H$.
2. By boiling in alcoholic solution with sulphur, giving bismuth sulphide Bi_2S_3; the trialkyl phosphines, arsines, and stibines do not react in this way with sulphur, but form the trialkyl-sulphides $R_3A \rightarrow S$. The same change to the sulphide and the hydrocarbon occurs on standing in the cold with an ethereal solution of hydrogen sulphide.
3. By the action of chlorine or bromine, giving the dialkyl halide $Alk_2Bi \cdot X$ and the alkyl halide $Alk \cdot X$.
4. By treatment with methyl iodide at 200° as mentioned above. This is a very remarkable reaction: the bismuthine behaves like a Grignard reagent or zinc alkyl:

$$(CH_3)_3Bi + 2\ CH_3 \cdot I = CH_3 \cdot BiI_2 + 2\ CH_3 \cdot CH_3.$$

As an example, $(CH_3)_3Bi$ boils at 110° at 760 mm.; it is colourless, fumes in air, and is insoluble in water.

R. A. Mortensen and P. A. Leighton[759] find that if lead tetramethyl containing some radioactive lead (RaD) is left to stand for a month in absence of air, the vapour above it contains both RaE (an isotope of bismuth) and RaF (of polonium); they conclude that volatile compounds of these two elements are present, which must be the methides, and that the lead atoms have undergone their two radioactive changes (both β-ray) while keeping first three and then two methyl groups attached to them:

$$^{210}_{82}PbMe_4 \qquad ^{210}_{83}BiMe_3 \qquad ^{210}_{84}PoMe_2$$

This seems very remarkable.

Bismuth triethyl was the first bismuth alkyl made (Löwig, 1850); at 150° it decomposes with explosion. Other alkyl compounds are known, including a ring-compound $(CH_2)_5Bi \cdot Et$, b.pt. 110°/20 mm.

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[758] **S. Hilpert and M. Ditmar, *Ber.* 1913, 46, 3741.**

[759] **R. A. Mortensen and P. A. Leighton, *J.A.C.S.* 1934, 56, 2397.**

Bismuth aryls are usually made from the aryl halide and a sodium-bismuth alloy, or by treating bismuth trihalide with the Grignard reagent or with mercury aryl. Gilman has shown[760] that diazonium halides form double salts $(Ar\cdot N_2)_3[BiCl_6]$ with bismuth trichloride, which in acetone solution react with copper to give bismuth triaryl.

Triphenyl bismuthine Φ_3Bi is colourless, stable in air, and dimorphic, with the melting-points 75° and 78°. Its dipole moment is very small, being the last member of the decreasing series[761]:

$$\Phi_3P\ 1{\cdot}45;\ \Phi_3As\ 1{\cdot}07;\ \Phi_3Sb\ 0{\cdot}57;\ \Phi_3Bi\ ca.\ 0.$$

This presumably means not that the valencies of the central atom lie in a plane, but that the moment of the Bi—C link is very small. Triphenyl bismuthine will volatilize undecomposed in a vacuum.

The link of carbon to bismuth in these aryl compounds is weaker than its link to arsenic or antimony. Chlorine and bromine will indeed add on to form dihalides, but iodine only does so at $-80°$, and the product decomposes at the ordinary temperature to give the mono- and di-phenyl bismuth iodides $\Phi\cdot BiI_2$ and $\Phi_2Bi\cdot I$. Bismuth triphenyl is also completely decomposed by warming with concentrated hydrochloric acid, with the production of bismuth trichloride (very different from the behaviour of antimony triphenyl), or by sulphuric acid. On the other hand, the phenyl groups can be nitrated with nitric acid without separation from the bismuth, the di-nitrate $(NO_2\cdot C_6H_4)_3Bi(NO_3)_2$ being formed.

Bismuth triphenyl is an active poison for spirochetes and trypanosomes.

Oxy-compounds of Bismuthines

The oxide $CH_3\cdot BiO$, got by treating the dibromide with ammonia,[762] is a white powder easily set on fire, which is insoluble in water but readily soluble in sodium hydroxide, so that it is amphoteric.

The bismuthonic and bismuthinic acids, which are Bi^V compounds, are not known.

Halides

$R\cdot BiX_2$. A few aryl compounds of this type are known; they are yellow or orange solids. If phenyl bismuth dibromide $\Phi\cdot BiBr_2$ is heated in toluene with sodium, it gives bismuth triphenyl, metallic bismuth, and sodium bromide.[763] The diazonium double salt $(Ar\cdot N_2)[BiCl_4]$ decomposes[764] in presence of copper bronze to give the mono- and di-aryl chlorides $Ar\cdot BiCl_2$ and Ar_2BiCl, and some bismuth triphenyl.

R_2BiX. The alkyl compounds are spontaneously inflammable in the air if they are warmed. The aryl compounds Ar_2BiX are formed at once in the cold from bismuth triaryl and bismuth trihalide in ether or benzene.

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[760] H. Gilman and A. C. Svigoon, ib. 1939, **61**, 3586.

[761] E. Bergmann and W. Schütz, *Z. physikal. Chem.* 1932, B **19**, 401.

[762] A. Marquardt, *Ber.* 1887, **20**, 1517.

[763] F. Challenger, *J.C.S.* 1916, **109**, 250.

[764] H. Gilman and H. L. Yablunky, *J.A.C.S.* 1941, **63**, 949.

Attempts to convert them into 'cacodyls' have so far failed.[765] [These have probably been got by means of the free alkyls.]

If sodium is added to diphenyl bismuth bromide in liquid ammonia,[766] the solution first turns green (possibly from the formation of a diphenyl bismuth radical), and then dark red, evidently from the formation of the sodium compound $\Phi_2Bi\cdot Na$; this compound was not isolated, but its formula is proved by its reacting with α-iodo-naphthalene to give diphenyl naphthyl bismuthine, $\Phi_2Bi\cdot C_{10}H_7$. On keeping, the diphenyl bismuth sodium decomposes of itself to give triphenyl bismuthine and metallic bismuth. All the other alkali metals behave in exactly the same way.[766]

Pentavalent Bismuth Compounds

These are rare; they are formed by the triaryls, but not by the trialkyls; the triaryls can take up two halogen atoms, and various other groups as well, all of the (only known pentavalent) type Ar_3BiX_2 or $Ar_3Bi{\rightarrow}O$. All attempts to make R_4BiX compounds have failed. Even the triaryl-dihalides are unstable: the dibromide loses $Ar\cdot Br$ at about 100°, and the iodide $Ar\cdot I$ at the ordinary temperature.

The known compounds of the type Ar_3BiX_2 are numerous; the chloride and bromide are made by direct addition, and the other pentavalent compounds from them. These are some examples:

Φ_3BiF_2: made[767] from the dichloride and potassium fluoride in aqueous alcohol; m. pt. 158-9°: easily soluble in ether and chloroform, insoluble in ligroin. It loses fluorobenzene at 190-200°.

Φ_3BiCl_2: m. pt. 141°; soluble in alcohol, benzene, and chloroform; it loses chlorobenzene when heated to 150°, or slowly in boiling benzene.

Φ_3BiBr_2: melts with some decomposition at 123-4° if quickly heated. In 20 minutes at 100° it is converted into the diphenyl bromide Φ_2BiBr and bromobenzene.

Φ_3BiI_2: this is formed[768] when iodine acts on triphenyl bismuthine in ligroin at $-78°$, but it decomposes below 0° into $\Phi_2BiI+\Phi\cdot I$. The cyanide and thiocyanate are equally unstable and impossible to isolate. But a cyanate (m. pt. 129°), nitrate, sulphate (very insoluble and not melting up to 280°), acetate (m. pt. 162°), and benzoate (m. pt. 173°) are known (for refs. see Krause and v. Grosse, p. 648), as well as a carbonate Φ_3BiCO_3,[769] which can be made by treating the bromide with potassium hydroxide solution and passing in carbon dioxide. It melts at 136°, and is easily soluble in benzene and chloroform.

The free base $\Phi_3Bi(OH)_2$ is made[770] by treating the chloride with silver oxide; it is an amorphous powder which is decomposed by solvents or by

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[765] F. F. Blicke, U. O. Oakdale, and F. D. Smith, *J.A.C.S.* 1931, **53**, 1025.

[766] H. Gilman and H. L. Yablunky, ib. 1941, **63**, 212.

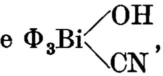
[767] F. Challenger and J. F. Wilkinson, *J.C.S.* 1922, **121**, 91.

[768] J. F. Wilkinson and F. Challenger, ib. 1924, **125**, 854.

[769] F. Challenger and A. E. Goddard, ib. 1920, **117**, 762.

[770] F. Challenger and O. V. Richards, ib. 1934, **405**.

heating at 100°, giving amongst other things triphenyl bismuthine and bismuth hydroxide $Bi(OH)_3$; it is slightly soluble in water, and reacts with ethyl alcohol to give triphenyl bismuthine and acetaldehyde. With potassium cyanide it gives the hydroxy-cyanide



$\Phi_3Bi\begin{smallmatrix}OH\\CN\end{smallmatrix}$, moderately soluble in benzene. Its whole behaviour shows that the hydroxide is a covalent compound and not a true base.

Bi—Bi *Compounds* (‘*Bismuth cacodyls*’)

These have not been isolated, but Paneth and Loleit[754] showed that while the attack of free radicals on a cold bismuth mirror only gave Alk_3Bi (with antimony this would give some cacodyl), if the mirror was heated the methyl and the ethyl dibismuthines could be formed. The methyl compound $(CH_3)_2Bi—Bi(CH_3)_2$ is a violet-red solid, melting below room temperature to a yellow oil, which at once changes to a black solid. With ethyl radicals, the black solid was formed at once. There was not enough of the product to analyse, but the highly characteristic loss of colour on fusion is sufficient to show that the cacodyl was formed.

Comparison of the Carbon Compounds

The following are some of the more important changes in the properties of these compounds as we go along the series from the lighter 5th Group elements to the heavier (R = alkyl or aryl).

With nitrogen the covalency cannot exceed 4; with bismuth the stability of the inert-pair form is so great that the pentavalent compounds are confined to the types $Ar_3Bi(hal)_2$ and Ar_3BiO. The heats of the linkages A—A,* A—H, and A—C all fall, but A—H the quickest. A—H is weaker than A—C for all except nitrogen, and hence alkyls which have some unreplaced hydrogen on A become increasingly unstable, and are unknown with Sb or Bi; as A—C also gets weaker, the trialkyl derivatives become less stable. The alkyls are in every case less stable than the corresponding aryls, and the benzyls for some reason the least stable of all.

The basicity and the donor power of the R_3A compounds also diminish. Their behaviour with the halide acids like HCl is peculiar. $NAlk_3$, $PAlk_3$, and $AsAlk_3$ form salts $[A(Alk)_3H]Cl$ with diminishing avidity. $SbAlk_3$ (not $SbAr_3$) reduces the hydride, the Sb becoming pentavalent:

$$SbAlk_3 + 2\,HCl = Alk_3SbCl_2 + H_2.$$

$BiAlk_3$ behaves like $ZnAlk_2$ and forms the binary chloride and the paraffin:

$$BiAlk_3 + 3\,HCl = BiCl_3 + 3\,AlkH.$$

The number of aryl groups that can occur in the onium cations $[R_4A]^+$ is oppositely affected along the series by the weakening of the A—C link and the decrease of the crowding round A as A grows larger; the observed numbers are N 1 (though NAr_3 occurs); P 3; As 4; Sb 1 (Bi 0).

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* Except that of N—N, which is less than that of P—P; compare the similar behaviour of the halogens.

A—A compounds are formed by all five elements, though they have not been isolated with Bi. $H_2A—AH_2$ and $(hal)_2A—A(hal)_2$ are formed by nitrogen and phosphorus only. The tetra-alkyls $Alk_2A—AAlk_2$ are stable with N, of doubtful existence with P, readily formed by As, and less readily by Sb and Bi, those of Bi being very unstable. $Ar_2A—AAr_2$ compounds are formed by all but Bi, and have an apparently increasing tendency to dissociate into free radicals Ar_2A.

The A=A compounds are again formed by all but bismuth, but the As and Sb compounds relieve the strain of the A=A double link by polymerization.

[*Nitrides*

No nitrides of arsenic antimony or bismuth seem to be known.]

OXIDES AND OXY-ACIDS

Arsenic Trioxide, As_4O_6

THREE forms of this have been described (see ref. [771]) with transition points at −13° and +200°; recent work suggests[772] that there are only two, the second (monoclinic) being stable from −13° to the m.pt. 315°; the b.pt. is 465°. X-ray examination shows[773] that the molecules in the ordinary solid have the same structure as those of P_4O_6 (p. 737), the 4 As atoms being at the points of a tetrahedron, and each pair joined through an oxygen; the As—O distance is 1·80 A (theory 1·87). Electron diffraction measurements[774-5] of the vapour confirm these results, and show that the angles are O—As—O 100±5°, As—O—As 126±3° (similar differences were found with P_4O_6). Sb_4O_6 has the same structure. The vapour, which has neither smell nor taste (the lethal dose for a man is 0·1 g.), is As_4O_6 up to 800°, and becomes As_2O_3 at 1,800°. The molecular weight in nitrobenzene is by the freezing-point that of As_4O_6. It dissolves in water up to 2 per cent. at 20°, becoming hydrated in the process.

The hydrate $As(OH)_3$ behaves as a weak acid, with a dissociation constant of about 8×10^{-10} at 25° (determined with a glass electrode).[776] It also behaves in some ways like a weak base, but it is doubtful whether it really gives $[As(OH)_2]^+$ ions, and practically certain that, unlike antimony, it forms no As^{+++} ions. The 'basic' properties should rather be called alcoholic: they consist in the formation of covalent derivatives such as the halides (formed reversibly from the hydroxide and a halogen acid) and a triacetate $As(O \cdot CO \cdot CH_3)_2$ (m.pt. 82°, b.pt. 165–70°), which, like boron triacetate, behaves as a mixed anhydride, being hydrolysed by moist air to arsenious and acetic acids.

[771] A. Smits and E. Beljaars, *Proc. K. Akad. Amst.* 1931, **34**, 1141, 1318.

[772] J. H. Schulman and W. C. Schumb, *J.A.C.S.* 1943, **65**, 878.

[773] K. E. Almin and A. E. Westgren, *Arkiv. Kemi, Min., Geol.* 1942, **15** B, no. 22.

[774] L. R. Maxwell, S. B. Hendricks, and L. S. Deming, *J. Chem. Phys.* 1937, **5**, 626.

[775] G. C. Hampson and A. J. Stosick, *J.A.C.S.* 1938, **60**, 1814.

[776] F. Ishikawa and I. Aoki, *Bull. Inst. Phys. Chem. Res. Japan*, 1940, **19**, 136.

In the same way it forms a series of esters $As(OR)_3$, which can be made by treating the alcohols with $AsCl_3$, or even, with the higher alcohols,[777] by heating the alcohol with As_2O_3 in presence of a hydrocarbon which removes the water formed with its vapour. Unlike phosphorus, it gives no ester-acids. The esters resemble those of the so-called metallic acids, such as $B(OR)_3$ and $Al(OR)_3$—and also the nitrous esters—in being at once hydrolysed by water.

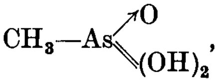
Boiling-points of Arsenious Esters $As(OR)_3$

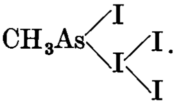
R=	CH_3	C_2H_5	C_3H_7	C_4H_9	*iso*-C_5H_{11}
B. pt.	129°	166°	217°	263°	288°

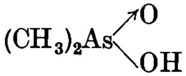
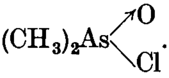
Arsenious acid is a true but very weak acid, and forms a series of salts, the arsenites. The alkaline salts are very soluble in water, those of the alkaline earths less so: the heavy metal salts are insoluble. Most of the salts are not derived from the ortho but from the meta acid $HAsO_2$, for example, Scheele's Green, $Cu[AsO_2]_2$.

The arsenite ion (the alkaline solution) is readily oxidized to the pentavalent arsen*ic* state by air or by iodine; but (unlike phosphorous acid) the free acid is not.

Arsenious acid, like phosphorous acid, is tautomeric. With methyl iodide the silver salt gives the true ester $As(OCH_3)_3$, while the sodium salt gives the ester of the isomeric acid with one methyl attached to the arsenic,


$\mathrm{CH_3{-}As}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow (\mathrm{OH})_2}$, which is a strong acid. On treatment with hydriodic acid this has all its oxygen replaced by iodine, forming a compound of the composition $CH_3 \cdot AsI_4$, which may possibly be a methyl substitution product of the non-existent AsI_5: but these poly-iodine compounds are always uncertain of structure, as they may be poly-iodides, such as


$\mathrm{CH_3As}\genfrac{}{}{0pt}{}{/\mathrm{I}}{\backslash \mathrm{I}\genfrac{}{}{0pt}{}{/\mathrm{I}}{\backslash \mathrm{I}}}$.

The corresponding dimethyl compound  $\mathrm{(CH_3)_2As}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{OH}}$ is cacodylic acid, a monobasic acid, easily soluble in water; $k = 6{\cdot}4 \times 10^{-7}$ (not much stronger than H_2S 1·3 or carbonic 3·2). It behaves as an amphoteric substance, diminishing the conductivity of hydrochloric acid; but this must be due[778] to its reacting with HCl to give a covalent chloride, as  $\mathrm{(CH_3)_2As}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{Cl}}$. (As—Cl is normally less hydrolysed than P—Cl.)

On treatment with PCl_5 cacodylic acid, like the monomethyl compound, has all its oxygen replaced by chlorine, giving $(CH_3)_2AsCl_3$. This contains

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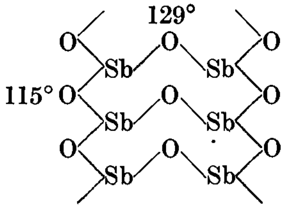
[777] P. Pascal and A. Dupire, *C.R.* 1932, **195**, 14.

[778] A. Hantzsch, *Ber.* 1904, **37**, 1076, 2705.

true pentacovalent arsenic, and accordingly is very unstable, and breaks up below 50° to form methyl chloride and CH_3AsCl_2. The higher valency seems to be always less unstable in these mixed halides: almost the only pentacovalent bismuth compounds are the mixed aryl halides $Ar_3Bi(hal)_2$.

Antimony Trioxide and the Antimonites

Antimony 'trioxide' Sb_4O_6 melts at 548° and boils at a higher temperature. The vapour density at 1,560° corresponds to Sb_4O_6. The solid is dimorphic, with a cubic form A below 570° and an orthorhombic B above.[779] These results were confirmed by Buerger and Hendricks,[780-1] who showed that the A form is made up of Sb_4O_6 groups of the same structure as P_4O_6 or As_4O_6, but that the structure of B is quite different, and consists of chains of this kind, with the angles O—Sb—O 79°, 92°, 100°; Sb—O—Sb 115° and 129°.



It is insoluble in water and also in dilute acids, but it is converted by strong HCl into the trichloride.

It is less acidic and more basic than As_4O_6. As a true base $Sb'''[OH]_3$ it forms a sulphate and a nitrate, but only with concentrated acids, and these salts are readily hydrolysed by water with separation of the basic salt or the trioxide. Most of its apparently basic properties are due to the formation of covalent compounds like the halides. Its acidic character is that of the anhydride of a very weak acid, $Sb(OH)_3$. The free acid can be obtained in a voluminous and apparently colloidal hydrated form, giving definite hydrates. It loses water slowly even on standing under water, to form Sb_4O_6, a sign of the more metallic character of the element.

The antimonites are very highly hydrolysed in water. The only alkaline salts yet isolated are those of sodium, which belong to the meta series ($NaSbO_2$, 3 H_2O and $NaSbO_2$, 2 H_2O), and are very slightly soluble in water. The potassium salts are much more soluble, as is usual with a weak acid. They precipitate the antimonites of the heavy metals. The solution reduces silver nitrate to metallic silver, and chromates to chromites.

The trialkyl antimonites $Sb(OAlk)_3$ (b.pts. at 30 mm.: methyl 65°, ethyl 115–20°, propyl 143°, *n*-amyl 170°) like the arsenites are formed by boiling the trioxide with the required alcohol, and removing the water as it is formed. Like the arsenites and nitrites they are hydrolysed at once by water.

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[779] R. M. Bozorth, *J.A.C.S.* 1923, **45**, 1621.

[780] M. J. Buerger and S. B. Hendricks, *J. Chem. Phys.* 1937, **5**, 600.

[781] Id., *Z. Krist.* 1937, **98**, 1.

Bismuth Trioxide

Bismuth trioxide (molecular weight unknown) is trimorphic; the liquid solidifies at 817° to a monoclinic α-form, which changes at 710° to a tetragonal β- with a large evolution of heat; there is a third cubic metastable form.[782-3] It sublimes at 1,010°, and is not decomposed at 1,750°. The solid conducts electricity, and more so at higher temperatures (unlike a metal), the conductivity being partly electrolytic, like that of the metallic oxide in a Nernst filament.

The hydroxide $Bi(OH)_3$ can be shown by the X-ray diagram to be crystalline, but no definite compound of Bi_2O_3 and water can be isolated.[784] It has no acidic character whatever and is quite insoluble in alkalies: in this it differs from all the other trioxides of the subgroup. It behaves as a weak metallic hydroxide, giving a whole series of salts such as thiocyanate, sulphate (isomorphous with the sulphates of yttrium lanthanum, and praseodymium), nitrate, perchlorate, etc. All these are readily hydrolysed to the corresponding bismuthyl salts $[Bi{=}O]X$.

PENTOXIDES AND -ATES

Arsenic Pentoxide and the Arsenates

Arsenic pentoxide, unlike the phosphorus compound, cannot be made by heating the element or the trioxide in air, but only by oxidation with a strong oxidizing agent such as nitric acid. It is amorphous, and its molecular weight is unknown. Its vapour is wholly dissociated into the trioxide and oxygen. Like phosphorus pentoxide it is very soluble in water (sol^y over 230/20°); the hydrates which separate from this solution are largely colloidal* and difficult to identify[785-7]; a solid of composition 3 H_3AsO_4, H_2O has been found to lose water below 100°, giving successively H_3AsO_4, $H_4As_2O_7$, and at 200° $HAsO_3$, which at a still higher temperature loses all its water to give the pentoxide. Its first dissociation constant is about half that of phosphoric acid, but the rest are much greater than those of the latter:

Classical Dissociation Constants at 20°

K	H_3PO_4	H_3AsO_4	*Ratio* As/P
K_1	11×10^{-3}	5×10^{-3}	1/2·2
K_2	$5{\cdot}6\times10^{-8}$	4×10^{-5}	700
K_3	$1{\cdot}2\times10^{-12}$	6×10^{-10}	500

All forms of the acid give the ortho modification on solution in water, and apparently (unlike phosphoric acid) at once. There is, however, some evidence that in concentrated solution the meta- and pyro-acids are

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* Colloid formation by the higher oxy-acids begins in Gp. V with As, but in IV with Si.

[782] W. C. Schumb and E. S. Rittner, *J.A.C.S.* 1943, 65, 1055.
[783] B. Aurivillius and L. G. Sillén, *Nature*, 1945, 155, 305.
[784] G. F. Hüttig, T. Tsuji, and B. Steiner, *Z. anorg. Chem.* 1931, 200, 74.

present[785-6]; but their strong tendency to go over into a colloidal form makes the investigation difficult.[787] The arsenates closely resemble the phosphates in composition and solubility. The crystal structures of Ag_3AsO_4 and KH_2AsO_4 have been determined[788]; in the silver salt the anion is a regular tetrahedron, with the As—O distance 1·75 (theory As—O 1·87, As═O 1·66 A); in KH_2AsO_4 the tetrahedron is slightly distorted, with the O—As—O angles 104° and 113°. The O—H··O bond is 2·54 A long.

Arsenic acid oxidizes sulphurous to sulphuric acid, and with concentrated hydrochloric acid gives chlorine and arsenic trichloride, presumably, like cacodylic acid $(CH_3)_2AsO \cdot OH$, first forming the unstable pentachloride. It is used as an oxidizing agent in organic chemistry.

The esters are known, such as $AsO(OCH_3)_3$, b.pt. 214° and $AsO(OC_2H_5)_3$, b.pt. 237°, but as with arsenious acid no ester-acids, such as $AsO(OCH_3)_2OH$.

Antimony Pentoxide and the Antimonates

Antimony pentoxide, like the arsenic compound, cannot be made by the direct action of oxygen, but is formed by treating the metal with concentrated nitric acid; the hydrated oxide is then dehydrated by heating, but great care is needed, as it begins to lose oxygen before the water is all removed. On heating the dry oxide, it loses oxygen, forming first an oxide Sb_2O_3, 2 Sb_2O_5, and then at 780° the tetroxide Sb_2O_4[789]: this reaction is extremely slow; at 400° Sb_2O_5 continues to give off oxygen for two months before the pressure becomes constant.

Sb_2O_5 is only very slightly soluble in water, but the solution reddens litmus.

Antimonic acid H_3SbO_4 can be got by the hydrolysis of $SbCl_5$, best in presence of chlorine to prevent reduction. It is colloidal: it dissolves both in acids and in alkalies.

The ordinary salts are of the type of $MSbO_3$, $x H_2O$, and are usually regarded as metasalts. Pauling[790] has, however, pointed out that on the ground of the atomic sizes we should expect the salts to have a structure corresponding to that of the tellurates and periodates, $M[Sb(OH)_6]$, and that they usually contain enough water to allow of this. This has been confirmed by Beintema,[791-2] who showed by X-ray analysis that the 'meta' salt $Ba(SbO_3)_2, 8H_2O$ is really $Ba[Sb(OH)_6]_2, 2H_2O$, and the pyroantimonate $Na_2H_2Sb_2O_7, 5H_2O$ is $Na[Sb(OH)_6]$, the antimony atom in the anions of both being surrounded octahedrally by 6 OH groups.[790]

Potassium pyroantimonate, $K[Sb(OH)_6], 0{\cdot}5\, H_2O$ is a reagent for sodium.

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[785] A. Rosenheim and H. Antelmann, *Z. anorg. Chem.* 1930, **187**, 385.

[786] A. Rosenheim, ib. **193**, 73.

[787] A. Simon and E. Thaler, ib. 1927, **161**, 143.

[788] L. Helmholz and R. Levine, *J.A.C.S.* 1942, **64**, 354.

[789] A. Simon and E. Thaler, *Z. anorg. Chem.* 1927, **162**, 253.

[790] L. Pauling, *J.A.C.S.* 1933, **55**, 1895.

[791] J. Beintema, *Proc. K. Akad. Amst.* 1935, **38**, 1015.

[792] Id., ib. 1936, **39**, 652.

The potassium salt is slightly soluble in cold water and much more in hot: the sodium salt is much less soluble: the same difference was noticed in the antimonites.

Bismuth Pentoxide and the Bismuthates

Bismuth trioxide can be made in various ways to take up more oxygen: by the action of atmospheric air in presence of alkalies, of chlorine or NaOCl, of electrolytic chlorine, or of fused KNO_3. The claim that an oxide Bi_2O_4 can be made in this way seems to be untrue. It would appear, however, that the pentoxide Bi_2O_5, and a series of alkaline bismuthates derived from it, can exist, although they are almost impossible to purify.

Ruff[793] passed chlorine into Bi_2O_3 suspended in 40 per cent. potash, dissolved the product in concentrated HF, and on adding NaOH at 0° obtained a bismuthate. On treatment with acids this gave a red-brown precipitate of nearly pure Bi_2O_5. It is, however, very unstable, and after drying at 100° half the extra oxygen was gone. See further, references[794-6].

TETROXIDES AND THEIR DERIVATIVES

Arsenic and antimony (but not bismuth) form oxides of the composition MO_2, usually written M_2O_4. They are probably mixed tri- and pentavalent derivatives, and should be written as As_4O_8, Sb_4O_8. This view is supported by the crystal structure[797] of Sb_4O_8, which is like that of stibiotantalite $SbTaO_4$, and contains both Sb^{iii} and Sb^{v} atoms.

The antimony compound is of remarkable stability, and in fact is the most stable oxide below 900°. It is the ultimate product of heating in air the element, the trioxide, the trisulphide, or the pentoxide above 300°. Above 900° it loses oxygen and forms the trioxide.

It is white (yellow when hot), non-volatile, and infusible, insoluble in water but reddening blue litmus, and very resistant to acids. It behaves in many ways like a mixture of the tri- and pentoxides, giving an antimonate and an antimonite on treatment with aqueous alkalies. Fusion with alkali converts it into a so-called hypoantimonate $M_2Sb_2O_5$, which may possibly be an antimonyl antimonate $M_2(Sb{=}O)[SbO_4]$.

SULPHIDES AND THIOACIDS

Many of these sulphides are of great stability; they include several of the more important ores of these elements.

ARSENIC COMPOUNDS

As_4S_4 is the red mineral realgar; it melts at 320° and boils at 565°. The vapour density corresponds to As_4S_4 at 550°, and to As_2S_2 at about

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[793] O. Ruff, M. Knoch, and J. Zedner, *Z. anorg. Chem.* 1908, **57**, 220.

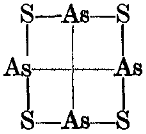
[794] A. Gutbier and R. Bünz, *J.C.S. Abstr.* 1906, ii. 174, 234, 551, 678.

[795] R. R. Worley and P. W. Robertson, *J.C.S.* 1920, **117**, 64.

[796] M. Haïssinsky and A. Sanielevici, *J. Chim. Phys.* 1939, **36**, 54.

[797] K. Dihlström and A. Westgren, *Z. anorg. Chem.* 1937, **235**, 153.

1,000°[798]; the electron diffraction of the vapour indicates a structure which may be written



with 2 As atoms above and 2 below the plane of the 4 S; the distances are As—S 2·23, As—As 2·49[799] (theory 2·25, 2·42). It is violently oxidized by heating with potassium nitrate ('Greek fire'); when warmed with alkaline hydroxides or sulphides it gives thioarsenites $M_3[AsS_3]$ with separation of elementary arsenic.

As_4S_6 is orpiment (auri pigmentum); yellow crystals, melting at 310° to a red liquid of b.pt. 707°. Electron diffraction shows the vapour to consist of As_4S_6 molecules, with a structure like that of As_4O_6.[800] It does not dissolve in acids even when concentrated, but does so readily in alkaline hydroxides or sulphides, giving thioarsenites. A colloidal form is easily got, for example, by treating a neutral As_2O_3 solution with hydrogen sulphide.

As_2S_5 (As_4S_{10}) can be made by fusing the elements together, or by treating As_2O_5 with hydrogen sulphide in fairly concentrated hydrochloric acid[801]; it is pale yellow and will sublime, but probably with decomposition to the trisulphide and sulphur.

Thioarsenites $M_3[AsS_3]$ are formed from the trisulphide, which they precipitate on treatment with hydrochloric acid. Their esters $As(S \cdot Ar)_3$ can be made[802] by warming arsenic trichloride and sodium thiophenate in alcohol. They are only slowly attacked by water even on boiling.

Thioarsenates $M_3[AsS_4]$ and $S \cdot As(S.R.)_3$ can be made from the pentasulphide, or by the action of sulphur on the thioarsenite esters.[802]

ANTIMONY COMPOUNDS

The trisulphide Sb_2S_3 can be made from the elements or by the action of hydrogen sulphide on an antimonite. It is the black mineral stibnite, the most important ore of antimony. It is precipitated from water as an orange usually colloidal solid, which goes over to the stable black form on heating. For the crystal structure see Wells.[803] It is soluble with decomposition in concentrated but not in dilute hydrochloric acid; it dissolves readily in alkaline hydroxides and sulphides.

Sb_2S_5 is made from its elements, or by treating a thioantimonate with acid; it is orange-yellow and insoluble in water, but decomposed by hydrochloric acid to antimony trichloride, hydrogen sulphide, and sulphur. It is used to vulcanize rubber, which is then red.

[798] E. C. Szarvasy and C. Messinger, *Ber.* 1897, **30**, 1345.

[799] Chia-Si Lu and J. Donohue, *J.A.C.S.* 1944, **66**, 824.

[800] C. S. Lu and J. Donohue, ib. 818.

[801] F. L. Usher and M. W. Travers, *J.C.S.* 1905, **87**, 1370.

[802] R. Klement and R. Reuber, *Ber.* 1935, **68**, 1761.

[803] *S.I.C.*, p. 392.

Thioantimonites, such as K_3SbS_3, are made by treating the trisulphide with alkaline sulphides in absence of air. The potassium salt is colourless and very soluble. The esters $Sb(S \cdot Ar)_3$ can be made from sodium thiophenates and antimony trichloride, but much less easily than their arsenic analogues; the reaction must be carried out at a high temperature under pressure and without a solvent; they are also much more readily hydrolysed by water.

Thioantimonates, such as $Na_3SbS_4, 9\,H_2O$, are got by boiling antimony trisulphide with sodium hydroxide and sulphur. Their esters $S \cdot Sb(S \cdot Ar)_3$ can be made from the thioantimonious esters by boiling with sulphur in carbon disulphide.[802]

BISMUTH TRISULPHIDE, Bi_2S_3

This, the only known sulphide of bismuth, is the mineral bismuthite. It can be made from its elements, when it is crystalline, or by precipitating a solution of a bismuth salt with hydrogen sulphide, when it comes out in a reddish-brown amorphous form, which changes to a dark grey solid, whose structure is given by Wells.[803] It is soluble in nitric acid and in hot concentrated hydrochloric acid, and slowly in alkaline sulphide solutions, with which it gives thiobismuthites such as $NaBiS_2$.

HALIDES

All these elements combine readily with the halogens. They all form trihalides $M(hal)_3$; those of arsenic, and those of antimony except the trifluoride, are definitely covalent, as is shown by their low conductivities. BiF_3 is definitely a salt; the other trihalides of bismuth, and SbF_3, have an intermediate character.

The relations of the pentavalent halides are peculiar. Phosphorus of course forms a stable pentafluoride, pentachloride, and pentabromide. Arsenic, as was pointed out before, shows an abnormal reluctance to take this form: it gives a pentafluoride but no pentachloride, apparently not even in the form of complexes. Antimony readily forms a pentachloride as well as a pentafluoride, and also perhaps complexes derived from a pentabromide. Bismuth forms no pentahalides. Halides $A_2(hal)_4$, analogous to P_2Cl_4 and P_2I_4, do not occur.

These are some boiling-points:

Trihalides

	AF_3	ACl_3	ABr_3	AI_3
A = N	−129°	+71°	. .	. .
P	−95°	+76°	172°	[M. pt. 61°]
As	+63°	130°	220°	*ca.* 400°
Sb	319°	221°	288°	*ca.* 410°
Bi	red heat	447°	453°	500°

Pentahalides

	AF_5	ACl_5	ABr_5
P	−75°	+*ca.* 100°	106°
As	−53°	. .	. .
Sb	+150°	+140°	. .

Specific Conductivities

PCl_3	*ca.* 0	PCl_5	*ca.* 0
$AsCl_3$	$1 \cdot 24 \times 10^{-6}$	$AsBr_3$	$1 \cdot 53 \times 10^{-6}$ (ord. T.)
$SbCl_3$	$0 \cdot 85 \times 10^{-6}$ (at 80°)	($RbNO_3$	0·415 at 300°)
$BiCl_3$	0·406 at 250°		

Dipole Moments in dioxane at 25°[804]

$AsCl_3$ 3·11 $AsBr_3$ 2·90 AsI_3 1·83.

Arsenic Halides

The arsenic trihalides are obviously covalent. The Raman spectra[805] show that the trifluoride and the trichloride have pyramidal molecules like PCl_3, and the same is proved for the solid tribromide by X-ray analysis.[806]

Arsenic trifluoride[807] melts at −5·95° and has a Trouton constant of 18·0.

Arsenic trichloride (m. pt. −13°) is colourless, and has a normal vapour density (T. E. Thorpe, 1876). Its dielectric constant (D.E.C.) is 12·8 at 20°,[808] and it is a good ionizing solvent, giving conducting solutions of tetramethyl ammonium iodide and of trimethyl sulphonium iodide.[809] It reacts with arsine to give elementary arsenic and hydrogen chloride.

The tribromide is similar; m. pt. 31°: D.E.C. 8·33 at 35°.[808]

The tri-iodide forms red-brown crystals, melting at 141°; the D.E.C. of the solid is 5·38 at 18°, and that of the liquid 7·0 at 170°. The vapour is yellow, and has the normal density. It is unstable; it decomposes in air, slowly at 100° but rapidly at 200°, to iodine, arsenic trioxide, and elementary arsenic. All its solutions decompose slowly, especially in presence of air or moisture.[810]

The trihalides are less completely hydrolysed by water than those of phosphorus, the reaction being reversible (compare silicon and germanium). The only known pentahalide is the *fluoride* AsF_5, a colourless gas, condensing to a yellow liquid at −53°. It is to be noticed that with phosphorus the pentafluoride boils 20° higher than the trifluoride, with arsenic 116° lower, and with antimony 170° lower. The density of AsF_5 vapour indicates some dissociation. The pentachloride $AsCl_5$ has been said to exist

[804] P. H. McCusker and B. C. Curran, *J.A.C.S.* 1942, **64**, 614.

[805] D. M. Yost and J. E. Sherborne, *J. Chem. Phys.* 1934, **2**, 125.

[806] H. Braekken, *Kong. Norsk. Vid. Forh.* 1935, **8**, no. 10.

[807] H. Russell, R. E. Rundle, and D. M. Yost, *J.A.C.S.* 1941, **63**, 2825.

[808] P. Walden, *Z. physikal. Chem.* 1903, **46**, 103.

[809] Id., *Z. anorg. Chem.* 1902, **29**, 375.

[810] W. H. Madson and C. Krauskopf, *Rec. Trav.* 1931, **50**, 1005.

at low temperatures, but there is no satisfactory evidence of this: Biltz[811] has shown that the freezing-point curve of the system $AsBr_3$—Br_2 gives no indication of any other solid compound than $AsBr_3$.

Antimony Halides

Antimony forms trihalides with all the halogens, and pentahalides with fluorine and chlorine; the pentabromide is only known (if at all) in complexes.

The following are some physical constants (for boiling-points see p. 791):

	SbF_3	$SbCl_3$	$SbBr_3$	SbI_3	SbF_5	$SbCl_5$
M. pt. . .	*ca.* 290°	72·9°	96·0°	170·3°	+7°	+5°
Crit. temp.[a] .	. .	518° C.	631°	828°	. .	. .
Dip. mom.[b] .	. .	5·16	5·01 D.	. .	. .	. .

a = [812], *b*: in dioxane at 25°; reference[805]

Electron diffraction has shown[813] that $SbCl_3$, $SbBr_3$, and SbI_3 all have pyramidal molecules in the vapour, the Sb-hal distances being 2·37, 2·52, and 2·75 A (theory 2·40, 2·55, 2·74). The X-ray analysis of solid $SbBr_3$ has confirmed this.[806]

The trihalides show an increase of metallic character as we go from arsenic to antimony. An aqueous solution of $SbCl_3$ must contain a certain concentration of Sb^{+++} ions, since it gives a precipitate of the sulphide with H_2S, and the metal can be obtained from it by electrolysis. But it mainly contains the univalent ion $[Sb{=}O]^+$, the stability of which is characteristic of antimony as compared with arsenic, and which is derived from a much stronger base than $Sb(OH)_3$ (while the stable oxychloride of phosphorus is $POCl_3$, that of antimony is SbOCl). The hydrolysis of the antimony trihalides leads to the precipitation of the basic antimonyl halide when the solution becomes dilute: when it is strong it remains clear, probably owing to complex formation. The addition of an alkaline halide prevents precipitation and at the same time greatly reduces the acidity, which is clear evidence of complex formation.

Antimony trifluoride, m. pt. 292°, b. pt. 319°: both of these are very high, especially as compared with the trichloride (73°, 221°). This is evidence of the preference of the fluoride for the ionic state, as with mercury, aluminium, and tin. SbF_3 is made by the action of concentrated hydrofluoric acid on the trioxide. Its aqueous solution has an acid reaction, but it is much less hydrolysed than any of the other halides, and it does not precipitate a basic salt; on evaporation hydrogen fluoride is evolved, and a basic salt remains.

$SbCl_3$, b. pt. 221°, has a normal vapour density, and is soluble in carbon

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[811] W. Biltz and K. Jeep, *Z. anorg. Chem.* 1927, **162**, 32.

[812] L. Rotinjanz and W. Suchodski, *Z. physikal. Chem.* 1914, **87**, 635.

[813] A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Far. Soc.* 1937, **33**, 852.

disulphide and in ether; so that it is obviously covalent. But it forms a dissociating medium for certain salts, such as potassium bromide.

Antimony tribromide is monomeric in benzene by the freezing-point,[814] and the crystals have pyramidal $SbBr_3$ molecules.[806]

The pentafluoride SbF_5 is a remarkably stable substance. It is formed by the prolonged action of hydrogen fluoride on $SbCl_5$, which is a proof that the affinity of antimony for fluorine is stronger than for chlorine (the heat of formation of H—F is already 29·7 k.cals. greater than that of H—Cl, so that since Sb—Cl = 68 k.cals., Sb—F must be greater than 98). It dissolves in water with a hissing sound (like $AlCl_3$ or quicklime) to a clear solution, from which $SbF_5, 2\,H_2O$ (perhaps $H(H_2O)[SbF_5OH]$) crystallizes out. In water it is precipitated by H_2S, converted by alkalies into the antimonate M_3SbO_4, and reduced by iodide ions; but all these reactions occur very slowly (much more slowly than with the chloride), which points to the formation of very stable complexes.

$SbCl_5$, which is formed by the direct combination of $SbCl_3$ and chlorine, melts at +2°, and begins to boil at 140°, but with considerable dissociation into $SbCl_3+Cl_2$: at 14 mm. it boils undecomposed at 68°. At low pressures the vapour density is normal, but this may be due to the dissociation at low temperatures being slow. Its D.E.C. at 21° is 3·78. It is a non-conductor of electricity, and solutions of salts in it do not conduct, but its solutions in SO_2 and in $AsCl_3$—two donor solvents—do so. It loses chlorine very easily, being reduced to the trichloride by ethylene, while sulphur converts it into $SbSCl_3$. It forms two hydrates (possibly complex acids) $SbCl_5, H_2O$, and $SbCl_5, 4\,H_2O$.

Bismuth Trihalides

Bismuth is much more metallic than the other elements in these compounds, which in many ways resemble those of the third-group metals. But all except the fluoride can assume the covalent state.

BiF_3 has all the characteristics of a salt. It is a white powder, which is scarcely volatile at a red heat: it is much the most stable of the trihalides.[815] It is insoluble in water, but dissolves in concentrated hydrofluoric acid, with the formation of complexes. Some indications have been obtained that BiF_3 can absorb more fluorine to form a pentafluoride[817-18]; but no recent evidence of this has been produced.

$BiCl_3$ dissolves in water and is hydrolysed to the oxychloride BiOCl. Its specific conductivity at 250° is that of a salt, but it has a normal vapour density, and it dissolves in acetone, methyl cyanide, and nitro-benzene (all donor solvents, with which it presumably forms complexes $Cl_3Bi \leftarrow X$, where the Bi has an inert electron pair (2, 8)). Electron diffraction[816]

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[814] R. Wright, *J.C.S.* 1916, 109, 1134.

[816] A. C. Vournazos, *Z. anorg. Chem.* 1926, **150**, 153.

[815] H. A. Skinner and L. E. Sutton, *Trans. Far. Soc.* 1940, **36**, 681.

[817] R. F. Weinland and O. Lauenstein, *Z. anorg. Chem.* 1899, **20**, 47.

[818] O. Ruff, M. Knoch, and J. Zedner, ib. 1908, **57**, 220.

shows that in the vapour $BiCl_3$ is pyramidal, with Bi—Cl 2·48 A (theory 2·45) and the Cl—Bi—Cl angles $100 \pm 6°$. It is monomeric in ether as long as the solution is less than 0·1 normal; above this it is associated.[817]

Bismuth tribromide is similar; it is soluble in xylene.

Bismuth tri-iodide forms black or brown crystals, melting at 408°. It is soluble in methylene iodide, but is much less soluble in water than the other halides, and so can be precipitated from a solution of bismuth trichloride on addition of potassium iodide. Owing to its insolubility it is not hydrolysed to the oxy-iodide BiOI in the cold, but only on boiling.

Salts of Sb^{+++} *and* Bi^{+++}

Antimony and bismuth, but not to any perceptible extent arsenic, are sufficiently metallic to form trivalent cations of the structure —(18), 2, that is, with two electrons inert. (This inertness is shown by arsenic in a few complexes.) They therefore form definite salts, especially with strong oxy-acids.

With antimony the tendency to do this is small; $Sb(OH)_3$ is a very weak base, and so the salts are formed only by strong oxy-acids, and are completely hydrolysed by water. In concentrated sulphuric acid Sb_2O_3 forms a crystalline sulphate $Sb_2[SO_4]_3$, which on the addition of a small quantity of water forms a hydrate, but with more water is hydrolysed to the antimonyl salt $[Sb{=}O]_2SO_4$. In the same way in concentrated nitric acid the nitrate $Sb[NO_3]_3$ is formed, but this is completely hydrolysed by water.

With bismuth the cation is much more stable, and this element behaves in many compounds like a metal of Group III such as lanthanum. The base $Bi(OH)_3$, like trivalent bases in general, such as $Al(OH)_3$ and $Fe(OH)_3$, is not very strong, and so salts are not formed with weak acids such as carbonic; also the great stability of the much more basic cation $[Bi{=}O]^+$ or $[Bi{\rightarrow}O]^+$, to which there is no analogue among the Group III metals, leads to the ready formation of bismuthyl salts, which are the only salts formed by bismuth with weak acids in presence of water.

Bismuth nitrate, $Bi[NO_3]_3$, 5 and 1·5 H_2O, is formed in fairly concentrated HNO_3, but is readily hydrolysed on dilution to $[Bi{=}O]NO_3$, which is also formed from the trioxide in dilute nitric acid. The nitrate gives a stable series of isomorphous double nitrates of the type $3\,M''(NO_3)_2$, $M'''(NO_3)_3$, $24\,H_2O$, where M'' is Zn, Cd, Co″, and Ni, and M''' can be bismuth or any of the rare earth metals La, Ce, Pr, Nd, Sm, and Gd.

The sulphate $Bi_2[SO_4]_3$ (7 and 2 H_2O) is similarly stable in fairly concentrated acid, and in the absence of water it can be heated to 400° without decomposition. It is isomorphous with the sulphates of yttrium, lanthanum, and praseodymium. It is very hygroscopic and on dilution gives various basic salts.

The perchlorate $Bi[ClO_4]_3$, $5\,H_2O$ is similar; it is extremely sensitive to traces of water, giving basic compounds such as the bismuthyl salt

$BiO(ClO_4)\ 4\ H_2O$.[819-20] It must be remembered that the readiness with which the basic salts are formed depends partly on their relative solubilities.

'Yl' *Compounds of Antimony and Bismuth*

The power of forming compounds of the univalent $A{=}O$ (or $A{\rightarrow}O$) radical, usually ionized $[A{=}O]X$ but apparently sometimes covalent $O{=}A{-}X$, first appears in this group in antimony, as it does in Group IV in zirconium, in the same period; it is much more marked in bismuth.

Antimony trichloride on addition of excess of water forms the oxychloride antimonyl chloride $SbOCl$, a crystalline substance insoluble in alcohol and ether, and only slowly soluble in water as it hydrolyses to more complicated oxychlorides. It is soluble in carbon disulphide, benzene, and chloroform, which indicates that it can at least go over into the covalent state $O{=}Sb{-}Cl$. More complicated oxychlorides have been made such as $Sb_4O_5Cl_2$, but their structures are not known. The only oxyfluorides, bromides, and iodides also belong to these more elaborate types, with more than one Sb atom in the molecule.

In the same way antimony sulphate and nitrate give as the first stage of their hydrolysis the antimonyl salts $[Sb{=}O]_2SO_4$ and $[Sb{=}O]NO_3$.

The base $[Sb{=}O]OH$ from which these compounds are derived, though obviously much stronger than the very weak base $Sb(OH)_3$, is still weak, and the antimonyl salts (excluding covalent $-Sb{=}O$ derivatives such as the complex tartrate) are readily hydrolysed further to free $Sb(OH)_3$.

With bismuth, as we should expect, the corresponding compound $[Bi{=}O]OH$ is a much stronger base, and its salts are much more stable; there is no indication that they ever go over into the covalent form.

Bismuthyl halides BiO(hal) can be made by the due dilution of a solution of the halide in water.

$[Bi{=}O]F$ is formed by the continued action of water on the insoluble trifluoride, or from the hydroxide and somewhat diluted hydrofluoric acid. It is crystalline and not hygroscopic. It is stable up to a moderate red heat, but decomposes at higher temperatures.

$[Bi{=}O]Cl$ is colourless: it melts at a red heat with little decomposition. It is insoluble in water, and is not attacked by it even on boiling, nor by cold dilute alkali: but hot concentrated alkalies convert it into the hydroxide.

$[Bi{=}O]Br$ is similar.

$[Bi{=}O]I$ is a brick-red powder, melting at a red heat, which is not attacked by boiling water.

The bismuthyl salts, of both weak and strong acids, form the largest class of bismuth salts. Thus we have a carbonate $(BiO)_2CO_3$, a nitrate $[BiO]NO_3$, a chlorate, a perchlorate $[BiO]ClO_4$, H_2O (hygroscopic: loses its water at 80–100°), and a nitrite $[BiO]NO_2$, $1/2\ H_2O$.

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[819] F. Fichter and E. Jenny, *Helv. Chim. Acta*, 1923, 6, 225.

[820] M. Prytz and P. Nagel, *Z. anorg. Chem.* 1936, 227, 65.

COMPLEX COMPOUNDS

THESE are very numerous and diverse, and we can distinguish four separate classes.

I. Trivalent donor compounds, in which the arsenic or other atom acts as a donor, like nitrogen in an ammine.

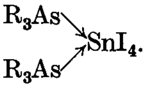
II. Acceptor compounds formed from the trivalent atom, as $K[SbCl_4]$. These are of peculiar interest, because they imply that two of the electrons are inert. The central atom has a valency group of $5+4+1 = 10_4$, or 2, $\underline{\underline{8}}$. The existence of complexes derived from the trivalent halide is a proof (and in the case of arsenic the only proof we have) that in this element the first pair of valency electrons can be inert. (The same argument applies to $K_2[AX_5]$, with 2, $\underline{\underline{10}}$, and to $K_3[AX_6]$ with 2, $\underline{\underline{12}}$.)

III. Acceptor compounds derived from the pentavalent atom, such as $K[SbF_6]$. There is no inert pair in these compounds, all the electrons being shared: here, for example, the valency group of the antimony is $5+6+1 = 12_6$ or $\underline{\underline{12}}$.

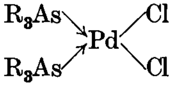
IV. A group of complexes which appear to be derived from a tetrahalide MX_4 or the tetroxide M_2O_4; an example is $(NH_4)_2[SbCl_6]$.

I. *Trivalent Donor Complexes*

The trialkyl arsines R_3As form compounds analogous to the ammines with many acceptors, such as



Various compounds of the type of



and similar forms have been obtained by Mann and others; they seem to be less stable than their phosphine analogues.

With the aryl arsines similar compounds have been obtained[821] with zinc, cadmium, and mercuric halides, for example, $(Me\Phi_2As)_2HgCl_2$, m.pt. 131°.

The donor power of the central atom falls off as the atomic weight rises; the phosphine and arsine compounds are less stable than the ammines; antimony has little tendency to react in this way, and bismuth apparently none at all.

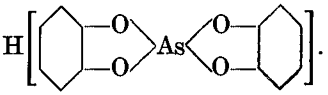
II. *Trivalent Acceptor Derivatives*

With arsenic, where the inert pair is scarcely capable of existence, only a small number of these compounds is known. ('Polynuclear' molecules, i.e. those containing two or more of the central atoms, as in $M[Sb_2Br_7]$, will not as a rule be considered unless their structure has been determined.)

[821] J. J. Anderson and G. J. Burrows, *Proc. Roy. Soc. N.S. Wales*, 1936, 70, 63.

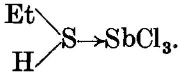
W. Petzold[822] has obtained a variety of salts of organic bases of the types of $Me_2NH_2[AsCl_4]$, $Et_2NH_2[AsBr_4]$, and $(EtNH_3)_2[AsBr_5]$. The chlorides are colourless, and the bromides pale yellow. They are not very stable: they can be recrystallized unchanged from the concentrated acid, but are at once hydrolysed by water or alcohol. Another example is (Quin. H) $[AsCl_4]$.[823] A more complicated salt of this kind, $Cs_3As_2Cl_9$, has been shown to be truly complex from its crystal structure.[824]

Another class consists of derivatives of catechol; the extra stability of the chelate ring obviously makes these possible. Rosenheim[825-6] found that arsenic trioxide forms a very stable complex acid with catechol of the formula, $H[As(C_6H_4O_2)_2],4\,H_2O$. This must be written



The arsenic atom is obviously in the same valency state as in the tetrachloride $M[AsCl_4]$: valency group 2, $\underline{8}$.

With antimony, where we should expect the first valency pair to be more inert, complexes of this kind, in which the trivalent atom acts as an acceptor, are much more numerous.

Antimony trichloride and tribromide form addition compounds with ethers, aldehydes, and mercaptans, such as $\Phi CHO\rightarrow SbCl_3$, $Et_2O\rightarrow SbBr_3$, and  $\begin{matrix}Et\\H\end{matrix}\!\!>\!S\rightarrow SbCl_3$. There is also a series of remarkable addition compounds of $SbCl_3$ with the aromatic hydrocarbons benzene, toluene, mesitylene, etc. (not with paraffins), mostly 1:1, but some of the type of $2\,SbCl_3, C_6H_5{\cdot}CH_3$; their structure is uncertain, but they presumably belong to this class; in the co-ordination compounds of unsaturated and aromatic hydrocarbons, the carbon atom probably always acts as a donor. Most of these addition compounds of hydrocarbons have been imperfectly investigated, so that we cannot be sure that they are more than crystal aggregates. They are crystalline substances of low melting-point (mostly 0° to 80°), which seem to dissociate entirely on melting. Substitution products of the aromatic hydrocarbons will also combine, but less strongly. Menschutkin[827] describes 39 compounds with 14 aromatic components, all either 1:1 or 1:2. No such compounds with hydrocarbons are formed by the pentahalides.

The antimony trihalides form a great variety of complex halides, with covalencies rising to 6, that is, of the types of $M[SbF_4]$, $M_2[SbCl_5]$, and $M_3[SbCl_6]$.

[822] W. Petzold, *Z. anorg. Chem.* 1933, **214**, 355, 365.

[823] W. Dehn, *J.A.C.S.* 1926, **48**, 275.

[824] J. L. Hoard and H. Goldstein, *J. Chem. Phys.* 1935, **3**, 117.

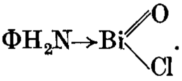
[825] A. Rosenheim and I. Baruttschisky, *Ber.* 1925, **58**, 891.

[826] A. Rosenheim and W. Plato, ib. 2000.

[827] See B. Menschutkin, *Chem. Centr.* 1910, i. 167; ii. 378, 379, 381; 1911, ii. 751; 1912, i. 408, 409, 410, 807; ii. 1439; 1913, i. 805.

A series of chelate 'ato' compounds of trivalent antimony are also known, of covalencies 4 and 6, such as $M[Sb(SO_4)_2]$:$M[SbOx_2]$ and $M_3[SbOx_3]$. Their chelation is proved by their relative stability to hydrolysis, as compared with the corresponding simple antimony salts.

Bismuth forms a large number of trivalent and 4–6 covalent complexes, but no pentavalent compounds of this kind (pentavalent bismuth compounds of any kind are very rare). $BiCl_3$ forms compounds with amines of the general formula $R_3N \rightarrow BiCl_3$ (Bi = 2, $\underline{8}$), and the oxychloride forms a similar compound with aniline, which perhaps is covalent, with the structure



$$\Phi H_2N \rightarrow Bi\begin{smallmatrix} \nearrow\!\!\!\!/ O \\ \searrow Cl \end{smallmatrix}.$$

$BiBr_3$ also combines with ether. The complex halide salts are of the types $M[BiCl_4]$, $M_2[BiCl_5]$, and less often $M_3[BiCl_6]$.[828-9] They are formed with all four halogens, but (perhaps owing to the great insolubility of BiF_3) the fluorides are less stable than the others; they seem to be limited to the 4-covalent type $M[BiF_4]$. The iodides appear to attain the highest covalencies, but there is the usual doubt here whether these compounds are periodides.

A series of bismuthinitrites have been prepared[830]; they are all of the type $M_3[Bi(NO_2)_6]$; their crystal structures are very like those of the cobaltinitrites.

Bismuth also forms the usual 'ato' complexes such as $M[Bi(SO_4)_2]$, $M[BiOx_2]$,[831] and at least one 6-covalent complex $(NH_4)_3[BiOx_3]$.[832] Catechol also forms 4-covalent derivatives $M[Bi(cat)_2]$.[825] These catechol derivatives are essentially of the same kind as the 'ato' complexes, except that they have a 5-ring in place of a 4-ring.

III. *Pentavalent Complexes*

These complexes are formed by arsenic and antimony, but, with one possible exception (p. 800), not by bismuth.

With arsenic they are limited by the absence of any pentahalides except the fluoride; it is obvious, for example, that a salt $M[AsCl_6]$ must decompose even if dissociated only to a minute extent into $AsCl_5$, since this loses chlorine at once. Accordingly, the complex halides are practically if not entirely confined to the hexafluorides $M[AsF_6]$ (almost the only 6-covalent compounds of phosphorus are the hexafluorides $M[PF_6]$).

With antimony, the number of co-ordination compounds is much greater. $SbCl_5$ forms 1:1 addition compounds with alcohols, ethers, aldehydes, nitriles, and esters; it also forms a compound with quinone $2\,SbCl_5,C_6H_4O_2$, in which both of the CO groups are co-ordinated.

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[828] A. Gutbier and M. Müller, *Z. anorg. Chem.* 1923, **128**, 137.

[829] F. Ephraim and P. Mosimann, *Ber.* 1921, **54**, 396.

[830] A. Ferrari and Z. Ciccioli, *Gaz.* 1936, **66**, 581.

[831] See S. Skramousky, *Coll. Czech. Chem. Comm.* 1930, **2**, 292.

[832] *Z. anorg. Chem.* 1901, **27**, 437; **28**, 210.

The complex halide salts of antimony are numerous. Antimony forms of course a pentafluoride and a pentachloride, but no pentabromide. Complex salts occur which, as far as composition goes, seem to belong to all three types, $M[SbF_6]$, $M[SbCl_6]$, and $M[SbBr_6]$. The hexafluorides and hexachlorides, which are colourless, are no doubt 6-covalent compounds of pentavalent antimony, but the structure of the bromides is less certain.

The hexafluorides resemble the phosphorus compounds in many ways.[833] Like them, they can be made by adding an alkaline fluoride to a solution of the pentoxide in concentrated hydrofluoric acid. In solubility they resemble the phosphorus salts, but they are rather more soluble. The diazonium salts, like those of HPF_6, are slightly soluble (most diazonium salts are very soluble in water) and are not explosive. But the antimony compounds are much more easily hydrolysed than those of phosphorus; water hydrolyses them at once, though not completely, replacing one, two, and ultimately three fluorine atoms by hydroxyl. Alkalies at once convert them into antimonic acid $H[Sb(OH)_6]$, whereas the HPF_6 ion is not attacked by alkalies at all. ($[PF_6]^-$ is covalently saturated: so is $[AsF_6]^-$ but not $[SbF_6]^-$.) The hydrolysis of $[AsF_6]^-$ does not seem to be described. Schrewelius[834] has shown by X-ray analysis that both $Na[SbF_6]$ and $Na[Sb(OH_6)]$ have their ions in NaCl lattice, and the arrangement round the Sb is octahedral. $Ag[Sb(OH)_6]$ and $Li[Sb(OH)_6]$ are similar. As we have seen, the corresponding compounds occur with arsenic, but efforts to make bismuth hexafluoro-salts $M[BiF_6]$ have all failed,[835] though a rather similar compound $K_3[BiOF_6]$ has been obtained. Hexafluoro-salts are formed by niobium and tantalum, but not by vanadium. A heptafluoro-antimony anion is known in the salts K_2SbF_7,H_2O, $(NH_4)_2SbF_7,1/2H_2O$, (quin. H) SbF_7, but their structure is unknown.

The hexachloro-antimonates $M[SbCl_6]$ are also fairly stable. The free acid $HSbCl_6$, $4{\cdot}5\,H_2O$, is a strong acid from whose freshly prepared solution silver nitrate immediately precipitates only a quarter of the chlorine (the stability of this complex is remarkable, since $SbCl_5$ reacts violently with water to give $Sb(OH)_5$ and HCl). On long standing the solution of $HSbCl_6$ deposits antimonic acid. Its salts are pale green. Salts of Mg, Fe''', and Cr''' are known which appear to have a higher covalency, their formulae being $MgSbCl_7$, $FeSbCl_8$, and $CrSbCl_8$: but they can be shown to contain the $[SbCl_6]$ ion, and to be properly written $[Cl]Mg[SbCl_6]$, $[Cl]_2Fe[SbCl_6]$, and $[Cl]_2Cr[SbCl_6]$, since with silver nitrate they precipitate little more than one and two chlorine atoms respectively. The ferric salt has 8 and the chromic salt 10 molecules of water of crystallization[836] and the beryllium salt $Be[SbCl_6]_2$ also has 10: this may indicate that the anion is hydrated, or it may be an example of a large anion causing an abnormally large hydration of the cation.

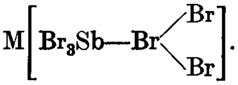
[833] W. Lange and K. Askitopoulos, *Z. anorg. Chem.* 1935, **223**, 369.

[834] N. Schrewelius, ib. 1938, **238**, 241.

[835] O. Ruff, ib. 1908, **57**, 220.

[836] R. F. Weinland and C. Feige, *Ber.* 1903, **36**, 252.

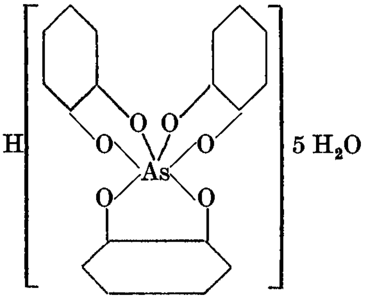
The complex bromides are formed[837-8] by adding bromine to a solution of $SbBr_3$ and the simple bromide, since no $SbBr_5$ exists. They have compositions corresponding to those of the fluorides and chlorides, $MSbBr_6$, and some contain even more bromine, such as the pyridine and dimethyl-pyridine salts $MSbBr_7$, and some are even of the type $MSbBr_9$. Petzold points out[838] that they differ markedly in properties from the fluorides and chlorides, and are likely to be polybromides of trivalent antimony, with such a structure as



$$\mathrm{M}\left[\mathrm{Br_3Sb{-}Br}\begin{matrix}\diagup\mathrm{Br}\\ \diagdown\mathrm{Br}\end{matrix}\right].$$

Whereas the fluorides and chlorides are colourless or nearly so, the bromides are black or dark violet-brown. While the fluorides and chlorides, as we have seen, are only hydrolysed very slowly, the bromides are converted into antimonic acid by water at once, and they lose bromine in the dry state with great ease.

Both arsenic and antimony can form pentavalent chelate compounds. The catechol derivatives of arsenic made it possible to resolve a 6-covalent arsenic compound into its optical antimers, and so prove that the distribution of the valencies is octahedral. 4-covalent arsenic had been shown to be tetrahedral by Mills and Raper.[839] Almost simultaneously Rosenheim and Plato[826] succeeded in resolving the 6-covalent arsenic compound of catechol $H[As(cat)_3], 5\,H_2O$ through its alkaloid salts. From these they made the ammonium, potassium, and barium salts, and the free acid. All these are active, the rotation of the free acid in acetone being $[M]_D = \pm 2{,}200°$. The salts are stable in water and in presence of alkali, but with traces of mineral acids they racemize at once. This was the first element which was shown to be capable of acting as a centre both of tetrahedral and of octahedral symmetry.



Pentavalent antimony can form catechol compounds of several kinds.[840] The first is the simple 6-covalent form like the arsenic compound

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[837] For more salts of the $[SbBr_6]$ type see R. F. Weinland and C. Feige, ib. 244.

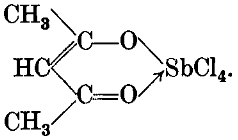
[838] W. Petzold, *Z. anorg. Chem.* 1933, **215**, 92.

[839] W. H. Mills and R. Raper, *J.C.S.* 1925, **127**, 2479.

[840] R. Weinland and R. Scholder, *Z. anorg. Chem.* 1923, **127**, 343.

$M[Sb(cat)_3]$: of this the free acid is unknown, and the only salts so far prepared are those of pyridine and quinoline. The other mononuclear types are antimonyl compounds, $M[O{=}Sb(cat)_2]$, which is obviously 6-covalent, and a remarkable series $M_3[O{=}Sb(cat)_3]$, which must be 8-covalent, and which form probably the only known series of compounds in which antimony shows its maximum covalency of 8. The free acid $H_3[O{=}Sb(cat)_3]$, 6 H_2O is known: the allowance of 2 H_2O for each H ion is the normal.

Other chelate compounds of pentavalent antimony are known, as with β-diketones such as acetyl acetone: these are monochelate:



IV. *Derivatives of Antimony Tetrachloride*

There is a series of complex salts which appear to be derived from a chloride $SbCl_4$, and a bromide $SbBr_4$, for example, $M_2[SbCl_6]$. They are all strongly coloured, including the chlorides. The tetrahalides themselves cannot be isolated, and their existence is doubtful.

In hydrochloric acid solution antimony trichloride is colourless, and so (practically) is antimony pentachloride; but if the two solutions are mixed, they become dark brown, and this colour increases on adding more hydrochloric acid or on warming, while it fades on cooling. This colour has been shown[841] to be proportional to the products of the concentrations of $SbCl_3$ and $SbCl_5$ used, as it would be if it were due to a dimeric Sb_2Cl_8. With rubidium and caesium chlorides the solution precipitates the dark violet anhydrous salts Rb_2SbCl_6 and Cs_2SbCl_6: they are stable in air, but are at once decomposed by water to Sb_2O_3 and Sb_2O_5; a corresponding bromide $(NH_4)_2[SbBr_6]$ can also be prepared.[842-3] If the tri- and pentachlorides are heated together without solvent, alone or with gaseous hydrogen chloride, the colour deepens only slightly. But if solid ammonium chloride is added, the liquid becomes black at once, and if enough of the salt is used there separates on cooling a dark violet mass, which is no doubt $(NH_4)_2SbCl_6$. This salt is unstable, and in the cold gradually loses its colour and becomes white, not, however, uniformly, but by single crystals, being evidently converted into a mixture of the tri- and pentavalent complexes, for example, into

$$(NH_4)_3[Sb^{'''}Cl_6] + (NH_4)[Sb^{v}Cl_6].$$

If the excess of tri- or pentachloride is removed by washing with chloroform, the violet colour may remain for several hours. The ammonium and

[841] J. Whitney and N. Davidson, *J.A.C.S.* 1947, **69**, 2076.

[842] R. F. Weinland, and H. Schmid, *Ber.* 1905, **38**, 1080.

[843] F. Ephraim and S. Weinberg, ib. 1909, **42**, 4447.

potassium salts $M_2[SbCl_6]$ cannot be isolated, partly no doubt because they are too soluble; but it is very remarkable that they can be got as isomorphous mixtures with the corresponding chlorostannates, -plumbates, and -platinates, which are typical salts of octahedral $[MX_6]$ ions.

Now if these salts are really M_2SbX_6 they have odd molecules, and should be paramagnetic; if, however, their molecular weights are twice this ($M_4Sb_2X_{12}$), they would be diamagnetic. Recently Jensen[844] has shown that Rb_2SbCl_3, Rb_2SbBr_6, and $(NH_4)_2SbBr_6$ all have the K_2PtCl_6 lattice, and all the Sb atoms occupy similar positions; so the anions cannot be doubled.

On the other hand, the magnetism of these salts was investigated by N. Elliott,[846] who found that $(NH_4)_2SbBr_6$ is diamagnetic; and Jensen[844] confirms this conclusion for $(NH_4)_2SbBr_6$ and for $Rb_2[SbBr_6]$.

Thus we are apparently faced by a complete contradiction.[845] Pauling has suggested that the crystals contain the anions $[Sb'''Cl_6]^{---}$ and $[Sb^{v}Cl_6]^{-}$, with resonance between the two.

Supposed Divalent Bismuth

It has been claimed that an oxide BiO and di-halides BiX_2 of divalent bismuth exist. The evidence is that these claims are erroneous; see references [847–51].

[844] K. A. Jensen, *Z. anorg. Chem.* 1937, **232**, 193.
[845] Id., ib. 1944, **252**, 317.
[846] N. Elliott, *J. Chem. Phys.* 1934, **2**, 298.
[847] W. Herz and A. Guttmann, *Z. anorg. Chem.* 1907, **53**, 63.
[848] H. G. Denham, *J.A.C.S.* 1921, **43**, 2368.
[849] E. Neusser, *Z. anorg. Chem.* 1924, **135**, 313.
[850] E. Montignie, *Bull. Soc. Chim.* 1937, [v] **4**, 588.
[851] A. Baroni, *Atti. R.* 1937, [vi] **25**, 195.

GROUP V A

VANADIUM, NIOBIUM, TANTALUM, PROTOACTINIUM

Physical Properties

	Vanadium	*Niobium*	*Tantalum*	*Protoactinium*
At. wt. (1947)	50·95	92·91	180·88	231
At. radius, A.U.	1·23	1·34	1·34	..
Parts per million				
in volcanic rocks[a]	200	0·37	0·24	7×10^{-7}
in earth's crust[b]	100	15	..	..
Metal, m. pt.	1,720° C.	1,950°	3,027°	..
XC, m. pt.	2,830°	3,500°	3,880°	..
XN, m. pt.	*ca.* 2,050°	*ca.* 2,050°	3,100°	..
XF_5 b. pt.	111·2°	217–20°	229·5°	..
XF_5 m. pt.	..	75·5°	96·8°	..
XCl_5 b. pt.	..	241°	241·6°	..
XCl_5 m. pt.	..	194°	211·3°	301°

a = 852, *b* = 853

THESE elements form on the whole a very regular series; as is usual in an A subgroup, the difference between the first and the second member is very much greater than that between the second and third; the resemblance between niobium and tantalum is very close, though not quite so close as that between their predecessors zirconium and hafnium. The chemistry of protoactinium is so little investigated that all we can say is that all its known properties are those to be expected from its position in the series.

As we pass down the subgroup the lower valencies (as in all A subgroups) become relatively less stable. The known valencies, and their relative importance, are shown in the following table:

Vanadium	$\underline{\underline{\underline{5}}}$	$\underline{\underline{4}}$	$\underline{\underline{3}}$	$\underline{2}$
Niobium	$\underline{\underline{\underline{5}}}$	? 4	3	..
Tantalum	$\underline{\underline{\underline{5}}}$	? 4	3	$\underline{\underline{2}}$
Protoactinium	5	..	..	..

With vanadium all four valencies are of some importance, while with niobium and tantalum only the group valency is found in any considerable number of compounds; further, while the lower valencies of niobium can be obtained in solution by electrolytic reduction, this is not so with tantalum, where they are oxidized by the water. So too zinc and acid reduce V^v to V'', Nb^v to Nb^{iii}, and have no action on Ta^v.

Another usual and characteristic difference is that the oxides of the group valency, which in the first member are amphoteric, become less acidic but not less basic as the atomic weight rises. Vanadic acid is both acidic and basic; niobic is still an acid, but an excessively weak one; tantalic is almost exactly like niobic; while the pentoxide of protoactinium

[852] G. v. Hevesy, E. Alexander, and K. Würstlin, *Z. anorg. Chem.* 1929, **181**, 95.
[853] V. M. Goldschmidt, *J.C.S.* 1937, 656.

has no acidic properties at all, and is quite insoluble in fused sodium carbonate.

A curious and marked change is that with vanadium, the oxyhalides are far more stable than the pentahalides, both in the simple compounds and in the complex salts, while with tantalum the opposite is the case, niobium occupying an intermediate position.

A list may be given of the oxides and sulphides of these elements; it must be remembered that owing to the much stronger tendency of sulphur (as compared with oxygen) to form links with itself, the valency of the other element is not necessarily the same in a sulphide as it would be in an oxide of the corresponding formula.

Oxides

	XO	X_2O_3	XO_2	X_2O_5
Vanadium . .	0	+	+	+
Niobium . . .	0	?	+	+
Tantalum . .	0	0	+	+

Sulphides

	XS	X_2S_3	XS_2	X_2S_5	XS_3	XS_4
Vanadium . .	? +	+	?	0	0	+
Niobium . .	+	+	0	0	0	0
Tantalum . .	+	+	+	0	+	0

The peroxy-acids (peroxyvanadic, etc.) with —O—O links, which are characteristic of the whole subgroup, become more stable as the atomic weight rises.

VANADIUM

VANADIUM is the least rare of the elements of this subgroup, but few minerals contain any large percentage of it: most of these are vanadates (like vanadinite, which is lead vanadate and chloride), but some are sulphides, such as patronite VS_4.

Vanadium occurs in all valencies from 5 to 2; their chief characteristics are as follows:

Valency 5

These compounds, the only ones that show a resemblance to those of the B elements, such as arsenic, are usually colourless.

The vanadic acids are definite and not very weak acids, but the pentoxide also has weak basic properties, and dissolves in strong acids to form vanadyl salts of the type $[VO]X_3$. There is only one pentahalide, the fluoride.

The complexes, which are not very numerous, the halides being the most important, are all without exception vanadyl ($VO^{\prime\prime\prime}$ or $VO_2^{\cdot}$) compounds.

Valency 4

The oxide VO_2 is still both basic and acidic, but the acidity is very slight, and shown only in highly condensed forms of the acid; the vanadites are nearly all of the type $M_2V_4O_9$, and are few and unstable; the salts formed with acids are all vanadyl compounds, such as $VOSO_4$, and are less readily oxidized than the vanadites. The vanadyl ion $[VO]^{++}$ is blue.

The complex salts, which include a variety of 'ato' (for example, oxalato) derivatives, are all vanadyl.

Valency 3

Trivalent vanadium is a reducing agent, and on warming will reduce copper sulphate solution to the metal; but it is not readily oxidized by air, and not at all by water. The vanadium is now no longer acidic, and the oxide is quite insoluble in alkalies, like ferric oxide; the element behaves as a trivalent metal, like trivalent chromium or iron, and forms a series of salts, the ion being green or blue.

It gives rise to a series of complexes, which, in exact opposition to the complexes of pentavalent and tetravalent vanadium, are never vanadyl compounds. In these complexes, like ferric iron, but unlike trivalent chromium or cobalt, it shows no preference for nitrogen over oxygen. Partly for this reason nearly all its complexes are anionic. The co-ordination number is always 6.

Valency 2

In this valency it is purely metallic (cationic), and resembles divalent chromium and iron, but is more readily oxidized even than divalent chromium: it decomposes water in neutral solution rapidly, though less readily in presence of concentrated acid. The V^{++} ion is violet.

Divalent vanadium forms scarcely any complexes except the double cyanides, which are all of the type $M_4[V(CN)_6]$, $3 H_2O$, corresponding to the ferro-cyanides, but of course much more easily oxidized.

Metallic Vanadium

Metallic vanadium is largely used as a constituent of ferrous alloys, but the pure metal is extremely difficult to obtain, as it readily combines with carbon, nitrogen, and oxygen, and forms solid solutions with some of the products.

The purest metal (still containing 1 or 2 per cent. of carbon or oxygen) is got by reducing the pentoxide, or more conveniently the trioxide V_2O_3, with 'Mischmetall'[854] (a mixture of rare earth metals, mainly cerium), or with aluminium. Aluminium will not reduce it below the trioxide,[855-6] except on addition of carbon or of calcium fluoride, which probably acts as a flux.[857]

[854] W. Muthmann, L. Weiss, and R. Riedelbauch, *Ann.* 1907, **355**, 58.

[855] W. Prandtl and B. Bleyer, *Ber.* 1910, **43**, 2602.

[856] O. Ruff and W. Martin, *Z. angew. Chem.* 1912, **25**, 49.

[857] W. Prandtl and H. Manz, *Z. anorg. Chem.* 1912, **79**, 209.

Vanadium is a bright white metal which is easily powdered in a steel mortar. The melting-point extrapolated to that of the pure metal[857] is 1,717°. It is stable in air, and resists the action of acids except hydrofluoric and oxidizing acids such as nitric. Its chief use is to increase the strength and toughness of iron and steel (e.g. for aeroplane engines) for which a very small quantity (0·1 to 0·2 per cent.) is sufficient.

Vanadium and Hydrogen

Vanadium absorbs hydrogen very slowly below 300° and rapidly above 400°[858]; there is no hysteresis, and above 400° the amount absorbed at equilibrium is proportional to the square root of the hydrogen pressure. If the metal is allowed to cool to the ordinary temperature in hydrogen at 1 atmosphere pressure, it will take up the gas to a composition $VH_{0\cdot56}$.

Vanadium and Boron

A very hard compound VB, indifferent to acids, can be made[859] by fusing the elements in an electric furnace.

Vanadium and Carbon

Moissan[860], by fusing vanadium pentoxide and carbon in an electric furnace, obtained the carbide VC, as a very hard mass. It melts at 2,750°.[861] As we should expect with an A element, vanadium forms no alkyl compounds; all attempts to make them, e.g. from the halides and the Grignard reagents,[862-3] have failed.

Vanadium and Silicon

If vanadium pentoxide is heated with silicon in an electric furnace or with thermite, especially in presence of a little calcium fluoride,[866] the disilicide VSi_2 remains as bright prisms which scratch glass and are scarcely attacked by anything in the cold except hydrogen fluoride, or on heating by halogens and sulphur.[864]

If a large excess of vanadium pentoxide is used, another compound V_2Si is formed, in silver-white crystals, very like the disilicide, and very stable, but much more easily attacked by halogens or by hydrochloric acid.[865]

Vanadium and Nitrogen

The only known nitride of vanadium seems to be VN. This can be obtained[867] in a practically pure state by heating a mixture of the trioxide

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[858] H. Huber, L. Kirschfeld, and A. Sieverts, *Ber.* 1926, **59**, 2891.

[859] E. Wedekind and C. Horst, ib. 1913, **46**, 1198.

[860] H. Moissan, *C.R.* 1896, **122**, 1297.

[861] O. Ruff and O. Goecke, *Z. angew. Chem.* 1911, **24**, 1459.

[862] J. Supniewski, *Rocz. Chem.* 1927, **7**, 172.

[863] C. C. Vernon, *J.A.C.S.* 1931, **53**, 3831.

[864] H. Moissan and A. Holt, *C.R.* 1902, **135**, 78.

[865] Id., ib. 493.

[866] J. Meyer and R. Backa, *Z. anorg. Chem.* 1924, **135**, 177.

[867] E. Friederich and L. Sittig, ib. 1925, **143**, 293.

V_2O_3 and carbon in nitrogen to 1,250° in a molybdenum boat. It is a grey-brown powder, which has a violet tinge when it is quite pure. It melts at 2,300°; its specific resistance at the melting-point is only 8·5 ohms. This is an 'interstitial' compound, with a sodium chloride lattice; it is probably ionized, though N^{---} ions are only known in nitrides of this kind; it is exceptionally stable for a compound of trivalent vanadium (see p. 664 above). It is insoluble in hydrochloric and sulphuric acids, but in boiling nitric acid forms a solution which as it is blue must now contain quadrivalent VO^{++} ions. If heated with soda-lime or boiled with potassium hydroxide solution it evolves ammonia.

Vanadium and Phosphorus[868]

If a solution of vanadium pentoxide in fused alkaline phosphate is electrolysed, two crystalline phosphides of vanadium can be made to separate, of the compositions VP and V_2P.[868] Both form metallic needles, which resist acids, but are decomposed by fusion with alkalies or alkaline salts. By tensimetric and X-ray studies of the system vanadium, phosphorus, Biltz[869] has obtained evidence of three compounds, V_3P, VP, and VP_2.

Vanadium Oxides, Sulphides, etc.

The binary compounds of vanadium with oxygen and the elements of the sulphur group have certain peculiarities in common, which may be mentioned here, though many of the individual compounds are dealt with under the various valencies of vanadium.

Biltz and Klemm and their collaborators have investigated the oxides,[873] sulphides,[870-1] and selenides,[872] by phase-rule methods, by X-ray measurements, and by magnetic measurements. The concordant results of these methods indicate the existence of the following compounds:

	VX	V_2X_3	VX_2	V_2X_5	VX_4
X=Oxygen . .	0	+	+	+	0
Sulphur . .	[+]*	+	?	0	+
Selenium . .	+	+	+	0	0
Tellurium .	+	?	0	0	0

The heats of formation of the oxides at 20° per mole and per oxygen atom are[874]:

Oxide	*Per mole*	*Per* O.
V_2O_3	296	99 k.cals.
V_2O_4	342	85·5 ,,
V_2O_5	373	74·6 ,,

* The occurrence of the monosulphide VS is asserted by Biltz and Köcher[871] but denied by Hoschek and Klemm).[872]

[868] M. Chene, *C.R.* 1939, 208, 1144.

[869] M. Zumbusch and W. Biltz, *Z. anorg. Chem.* 1942, 249, 1.

Of the higher compounds the pentoxide, which is the only compound of the type V_2X_5, is a quite definite and distinct substance (see below). The curious tetrasulphide VS_4 evidently from its properties does not contain vanadium in a high valency, but is a polysulphide in which the metal is very possibly divalent. It is made by heating the sesquisulphide V_2S_3 with excess of sulphur, and after cooling removing the excess with carbon disulphide. It is a black powder: it occurs in nature as patronite. It resists acids which do not oxidize it, but is at once dissolved by potassium hydroxide solution to give a red solution. The polysulphide structure is supported amongst other things by the very small amount of heat evolved when it is formed from the sesquisulphide:

$$V_2S_3 \text{ (solid)} + 5\,S \text{ (rhomb.)} = 2\,VS_4 \text{ (solid)} + 10 \text{ k.cals.}$$

The lower compounds, V_2O_3 and VO_2 with oxygen, V_2S_3 and VS_4 with sulphur, VSe, V_2Se_3, and VSe_2 with selenium, are able in each series to form solid solutions with one another, and also occur in three separate phases—different crystalline modifications—which have been studied especially with the selenides[872]; two of these have a nickel arsenide structure or one very similar to it, and the third the cadmium iodide lattice.

Pentavalent Vanadium

Vanadium Pentoxide V_2O_5

Vanadium pentoxide can be made by igniting ammonium metavanadate $(NH_4)VO_3$, or precipitating a vanadate solution with acid, or in the pure state[875] by hydrolysing the oxychloride $VOCl_3$ with water, and finally heating it in oxygen to its melting-point. It then forms transparent yellow-brown prisms, which become cinnabar-red on heating, and melt at 658°. It is doubtful whether it is truly dimorphic. It cannot be sublimed except in an electric furnace, and it does not begin to lose oxygen even at 1,800°.

It is only slightly soluble in water, probably about 1·82 g. per litre (about 1/100 molar), but it readily becomes colloidal.

With water it forms one or two definite hydrates (see under vanadic acid). The aqueous solution behaves as an acid, and forms vanadates of very various types. It is readily reduced to the tetravalent and the trivalent states by heating in the dry state with hydrogen, or with carbon monoxide[876]: in solution by the halogen hydrides, and the more easily the heavier the halogen (vanadic acid has nearly the same oxidation potential as nitric); see further, under these lower oxides.

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[870] W. Klemm and E. Hoschek, ib. 1936, **226**, 359.

[871] W. Biltz and A. Köcher, ib. 1939, **241**, 324.

[872] E. Hoschek and W. Klemm, ib. 1939, **242**, 49.

[873] Id., ib. **242**, 63.

[874] H. Siemonsen and H. Ulich, *Z. Elektrochem.* 1940, **46**, 141.

[875] W. Prandtl and B. Bleyer, *Z. anorg. Chem.* 1910, **67**, 257.

[876] A. Morette, *C.R.* 1935, **200**, 134.

The pentoxide, either as such, or in the hydrated form as vanadic acid, or as a pentavalent vanadyl salt formed from the pentoxide in the presence of strong acids, is a powerful catalyst for many reactions, for example for the oxidation of sulphur dioxide to trioxide, for the sulphonation of aromatic hydrocarbons[884] or of pyridine,[885] for the reduction of olefines[885a], and especially for a variety of oxidations, such as that of hydriodic by bromic acid[877] or by hydrogen peroxide,[878] of sugar by nitric acid, of alcohol by air,[879] of stannous salts to stannic by nitric or chloric acid,[879] of various cyclic organic compounds by hydrogen peroxide,[880] of naphthalene and its substitution products by atmospheric air[886]; and also the reduction of aromatic hydrocarbons by hydrogen.[881] Many other vanadium compounds are remarkable for their catalytic power. Metallic vanadium strongly catalyses[866] the reaction

$$2\,CO = CO_2 + C.$$

Vanadium trioxide catalyses the dehydrogenation of cyclohexane at 380–440°[882]; and various vanadium compounds assist the electrolytic reduction of organic nitro-compounds.[883]

Vanadic Acid and the Vanadates

Vanadium pentoxide is precipitated from a vanadate solution by acids in a hydrated form. Hüttig and König have shown[887] by vapour-pressure and X-ray measurements that there are two definite hydrates, of the compositions V_2O_5, H_2O or HVO_3, and $2\,V_2O_5$, H_2O or $H_2V_4O_{11}$, which appear to be the free meta- and a kind of pyro-acid.

The behaviour of vanadic acid and its salts in presence of water is in many ways peculiar. The literature up to 1907 is collected by Chilesotti.[889] See further, Düllberg[888] and Jander and Jahr.[890-1]

The vanadates resemble the phosphates in having all the valency electrons of the central atom in use, and this leads to a similarity in properties and especially in crystalline form. But the differences are also very marked.

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[877] W. Ostwald, *Z. physikal. Chem.* 1888, **2**, 127.

[878] J. Brode, ib. 1901, **37**, 260.

[879] A. Naumann, L. Moeser, and E. Lindenbaum, *J. prakt. Chem.* 1907, [2] **75**, 146.

[880] W. Treibs, *Angew. Chem.* 1938, **52**, 698.

[881] G. D. Lubarski and M. J. Kagan, *C.R. Acad. Sci. U.R.S.S.* 1941, **29**, 575.

[882] H. S. Taylor and M. Yeddanapalli, *Bull. Soc. Chim. Belge*, 1938, **47**, 162.

[883] H. Hofer and F. Jakob, *Ber.* 1908, **41**, 3187.

[884] F. Thümmler, Deutsches Patent, *Chem. Centr.* 1909, ii. 1396.

[885] H. Meyer and W. Ritter, *Monatsh.* 1914, **35**, 765.

[885a] V. I. Komarewsky, L. B. Bos, and J. R. Coley, *J.A.C.S.* 1948, **70**, 428.

[886] A. Pongratz *et al.*, *Angew. Chem.* 1941, **54**, 22.

[887] G. F. Hüttig and A. König, *Z. anorg. Chem.* 1930, **193**, 81.

[888] P. Düllberg, *Z. physikal. Chem.* 1903, **45**, 129.

[889] A. Chilesotti, in Abegg's *Handbuch*, Bd. iii, Abt. 3, pp. 752–76 (Leipzig, 1907).

[890] G. Jander and K. F. Jahr, *Z. anorg. Chem.* 1933, **211**, 49.

[891] Id., ib. **212**, 1.

In its properties vanadic acid resembles chromic rather than phosphoric acid, to such an extent indeed that Berzelius thought that the formulae of the vanadates and chromates were similar.

The differences from the phosphates (or arsenates) are first that the rates of mutual conversion of the ortho, pyro, and meta forms which are slow with phosphorus are practically instantaneous with vanadium. A solution of an ortho-, meta-, or pyro-vanadate is the same at any given concentration of the salt and hydrogen ion, and by a suitable modification of these factors can be made to precipitate any one of the three salts. A similar case of transformation is found with the esters (see later, p. 813), which is an almost unparalleled phenomenon.

Secondly, the direction of the change with increasing acidity is the opposite in the two instances. With phosphoric acid the ultimate result of acidification whether of an ortho-, pyro-, or meta-phosphate is the production of a molecule containing only one atom of phosphorus, an orthophosphate such as NaH_2PO_4, or free orthophosphoric acid H_3PO_4. With vanadic acid the ultimate product of hydrolysis or acidification is the production, through a series of condensed acids of increasing complexity, of the highly polymerized pentoxide $(V_2O_5)_n$. This is like the behaviour of a chromate, which on acidification gives the dichromate ion $[Cr_2O_7]''$, and probably more complex forms.

A large number of vanadates of different types are known, which may be divided into two classes: (1) colourless salts which crystallize from alkaline or neutral solutions, and (2) coloured (brown or red) salts which are obtained only from more or less acid solutions; these differences of colour occur in the solution as well as in the solid. Of the colourless salts (with their M′:V ratios) the commonest are the ortho, M_3VO_4 aq. (3:1), the pyro (2:1) $M_4V_2O_7$ aq., and the meta (1:1) vanadate MVO_3 aq. (nearly all the vanadates are hydrated). Other types of colourless vanadates have been described, all having the M′:V ratio at least 1. With the coloured salts this ratio is always less than 1, and commonly 3:5 or 4:5.

Düllberg[888] and Jander and Jahr[890-1] have traced the changes which occur in the solution, and in the salts which separate from it, as the concentration of hydrogen ion alters from the strongly alkaline to a strongly acid solution. As the hydroxyl ion concentration falls, the salts which separate contain an increasing number of vanadium atoms in the molecule, the solution and the salts becoming coloured as the liquid passes the neutral point, until finally, at the isoelectric point for vanadium pentoxide (about $n/100$ acid), V_2O_5 separates in a hydrated and highly polymerised form. If the acidity is increased, the orange or brown colour changes to pale yellow, the colour of the $[VO_2]^+$ and $[VO]^{+++}$ ions of the vanadyl salts (such as $(VO)_2[SO_4]_3$) now present.

But there is more than this. The molecular weight of the ions in these solutions has been determined by Jander and Jahr from the rates of diffusion.[891] In this way they showed that as the alkalinity falls from the alkaline end, the molecular weight of the ions increases in a series of steps, indicating considerable ranges of p_H over which the ions present are mostly of one kind; this is supported by the sharpness of the electrometric titration.

Measurements of the p_H of the solutions indicated that the mono-vanadium form is present in strongly alkaline solutions, where on concentration the ortho-vanadate M_3VO_4, aq. separates; between p_H values of 12 and 10·6 this changes into a divanadic acid: after this point the pyrovanadates $M_4V_2O_7$ aq. can be made to separate. At p_H 9·0 to 8·9 the V_2 ions change over to V_4, giving a tetravanadic acid, and this solution produces the metavanadates, of which the true formulae must therefore be $M_4V_4O_{12}$, aq., $M_6V_4O_{13}$, aq., etc.; finally, at p_H 7·0 to 6·8, this goes over into the penta-acid which is coloured, giving solids of the compositions $M_3V_5O_{14}$, aq., $M_4HV_5O_{15}$, aq., and the like (no doubt some of the water often forms part of the complex ion). With an increase of the acidity beyond the neutral point, we come to a region where the hydrated pentoxide separates from a dark solution; this continues up to the isoelectric point of the pentoxide (about $p_H = 2·2$). If the acidity is carried farther, the solution turns pale yellow; the vanadium is now present entirely as a vanadyl salt; transport determinations show[888] that the vanadium is positively charged, and diffusion measurements[889] that the ion contains only one vanadium atom.

It is remarkable that while the reactions between the colourless salts (with 1, 2, and 4 vanadium atoms in the molecule) are practically instantaneous, the coloured salts only change slowly. Even in the colourless regions a drop of perchloric acid produces a brown colour where there is a local excess of acid, and this only gradually disappears. It is remarkable how much more rapidly these ions react with acid than with alkali; the brown solution of the pentavanadate only loses its colour quite slowly on addition of excess of alkali, the reaction taking several hours at the ordinary temperature; while the colourless solution of one of the less complex acids at once becomes coloured on addition of acid.

It is to be noticed that though vanadium pentoxide is only slightly soluble in water it will dissolve readily in hydrogen peroxide[892]; the solution soon loses its extra oxygen and becomes a metastable supersatured solution of vanadic acid, from which the pentoxide slowly crystallizes out. The primary product is no doubt a peroxyvanadic acid, probably $H_3[V(O_2)O_3]$.[893-4]

Vanadic Esters

These have been examined in detail by Prandtl and Hess[895-6], with results which on the whole confirm the conclusions reached for the salts. They have the property, almost alone amongst esters, of changing from

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[892] J. B. Cammerer, *Chem. Ztg.* 1890, **15**, 957.

[893] J. Meyer and A. Pawletta, *Z. physikal. Chem.* 1927, **125**, 49.

[894] Id., *Z. anorg. Chem.* 1927, **161**, 321.

[895] W. Prandtl and L. Hess, ib. 1913, **82**, 103.

[896] L. Hess, Deutsches Patent, *J.C.S. Abstr.* 1915, i. 1.

one form to another nearly as rapidly as the ions of ortho- and meta-vanadic acid, and far more rapidly than those of phosphoric.

The ortho-esters R_3VO_4, which are formed by the prolonged boiling of vanadium pentoxide with a large excess of alcohol, are pale yellow volatile liquids (b. pts.[896] Et_3VO_4 108°/26 mm.; $(iso\text{-}Pr)_3VO_4$ 124°/21 mm.); their molecular weights in solution are normal, and they are soluble in ether, benzene, and toluene. The addition of a small quantity of water to the alcoholic solution gives a pale yellow precipitate of the meta-ester $R_3V_3O_9$: with more water a yellow-red solid ester separates (see below), while in water alone the esters are at once hydrolysed to colloidal vanadic acid. Pyrovanadic esters ($R_4V_2O_7$) do not seem to exist.

The metavanadic esters obtained as above described give in phenol the molecular weight required by the formula $R_3V_3O_9$. The meta-acid was found (p. 812) to contain four vanadium atoms in the molecule; but the esters need not always correspond in structure to the salts. The meta-esters are hydrolysed with great ease; they are unstable, and even in an atmosphere of carbon dioxide undergo internal oxidation and reduction, with the formation of aldehyde.

The final products, the solid yellow-red esters described above, could not be analysed, because it was impossible to free them from colloidal vanadic acid, but their existence is proved by the red colour which they give in solution. The formula may be presumed to be that of the red 'acid' vanadates, $R_3V_5O_{14}$.

The alcoholic solutions of all these esters undergo remarkable changes of colour. Both the ortho- and the meta-esters are pale yellow, and perhaps colourless when pure, while the V_5-ester is red. The solution got by boiling vanadium pentoxide with alcohol has the colour of a dichromate solution when it is cold, but the colour disappears on heating and comes back again on cooling. This was shown to be due to a reversible hydrolysis in presence of traces of water in the alcohol:

$$\underset{\text{Colourless}}{5\,Et_3VO_4} + 6\,H_2O \rightleftharpoons \underset{\text{Red}}{Et_3V_5O_{14}} + 12\,EtOH$$

$$\underset{\text{Colourless}}{5\,Et_3V_3O_9} + 3\,H_2O \rightleftharpoons \underset{\text{Red}}{3\,Et_3V_5O_{14}} + 6\,EtOH$$

These reactions are promoted from left to right by a low temperature: in other words, the hydrolysis must evolve heat. Similarly the temperature at which the solution loses its colour is raised by the addition of water and lowered by its removal. The loss of colour is accompanied by a marked fall of conductivity (from 114 to 15 gemmhos on heating a 1·5 per cent. solution of the pentoxide in ethyl alcohol from 0° to 75°); the pure ortho-ester is practically non-conducting in alcohol (2·4 gemmhos at 18°). The conductivity of the penta-ester may perhaps be due to the presence of an acid ester such as $Et_2HV_5O_{14}$. A corresponding change of colour occurs with the salts: a vanadate solution which is orange when cold becomes pale yellow at its boiling-point, and the solid salts undergo a similar change.

Thiovanadates

Although the pentasulphide V_2S_5 does not appear to exist, a variety of thiovanadates are known, in which any number of the oxygen atoms of a vanadate from one to all may be replaced by sulphur.[897-8] These are known in the ortho, pyro, and meta series; examples are $(NH_4)_3VS_4$, very soluble permanganate-like crystals, and the deep purple $Na_4V_2O_2S_5$.

Peroxyvanadic Acid and its Salts

A vanadate solution is readily oxidized by hydrogen peroxide with the production of colour, and a variety of peroxyvanadates, such as KVO_4[899], have been obtained in this way. These are yellow or deep orange in colour, both in the solid state and in solution.

Free peroxyvanadic acid cannot be isolated. Its constitution has been disputed; there probably are at least two substances formed in the reaction. If a solution of vanadium pentoxide in dilute hydrogen peroxide is shaken with ether, the partition of the hydrogen peroxide between the two layers indicates that one molecule of H_2O_2 is bound by every vanadium atom, so that each vanadium must have one oxygen atom replaced by the —O—O group. Hydrogen peroxide acts at once[893] on a vanadium pentoxide solution to give a pale yellow solution of high conductivity, which probably contains the free acid $H_3[V(O_2)O_3]$. But if the pentoxide is dissolved in fairly concentrated sulphuric acid, a characteristic dark red colour is produced (presumably due to a new per-compound). If the peroxide and the sulphuric acid are added simultaneously to the pentoxide, this colour is only formed slowly; but if the pentoxide has been left for some time in the acid, or heated with it, the addition of the hydrogen peroxide at once causes the red colour to appear. Now we know that vanadium pentoxide reacts slowly with sulphuric acid to give a vanadyl salt such as $[VO]_2(SO_4)_3$. It is therefore at least very probable that the replacement of an oxygen atom attached to vanadium by the —O—O group is instantaneous: that the pale yellow solution formed at once from the vanadic acid is a true per-acid: and that the red-brown compound is the peroxide of a vanadyl salt, probably of the composition

$$[V\rightarrow O\rightarrow O]_2(SO_4)_3,$$

which is formed by the hydrogen peroxide at once from the vanadyl salt, as soon as that has been produced.[893]

These peroxide compounds all decompose readily. Melikov[900] has pointed out that the stability of the per-acids in any periodic subgroup rises with the atomic weight, and that of the series V—Nb—Ta the vanadium per-compounds are the least stable. In particular they promote the decomposition of hydrogen peroxide itself, and thus rapidly lose their

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[897] G. Krüss and K. Ohnmais, *Ber.* 1890, **23**, 2547; *Ann.* 1891, **263**, 39.

[898] J. Locke, *Amer. Chem. J.* 1898, 20, 373.

[899] L. Pissarjewsky, *Z. physikal. Chem.* 1903, **43**, 160, 173.

[900] P. Melikov and E. Jeltschaninov, *Ber.* 1909, **42**, 2291.

extra oxygen, especially in the presence of acid.[901] Another sign of their instability is that 'pervanadic acid', the product of the action of hydrogen peroxide on vanadium pentoxide, is found to be a powerful catalyst in promoting the oxidation of unsaturated hydrocarbons by hydrogen peroxide.[902]

Halides

Ruff points out[903] that vanadium is remarkable for giving halides in all four valencies 5, 4, 3, and 2; under some conditions all four can be observed in the same operation.

Vanadium Pentafluoride, VF_5

This was obtained by Ruff and Lickfett[904] by heating the tetrafluoride for several hours in nitrogen at 600°, when the pentafluoride distils over, and the trifluoride remains behind.

It is the only known compound of the type VX_5. It is pure white; it turns yellowish in air from the formation of the oxyfluoride VOF_3, and it attacks glass. It dissolves easily in water, alcohol, chloroform, acetone, and ligroin, giving yellow or reddish-yellow solutions; it is insoluble in carbon disulphide. It melts under pressure at above 200° and sublimes under 1 atm. at 111°.

The absence of a pentachloride or pentabromide of vanadium is an example of the reluctance of elements of the first long period to assume high co-valencies. Other examples of the same phenomenon, the absence of a compound of high covalency of an element in this period, while it formed by both the preceding and the following elements of the group, are these:

PCl_5	SF_6	PCl_5	SO_3	$[ClO_4]'$
No VCl_5	No CrF_6	No $AsCl_5$	No SeO_3	No $[BrO_4]'$
$NbCl_5$	MoF_6	$SbCl_5$	TeO_3	$[IO_4]'$

Vanadium Oxyfluoride, VOF_3

This can be made[904] from the oxychloride $VOCl_3$ with concentrated hydrofluoric acid in the cold; or by oxidizing the trifluoride VF_3 by heating it in a stream of oxygen to a red heat.

It forms a hard yellowish-white mass, which is very hygroscopic, and dissolves readily in water to give a brown solution. It attacks glass, especially when warm, forming the pentoxide V_2O_5. It dissolves in chloroform and in acetic acid on boiling, but is insoluble in other organic solvents.

It melts at 300°, and boils at about 480°, but it can be sublimed in a stream of oxygen even at 130°.

Vanadium Oxychloride, $VOCl_3$

This substance has repeatedly been used for the determination of the atomic weight of vanadium.[905-6,908]

[901] V. Auger, *C.R.* 1921, **172**, 1355.

[902] W. Treibs, *Ber.* 1939, **72**, 7, 1194.

[903] O. Ruff and H. Lickfett, ib. 1911, **44**, 506.

[904] Id., ib. 2539.

It can be made by the action of chlorine on vanadium pentoxide at 600–700° (with evolution of oxygen),[903] or on the trioxide V_2O_3.[905-6,908] It is a pale yellow liquid melting at −79·5° and boiling at 127°.[909] Its heat of evaporation is 8·7 k.cals.,[909] and hence the Trouton constant is 21·8. The dielectric constant is 3·42 at 21°.[907] The melting- and boiling-points are remarkably low:

	B. pt.	*M. pt.*
VF_5 . . .	111°	200°
VOF_3 . .	480°	300°
$VOCl_3$ . .	127°	−79·5°

This suggests that the fluorine compounds may be ionized in the solid state, and the pentafluoride covalent in the liquid state, like aluminium chloride and phosphorus pentachloride. The vapour density is normal.[905]

The oxychloride has no action on metals; mercury remains unchanged in it for months,[908] and it can be boiled with sodium for 12 hours under ordinary pressure without any reaction occurring.[906] It dissolves most non-metals, but not inorganic salts; it is miscible with the ordinary organic solvents, but it reacts with many of them, oxidizing the alcohols to aldehydes. It is violently hydrolysed by water.

Vanadium Oxybromide, $VOBr_3$

This has scarcely been investigated since the work of Roscoe 80 years ago.[910] It can be made by passing bromine vapour at a red heat over vanadium trioxide,[910] or over a mixture of the pentoxide and carbon.[911] It is a dark red liquid, which readily gives off bromine, and does so suddenly and completely at 180°.[910] It boils at 130–36° under 100 mm.,[910] and at 75–8° under 2 mm. pressure.[911]

Pentavalent Vanadyl Salts, $(VO)[X]_3$

The $[VO]^{+++}$ salts seem to be only known salts of V^{v}, and it is doubtful whether any of them have been isolated.[914] They can, however, certainly occur in solution. Vanadium pentoxide or its hydrate is amphoteric, and in a strongly acid solution forms salts which have the vanadium in the cation. These solutions are most easily obtained by adding excess of strong acid to a concentrated solution of a metavanadate, so that the vanadyl salt is formed before the pentoxide has time to separate out. Düllberg showed[888] that under these conditions the colour of the solution

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[905] W. Prandtl and B. Bleyer, *Z. anorg. Chem.* 1909, **65**, 152.

[906] H. V. A. Briscoe and H. F. V. Little, *J.C.S.* 1914, **105**, 1310.

[907] A. G. Loomis and H. Schlundt, *J. Phys. Chem.* 1915, **19**, 734.

[908] A. F. Scott and C. R. Johnson, *J.A.C.S.* 1930, **52**, 2638.

[909] H. Flood, J. Goerrissen, and R. Veimo, ib. 1937, **59**, 2494.

[910] H. E. Roscoe, *Phil. Trans.* 1870, **159**, 689; **160**, 317; *Ann. Splbd.* 1870, **7**, 70; 1872, **8**, 95.

[911] F. P. Nuñes and E. Figueroa, *C.R.* 1938, **206**, 437.

fades to pale yellow, and there is a slow but considerable fall in conductivity; this is the same whatever the strong acid used; transport experiments showed that in these solutions the vanadium has a positive charge.

Jander and Jahr[891] found that in solutions where the vanadium was about decinormal, the (nitric) acid varying from N/9 to 4·5 N., the rate of diffusion was always the same, and indicated that there was only one vanadium atom in the ion. They assumed that the salt is $[VO](NO_3)_3$, though $[VO_2]NO_3$ is not impossible, since the VO_2 group occurs in some complexes.

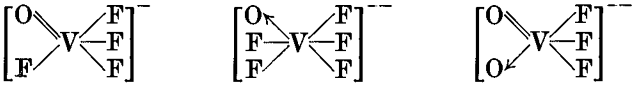
Complex Salts of Pentavalent Vanadium

These do not form a large group. The most important are the oxyhalides, and there are also some sulphato-, oxalato-, and similar complexes. They are all without exception vanadyl compounds, that is, they always have at least one oxygen atom (sometimes two) covalently linked to the vanadium and to nothing else.

Complex Fluorides[912-13,915]

A variety of these are known, both single (i.e. with one vanadium atom in the molecule) and multiple. They are all oxyfluorides, being derived either (*a*) from the oxyfluoride VOF_3, or (*b*) from the non-existent VO_2F. Thus we have the types (amongst others) (*a*) $M[VOF_4]$; $M_2[VOF_5]$; (*b*) $M_2[VO_2F_3]$; (K_2, Ba, Zn, etc.). These salts are made from the components, and they change readily into one another. In water they are considerably hydrolysed, often giving more complicated compounds; thus[913] $K_2[VO_2F_3]$ is colourless, but it gives a yellow solution in water, owing to the formation of a deep yellow salt of the composition 3 KF, 2 VO_2F.

The stability of these oxyfluoride complexes is no doubt increased by the fact that the oxygen atom can form (predominantly) either a single or a double link with the vanadium, so that they can all acquire a covalency of 6:



The valency of the vanadium of course remains 5 throughout.

Complex Chlorides

These are also oxy-compounds, being derived from the oxychloride $VOCl_3$, and probably also from the unknown VO_2Cl. They are very difficult to prepare, largely because of their high solubility[913]; it has, how-

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[912] P. Melikov and P. Kasanetzky, *Z. anorg. Chem.* 1901, 28, 242.

[913] F. Ephraim, *Ber.* 1903, **36**, 1177.

[914] A. Rosenheim, E. Hilzheimer, and J. Wolff, *Z. anorg. Chem.* 1931, **201**, 173.

[915] Most of the work on these compounds was done in the nineteenth century; for references see Abegg, *Vanadium*, pp. 745–9.

ever, been found possible, by working in alcoholic solution, to prepare the salts of one or two organic bases, such as (pyH)[$VOCl_4$].

All attempts to prepare complex oxybromides have been unsuccessful.

Vanadyl Sulphato-complexes

All the other complexes formed by pentavalent vanadium seem to contain chelate (ring) groups, usually of the 'ato' type, formed by dibasic acids.

Sulphato-compounds, of the type of $M[VO_2(SO_4)]$ aq., were obtained by Berzelius, and their existence was confirmed later.[916]

Oxalato-complexes

These, the best known of the 'ato' group, can be made by treating a vanadate solution with oxalic acid. They are all of the type

$$M_3[VO_2(C_2O_4)_2], \text{ aq.},$$

and are remarkably stable. Rosenheim has shown[918] by the conductivity that a solution of the sodium salt contains the neutral salt of a tribasic acid; and from transport measurements[919] that the vanadium is present wholly in the anion.

Tetravalent Vanadium

This is very readily produced from the pentavalent by reduction, for example, from the pentoxide by treatment with hydrogen halides. The fall in valency has, as usual, a marked effect in diminishing the acidity of the oxide. Vanadium tetrahydroxide $V(OH)_4$ is still amphoteric, and is about as basic as the pentoxide; it also resembles the latter in giving no simple salts $V[X]_4$, nor any complexes derived from them, but only derivatives, simple and complex, of the divalent radical VO″. As an acid, however, $V(OH)_4$ is much weaker than the pentavalent vanadic acid. It also seems that while the basic form is monomeric like $V(OH)_4$ and its derivatives, the acidic form (in the vanadites) can only occur with a condensed ion, which practically always is $[V_4O_9]''$.

Vanadium Dioxide and the Vanadites

Vanadium pentoxide can be reduced to the tetravalent state in many ways: by hydrochloric acid in aqueous solution[922-3]; by hydriodic acid[927]; by carbon at 400-700°, or by carbon monoxide[929]; or by hydrogen peroxide or peroxysulphates.[926] It is usually made by heating the

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[916] B. W. Gerland, *Ber.* 1877, **11**, 98.

[918] A. Rosenheim, *Ber.* 1893, **26**, 1191; *Z. anorg. Chem.* 1893, **4**, 368.

[919] Id. ib. 1896, **11**, 225.

[922] F. A. Gooch and L. B. Stookey, *Z. anorg. Chem.* 1920, **32**, 456.

[923] F. A. Gooch and R. W. Curtis, *Amer. J. Sci.* 1904, [4] **17**, 41.

[924] G. Gain, *C.R.* 1906, **143**, 283.

[925] Id., ib. 1907, **146**, 403.

[926] J. R. Cain and J. C. Hostetter, *J. Amer. Chem. Soc.* 1912, **34**, 274.

[927] G. Edgar, ib. 1916, **38**, 2369.

[928] E. Parisi, *Gaz.* 1926, **56**, 843.

[929] A. Morette, *C.R.* 1935, **200**, 134.

pentoxide with the trioxide, with oxalic acid, or with sulphur dioxide. It forms dark blue crystals with a rutile lattice, which dissolve easily, especially on heating, in acids or in alkalies. It is oxidized by concentrated nitric acid, or by heating in air, to the pentoxide.

A hydrated form $2\,VO_2, 7\,H_2O$ (or $V(OH)_4, 1{\cdot}5\,H_2O$) can be obtained as a grey precipitate by adding sodium carbonate to a solution of the oxychloride $VOCl_2$ in water, or to a solution of the dioxide in sulphuric acid. Another form, VO_2, H_2O, or $VO(OH)_2$, was got by Gain[924] by the hydrolysis of a solution of the sulphite, as a pale red powder. The supposed isomeric green form[925] of this last compound has been shown[928] not to exist.

Vanadites (*or Hypovanadates*)

These are few and rather unstable. They are all derived from condensed forms of the acid, and are nearly all of the type $M_2V_4O_9$. They are yellow or brown, and the alkaline salts are all very soluble in water, giving brown solutions.[930]

Tetrahalides

Vanadium forms a tetrafluoride and a tetrachloride, but as with the pentavalent compounds the majority of the tetravalent halide derivatives contain the vanadyl group VO'', which is here divalent.

Vanadium Tetrafluoride[931]

This can be made by the action of hydrogen fluoride on the tetrachloride VCl_4 at a low temperature; the reaction begins at $-80°$ and is completed at the ordinary temperature. It is a very hygroscopic brown powder, which in air or with water changes to a blue liquid. It gives a green solution in acetone, and a greenish-blue in acetic acid. It is slightly soluble in silicon tetrachloride, alcohol, and chloroform, but is insoluble in most inactive organic solvents. On heating it begins to decompose without melting at 325°, giving off the pentafluoride and leaving the trifluoride behind; this is the only way in which the pentafluoride has been prepared.

Vanadium Tetrachloride, VCl_4

This can be made in many ways: by passing the vapour of the oxytrichloride $VOCl_3$ with chlorine over red-hot charcoal, or that of carbon tetrachloride over vanadium pentoxide at 500-600°[933,935]: or by the action of chlorine on the metal, the nitride, or the silicide. To avoid the presence of the oxychlorides $VOCl_3$ and $VOCl_2$, it should be made from materials which are free from oxygen, best by passing air-free chlorine

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[930] J. Koppel and R. Goldmann, *Z. anorg. Chem.* 1903, **36**, 281.

[931] O. Ruff and H. Lickfett, *Ber.* 1911, **44**, 2539.

[932] A. T. Mertes, *J.A.C.S.* 1913, **35**, 671.

[933] O. Ruff and L. Friedrich, *Z. anorg. Chem.* 1914, **89**, 279.

[934] A. G. Loomis and H. Schlundt, *J. Phys. Chem.* 1915, **19**, 734.

[935] S. Bodforss, K. J. Karlsson, and H. Sjödin, *Z. anorg. Chem.* 1935, **221**, 382.

over ferrovanadium (the technical alloy FeV) in a combustion furnace.[932] The tetrachloride distils over while the less volatile ferric chloride remains behind, and the last of it can be removed by dissolving the vanadium tetrachloride in carbon disulphide, in which ferric chloride is insoluble.

Vanadium tetrachloride is a dark red oily liquid of density 1·84, which boils at 154°[930,933] (149·7°/731 mm.),[936] freezes at −25·7°,[936] and has a dielectric constant of 3·05 at 25°.[934] Electron diffraction[937] gives a tetrahedral structure with V—Cl 2·03 A (theory 2·22). Its freezing-point in carbon tetrachloride shows[936] that at this low temperature (about −23°) it is dimeric. It is an unstable substance. At the ordinary temperature it breaks up very slowly into the trichloride and chlorine; after several months in a sealed tube it was found that there was a high pressure of chlorine, and that scarcely any tetrachloride was left.[933] (Uranium pentachloride, antimony pentachloride, and iodine trichloride seem to behave in the same way.) This change is to be expected from the heats of formation (from the metal and chlorine gas) of the halides of vanadium, which are as follows:[933]

	VCl_2	VCl_3	VCl_4
	147±4.	187±8.	165±4 k.cals.
or per V—Cl	74	62	41

Thus the conversion of the tetrachloride into the trichloride and free chlorine evolves 187−165 = 22 k.cals. At higher temperatures, however (probably at 650° and above),[933] the tetrachloride is stable; at a red heat the trichloride changes into the tetrachloride and the dichloride.

The vapour density of the tetrachloride is that of VCl_4, but it very soon begins to fall owing to the dissociation into trichloride and chlorine. Water at once hydrolyses it to hydrochloric acid and the oxychloride $VOCl_2$.

A tetrabromide and tetraiodide are unknown (though oxybromides occur, p. 821).

Oxyhalides of Tetravalent Vanadium

These have the structure VO(hal)$_2$: the fluoride, chloride, and bromide are known.

Vanadyl Difluoride, VOF_2

This can be made[931] by heating the dibromide $VOBr_2$ in gaseous hydrogen fluoride, ultimately to a red heat.

It is a yellow powder which scarcely sublimes even at a red heat. It is insoluble in water, alcohol, ether, chloroform, and the ordinary organic solvents, but is slightly soluble in acetone.

Vanadyl Dichloride, $VOCl_2$

This is formed at once when water acts on the tetrachloride, and also from concentrated hydrochloric acid and vanadium pentoxide:

$$V_2O_5 + 6\,HCl = 2\,VOCl_2 + 3\,H_2O + Cl_2.$$

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[936] J. H. Simons and M. G. Powell, *J.A.C.S.* 1945, 67, 75.

[937] W. N. Lipscomb and A. G. Whittaker, ib. 2019.

The pure substance is best made either by passing a mixture of vanadyl trichloride vapour and hydrogen through a red-hot tube, or by the action of zinc on the vanadyl trichloride in a sealed tube at 400°.

Vanadyl dichloride $VOCl_2$ forms bright green crystals, which deliquesce in air and are decomposed by water. It crystallizes from concentrated hydrochloric acid as a hydrate (Berzelius).

Vanadyl Dibromide, $VOBr_2$

Though the tetrabromide is unknown, it is possible[938] to prepare the vanadyl bromide. If vanadium pentoxide is treated at a red heat with sulphur and chlorine, it gives vanadyl trichloride, $VOCl_3$. If bromine is used instead, a solid product is formed, from which vanadyl dibromide can be obtained. For this purpose mixed bromine and sulphur bromide S_2Br_2 vapours are passed over vanadium pentoxide in a boat heated at first to 500-600° and finally to 700-800°. A blackish-brown solid sublimes, which *in vacuo* at 260° loses bromine and S_2Br_2, and a pale yellow residue of nearly pure vanadyl dibromide $VOBr_2$ remains. If this is further heated *in vacuo*, it begins to sublime about 330°, but with considerable decomposition into bromine and the trivalent vanadyl monobromide VOBr, which stays behind.

Tetravalent Vanadyl Salts

Tetravalent vanadium forms no salts of the $V[X]_4$ type, but a considerable number of complex salts, and some salts which are apparently simple, containing the divalent vanadyl radical VO''.

'Simple' vanadyl Salts

These are almost confined to the sulphites and sulphates.

Sulphites.[939,940] Barium vanadate is reduced to the tetravalent state by sulphur dioxide, and from the liquid brown crystals separate, of the composition $3\ VO_2,\ 2\ SO_2,\ 4{\cdot}5\ H_2O$; they dissolve in water but slowly lose SO_2 in the air. Complex salts (perhaps of this acid) are known, of the formula $M_2O,\ 3\ VO_2,\ 2\ SO_2$, aq.

Sulphates. The sulphate $VO(SO_4)$ occurs in two forms, one soluble in water, and the other not. The latter is made by heating the acid salt $H_2SO_4,\ 2\ VOSO_4$ to 260° with concentrated sulphuric acid. It is a grey-green crystalline powder. If it is heated with water it is converted into a blue soluble form, which slowly hydrolyses, with separation of green dioxide VO_2, aq.

Recent work[939] on the system $VO_2,\ SO_3,\ H_2O$ at 30° shows that VO_2, SO_3, (or $[VO]SO_4$) occurs with 0, 3, and 5 H_2O; equilibrium in the system may take as much as two years to establish itself.

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[938] O. Ruff and H. Lickfett, *Ber.* 1911, **44**, 2534.

[939] C. S. Rohrer, O. E. Lanford, and S. J. Kiehl, *J.A.C.S.* 1942, **64**, 2810.

[940] G. A. Barbieri, *Atti R.* 1915, [5] **24**, 1; G. Canneri, *Gaz.* 1926, **56**, 637, 901.

Complex Salts of Tetravalent Vanadium

These are all vanadyl (VO″) derivatives, and nearly all have four links to the vanadium in addition to the oxygen link, so that if the latter is a double link, the co-ordination number is 6. They include open-chain compounds (such as the halides), and those in which the vanadium forms part of two rings (as the oxalato and diketone complexes).

Complex Vanadyl Fluorides

These are formed by the action of vanadium tetrafluoride on an aqueous solution of an alkaline fluoride. They are mostly of the type $M_2[VOF_4]$, $2\ H_2O$, but the potassium salt is anhydrous, and the ammonium salt has the unusual composition $(NH_4)_3[VOF_5]$. Its crystal structure is unknown.

Complex Chlorides

These are very soluble in water, but they can be made in alcohol, by using organic bases. The pyridine and quinoline salts have been made.[942] Each of these bases gives two salts, a blue one of the type $(pyH)_2[VOCl_4]$, aq., and a green one of the type $(pyH)_4[VOCl_6]$; the covalency of 7 or 8 which the last formula requires is beyond the covalency limit of vanadium, so probably the salt is really an aggregate.

Complex thiocyanates, of the type $M_2[VO(SCN)_4]$ aq., are easily formed[941]; examples are NH_4, $5\ H_2O$: K, $5\ H_2O$; they are blue.

Sulphito-complexes[939,940] are readily made by adding sulphur dioxide and an alkaline sulphite to a solution of a vanadate. They form two series, the first, which is green, of a simple type $M_2[VO(SO_3)_2]$, aq., and the second more complex, M_2O, $2\ VO_2$, $3\ SO_2$, aq., which is blue.

Sulphato-complexes[940,943,946] like the sulphites occur in a single form of the type $M_2[VO(SO_4)_2]$, which is dark blue, and in a multiple form, which is pale blue, of the type $M_2[V_2O_2(SO_4)_3]$. In the dry state the salts are fairly stable, but above 300° they break up into a mixture of pentavalent and trivalent vanadium compounds.

Oxalato-complexes[941] are formed with great readiness, and are of two types, corresponding exactly to the sulphates, (1) $(NH_4)_2[VO(C_2O_4)_2]$, $2\ H_2O$; and (2) $M_2[V_2O_2(C_2O_4)_3]$, aq. (NH_4 8·5 aq.: K 4 aq.). Both are blue; they are unusually stable: the solution gives no reactions for oxalate ion in the cold.

Malonato-complexes.[947] If a solution of ammonium vanadate is heated with malonic acid it is reduced to the tetravalent state, and if ammonium carbonate is added the malonato-compound $(NH_4)_2[VO(C_3H_2O_4)_2]$ separates as a blue tetrahydrate. This can be dehydrated to give successively

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[941] J. Koppel and R. Goldmann, *Z. anorg. Chem.* 1903, **36**, 281.

[942] J. Koppel, R. Goldmann, and A. Kaufmann, ib. 1905, **45**, 345.

[943] G. Gain, *C.R.* 1906, **143**, 1154.

[944] G. T. Morgan and H. W. Moss, *J.C.S.* 1913, **103**, 78.

[945] G. A. Barbieri, *Atti. R.* 1914, [5], **23**, ii. 408.

[946] A. Rosenheim and Hsin Yü Mong, *Z. anorg. Chem.* 1925, **148**, 25.

a violet trihydrate, a violet-pink monohydrate, and a pale violet anhydrous salt. The free acid forms blue-violet deliquescent crystals.

Many of these malonato-salts have been made, all remarkable for the number of hydrates they form and the diversity of their colours.

Complex citrates are also known.[940]

Salicylato-complexes[945-6]

These are of the type $M_2[VO(OC_6H_4COO)_2]$, aq. (e.g. NH_4, 3 aq.; K, 3 aq.). They are white or pale yellow solids which give a green solution in water. They are fairly stable; they can be recrystallized from water, and are not decomposed by dilute alkali. That they are ring-compounds is shown by the fact that meta- and para-hydroxy-benzoic acids do not form such salts.

Catechol complexes[946] are readily obtained from alkaline solutions of tetravalent vanadium. They all contain 'catechol of crystallization', which is a common phenomenon with catechol derivatives[948]; they are pale brown substances, all of the type $M_2[VO(C_6H_4O_2)_2]$, $C_6H_6O_2$, x H_2O.

β-Diketone Complexes

These were obtained by Morgan and Moss[944]; (1) by the air-oxidation of the diketone derivative of trivalent vanadium (VA_3), or (2) more conveniently by precipitating a solution of the oxy-dichloride $VOCl_2$ with alkali, and dissolving the precipitated oxide $VO(OH)_2$ in a warm alcoholic solution of the diketone. The products are all vanadyl-bis-diketones VOA_2.

The acetylacetone derivative VOA_2 forms green crystals, soluble in benzene, chloroform, or hot alcohol, but not in water or dry ether. Rosenheim[946] has obtained it in a hydrated form. By treating vanadyl sulphate $VOSO_4$ with acetylacetone he got fine blue-green crystals of the composition VOA_2, H_2O; this water no doubt completes the co-ordination number of 6, as in VA_3 (p. 832). If so, the vanadyl link must be $V\rightarrow O$ rather than $V{=}O$, or the water would not be needed. It is insoluble in water, but easily soluble in alcohol, ether, benzene, or chloroform, from which it can be crystallized, without losing its water, which is only lost with complete decomposition on melting. If the hydrate is boiled in ether with ammonia or an amine, the water is displaced by one molecule of the amine to give a compound VOA_2,B, where B = ammonia, pyridine, or quinoline.

Rather similar complexes are formed as lakes by tetravalent vanadium with hydroxy- and amino-azo dyes; they are fairly stable, and are all 6-covalent.[949]

TRIVALENT VANADIUM

Trivalent vanadium is easily obtained by reducing the higher oxides: for example, from the pentoxide by the action of carbon monoxide, or of carbon at 1,000°,[976] or of hydrogen iodide (and to some extent the

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[947] W. Schramm, ib. 1927, **161**, 231.

[948] R. F. Weinland and W. Denzel, *Ber.* 1914, **47**, 749, 2244.

[949] H. D. K. Drew and F. G. Dunton, *J.C.S.* 1940, 1064.

bromide[959,965]): by heating in hydrogen, or in solution by electrolytic reduction. For the redox potential V^{iii}/V^{iv} see Jones.[979–81]

The terminology is not very clear, but commonly the trivalent compounds are called vanadic, and the divalent vanadous; this usage may be adopted here.

In the trivalent state vanadium behaves as a metal, and in general resembles other trivalent metals such as aluminium, chromium, iron, and cobalt; the sesquioxide has no acidic character whatever, and is quite insoluble in aqueous alkalies, behaving in this respect like ferric iron, and unlike either aluminium or chromium. The trihalides are considerably hydrolysed by water, like ferric chloride.

Trivalent vanadium forms a certain number of simple salts, which in water show the characteristic green colour of the vanadic ion V^{+++}. It also forms a large number of complex salts, which unlike the pentavalent and tetravalent vanadium complexes are never vanadyl, but are always derived from VX_3; the co-ordination number is nearly always 6 but sometimes 4. It can also form ammines, usually of the type of $[V(NH_3)_6]X_3$; but the affinity of trivalent vanadium for nitrogen is no greater than that for oxygen, and so these ammines, like the ammines of aluminium or ferric iron, and in sharp contrast to those of trivalent chromium or cobalt, are decomposed by water.

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[950] E. Petersen, *Ber.* 1888, **21**, 3257: *J. Prakt. Chem.* 1889, [2] **40**, **44**, 194, 271.

[951] A. Piccini and G. Giorgis, *Gaz.* 1892, I. 55.

[952] A. Piccini, *L'Orosi*, 1896, **19**, 325 (C. 97, I. 223).

[953] J. Locke and G. H. Edwards, *Am. Chem. J.*, 1898, **20**, 594.

[954] A. Piccini and N. Brizzi, *Z. anorg. Chem.* 1899, **19**, 394.

[955] A. Cioci, ib., **19**, 308. [956] A. Stähler, *Ber.* 1904, **37**, 4405.

[957] Id., ib. 4411. [958] A. Bültemann, *Z. Elektrochem.* 1904, **10** 141.

[959] F. A. Gooch and R. W. Curtis, *Am. J. Sci.* 1904, [4], **17**, 41.

[960] T. F. Rutter, *Z. anorg. Chem.* 1907, **52**, 368.

[961] N. Costatchescu, Jassy, 1910, **6**, 117, (C. 10. ii. 1283).

[962] E. Renschler, *Z. Elektrochem.* 1912, **18**, 137.

[963] G. A. Barbieri, *Atti R.* 1915, [v], **24**, i. 435.

[964] Id., ib. 1916, [v], **25**, i. 723.

[965] G. Edgar, *J.A.C.S.* 1916, **38**, 2369.

[966] G. Scagliarini and G. Tartarini, *Gaz.* 1923, **53**, 876.

[967] J. Meyer and R. Backa, *Z. anorg. Chem.* 1924, **135**, 177.

[968] G. Scagliarini and A. Airoldi, *Gaz.* 1925, **55**, 44.

[969] J. Meyer and E. Markowicz, *Z. anorg. Chem.* 1926, **157**, 211.

[970] W. Schramm, ib. 1927, **161**, 231.

[971] A. Rosenheim, E. Hilzheimer, and J. Wolff, ib. 1931, **201**, 162.

[972] L. Passerini and R. Pirani, *Gaz.* 1932, **62**, 279. [973] R. Pirani, ib. 380.

[974] H. M. Spencer and J. L. Justice, *J.A.C.S.* 1934, **56**, 2306.

[975] S. Bodforss, K. J. Karlsson, and H. Sjödin, *Z. anorg. Chem.* 1935, **221**, 382.

[976] A. Morette, *C.R.* 1935, **200**, 134.

[977] Id., ib. 1938, **207**, 1218.

[978] E. Hoschek and W. Klemm, *Z. anorg. Chem.* 1939, **242**, 63.

[979] G. Jones and J. H. Colvin, *J.A.C.S.* 1944, **66**, 1563.

[980] G. Jones and W. A. Ray, ib. 1571.

[981] G. Jones and J. H. Colvin, ib. 1573.

Vanadium Sesquioxide, V_2O_3

This is best made by reducing the pentoxide with hydrogen, or with carbon monoxide at a high temperature.[974,976] It is a black almost infusible powder. It is slowly oxidized by air in the cold to the blue dioxide, and if it is heated in air it catches fire. It can form solid solutions and crystal aggregates with the dioxide.[978]

Vanadic Hydroxide, $V(OH)_3$

This can be got in a more or less hydrated form as a green flocculent precipitate, when ammonia or alkalies are added to a solution of vanadium trichloride, or when the tetravalent vanadyl dichloride $VOCl_2$ is reduced with sodium amalgam in an atmosphere of hydrogen, and precipitated with ammonia. It is very unstable and rapidly absorbs oxygen from the air: but if air is excluded it dissolves in acids to form vanadic salts.

Its behaviour is in general like those of trivalent iron and chromium, especially iron; but it differs markedly from both in its tendency to oxidize.

Halides of Trivalent Vanadium

Vanadium forms a trifluoride, a trichloride, and a tribromide: a triiodide has recently been described; but the affinity of the halogen for the vanadium falls off rapidly as its atomic number increases. It also forms an oxychloride and an oxybromide, but no oxyfluoride has yet been prepared.

Vanadium Trifluoride, VF_3

This was made[931] by Ruff and Lickfett by passing hydrogen fluoride over vanadium trichloride at 600° for 6 to 8 hours: this is the only case where the replacement by this method of other halogens by fluoride needs a high temperature; with vanadium tetrachloride, oxytrichloride $VOCl_3$, and oxydibromide $VOBr_2$ the reaction goes at the ordinary temperature. The trifluoride can also be made by heating the tetrafluoride VF_4 in nitrogen for several hours at 600°, when the pentafluoride VF_5 distils over and the trifluoride remains behind.

Vanadium trifluoride VF_3 is a greenish-yellow solid, which melts above 800°, and sublimes only at a bright red heat. The anhydrous compound is almost insoluble in water, although it is capable of forming a trihydrate. It is quite insoluble in all organic solvents (alcohol, ether, acetone, toluene, chloroform, carbon disulphide, etc.) and in liquid anhydrous inorganic chlorides.

The trihydrate VF_3, $3\ H_2O$ can be made by the electrolytic reduction of a solution of vanadium pentoxide in aqueous hydrofluoric acid.[966] It loses one molecule of water at 100°. It seems to dissolve to some extent in water, and no doubt forms auto-complexes in the solution, since this gives a green precipitate when treated with a solution of a magnesium salt.

Vanadium Trichloride, VCl_3

This can be made by passing gaseous hydrogen chloride over powdered vanadium at 300–400°,[967] or by heating the oxytrichloride $VOCl_3$ or the tetrachloride, or a mixture of the two, with sulphur at 150°, and finally distilling off the excess of sulphur at 440°.[836] The best way[967] is to make the tetrachloride by the action of chlorine on ferrovanadium and heat this in a current of an indifferent gas.

Vanadium trichloride is a practically non-volatile violet solid; if it is heated in nitrogen to a dark red heat a very small quantity sublimes in violet crystals, but nearly the whole breaks up into the dichloride and tetrachloride, this reaction, as well as the loss of chlorine from the tetrachloride, being reversible.

$$\begin{tikzcd} VCl_3 \arrow[r, shift left] & VCl_2 + VCl_4 \arrow[l, shift left] \arrow[d, shift left] \\ & VCl_3 + Cl_2 \arrow[u, shift left] \end{tikzcd}$$

Vanadium trichloride is very hygroscopic and excessively soluble in water, which must be carefully excluded in its preparation to prevent the formation of oxychlorides. It dissolves easily in alcohol or acetic acid, giving green or blue solutions, but is insoluble in ether,[975] chloroform, toluene, and carbon disulphide.

It can be recrystallized from water as a hexahydrate $VCl_3,6\,H_2O$,[956] also made by dissolving the trihydroxide in hydrochloric acid; very hygroscopic crystals, easily soluble in alcohol and ether; it corresponds to the violet chromic compound $CrCl_3, 6\,H_2O$.

Vanadium Tribromide, VBr_3

This can be made[938] in quantitative yield as a black sublimate by passing bromine vapour over vanadium carbide at 500–600°. Unlike the trichloride it can be made directly[967] by the action of the halogen on powdered vanadium, the reaction starting at 40°. On heating, vanadium tribromide sublimes unchanged, and does not change into the divalent and the tetravalent halides as the trichloride does.[938]

Vanadium tribromide forms a hexahydrate $VBr_3,6\,H_2O$, which is very like the hydrated chloride; it is easily soluble in alcohol, ether, and water; it is very hygroscopic, and is hydrolysed by water.[953,967]

Vanadium Tri-iodide, VI_3

This is the least stable of the tri-halides. All attempts to prepare it by the action of dry or dissolved iodine on powdered vanadium or ferrovanadium were unsuccessful.[967] But vanadium and iodine react *in vacuo* at 150° to give the tri-iodide as a brownish-black powder.[977] This decomposes reversibly above 280° into vanadium di-iodide VI_2 and iodine.

Vanadium tri-iodide is soluble in water and in alcohol; if heated in air it begins to oxidize at 130°. It reacts with chlorine to give vanadium tetrachloride VCl_4 and iodine trichloride.

A hexahydrate $VI_3, 6\,H_2O$ is made by electrolytically reducing a solution of vanadium pentoxide in aqueous hydriodic acid, and evaporating the solution at 0°.[954] It forms green deliquescent crystals, soluble in alcohol. The substance cannot be recrystallized without decomposition even from concentrated hydriodic acid at the ordinary temperature.

Attempts to make anhydrous vanadium tri-iodide by the action of iodine on vanadium nitride or vanadium pentoxide had no success.[954]

[*Vanadyl Monofluoride*, VOF

Though vanadium trifluoride is the stablest of the trihalides, the vanadyl derivative VOF has not been obtained.]

Vanadyl Monochloride, VOCl

This can be made by passing a mixture of hydrogen and vanadyl dichloride $VOCl_2$ vapour through a red-hot tube. It is best prepared[903] by heating the trichloride VCl_3 to 700° in a stream of carbon dioxide; the tetrachloride distils over, a very small quantity of trichloride sublimes away, and there remains a mass of brown crystals of the monochloride VOCl, with a golden yellow sublimate above it; the oxygen is, of course, derived from the reduction of the carbon dioxide to monoxide.

Vanadyl monochloride VOCl is a loose brown crystalline powder, dissolving with great difficulty in water, but readily in nitric acid.

Vanadyl Monobromide, VOBr

This is made,[938] like the chloride, by heating vanadyl dibromide *in vacuo*, but the attachment of the bromine being weaker, 4–5 hours at 360° is sufficient. The oxybromide forms violet octahedral crystals. *In vacuo* at 480° or above it slowly changes into the black tribromide which sublimes away, and the sesquioxide V_2O_3 which remains behind.

Vanadyl monobromide is slightly soluble in water, acetic anhydride, ethyl acetate, and acetone; it is quite insoluble in alcohol, ether, acetic acid, chloroform, toluene, and carbon tetrachloride.

Simple Salts of Trivalent Vanadium

The tendency of the trivalent vanadium atom to form complexes is very strong, and most of its derivatives with acids are complex. Many of those which have the composition of simple salts are probably chelate, and so are complex in the proper sense, in that the covalency of the vanadium in them is greater than its valency. The apparently simple vanadic salts are the sulphates, and certain derivatives of organic acids.

Vanadic Sulphates

The nature of these compounds is obscure.[957,962,969] They include the alums $M'V(SO_4)_2, 12\,H_2O$, which are mere double salts, the simple sulphates, $V_2(SO_4)_3$, aq., and an acid sulphate or complex acid $HV(SO_4)_2$, aq.

The alums are remarkable for crystallizing from strongly acid solutions in blue crystals (green or blue is the usual colour of vanadic salts), but from a nearly neutral solution in red crystals.[958] The red colour was shown by Meyer[969] to be due to a superficial adsorbed layer of the hydroxide $V(OH)_3$. In the same way ferric nitrate crystallizes from concentrated nitric acid in amethyst crystals, but is colourless from water, the violet being masked by a trace of colloidal ferric hydroxide. The vanadic alums are considerably hydrolysed by water; the solubilities in grammes per 100 gr. of water at 10° are[952]:

K 198·4; Rb 2·56; Cs 0·464; NH_4 39·8; Tl′ 11·1.

The 'simple' sulphates of trivalent vanadium are of unknown structures,[969] but certainly largely complex. Electrolytic reduction of $V^{iv}O\cdot SO_4$[960] will give $V_2(SO_4)_3$, aq., and the acid salt $HV(SO_4)_2$, which occurs with 8, 6 (2 forms), 5, and 4 (2 forms) H_2O. But sulphates (of this type) can also be made by the addition of sulphuric acid to a solution of (trivalent) vanadic acetate in glacial acetic acid, which are quite different in behaviour and even in colour from the others.[969] The structure of these compounds is still very uncertain, and there is good evidence (including that of the colour) that at least two different forms can exist in solution.

Two series of sulphates are also formed by trivalent titanium, chromium, and iron. The anhydrous normal sulphate $V_2(SO_4)_3$ is obviously complex; like the corresponding titanic, chromic, and ferric compounds it refuses to dissolve in water or sulphuric acid, and will only do so in boiling concentrated nitric acid.

The pale green salt $V_2(SO_4)_3, 3\,H_2O$ closely resembles the chromium compound in colour and other properties.

Organic Salts of Trivalent Vanadium. Apparently simple formates and acetates are known.[964,971] $V(O\cdot CO\cdot CH_3)_3, H_2O$ forms large grey-green crystals, and is a fairly definite and stable salt, but a variety of complicated acetates exist as well.

Complexes of Trivalent Vanadium

Like all trivalent metals, and especially those with smaller atoms, trivalent vanadium readily forms complexes, some positive (cationic), some negative (anionic), and a few neutral (mainly chelate). The anionic complexes are much more numerous and varied than the cationic, and (which is partly the cause of this) the affinity for nitrogen is no stronger than that for oxygen, so that the ammines are immediately decomposed by water. In both these points trivalent vanadium resembles aluminium and iron, and differs very markedly from chromium and cobalt. The co-ordination number is nearly always 6; it never exceeds this (which is its covalency maximum), and it is not certain that it ever falls below it.

Cationic Complexes

In these, so far as they are known, the element is always attached either to oxygen or to nitrogen. The oxygen-complexes include the hydrated vanadic ion; in solution this is presumably $[V(OH_2)_6]^{+++}$, which is also found in the hexahydrated chloride, bromide, and sulphate. Further evidence of the affinity of trivalent vanadium for oxygen is shown in the complex fluorides, where a water molecule can replace a halogen atom in the 6-fold complex.

The interaction of vanadium trichloride with ammonia is peculiar. In water there is no action, because the affinity for nitrogen is not strong enough to overcome that for oxygen. In the dry state gaseous ammonia acts on anhydrous vanadium trichloride even at −80° to give vanadium nitride VN and ammonium chloride.* If liquid ammonia is poured on to the dry trichloride and the excess allowed to boil away, the red-brown ammine $[V(NH_3)_6]Cl_3$ remains in a quantitative yield. A similar bromide and nitrate can be made. In these compounds the ammonia is much less firmly held than with trivalent chromium or cobalt; it is easily and quantitatively expelled by sodium hydroxide. In the air the ammine slowly turns white owing to its oxidation to the vanadate:

$$[V(NH_3)_6]Cl_3 + O + 2\,H_2O = NH_4VO_3 + 3\,NH_4Cl + 2\,NH_3.$$

In moist air it turns green (the colour of the vanadic ion V^{+++}), presumably through the formation of the aquo-complex. It is insoluble in cold water, alcohol, or ether; in hot water it is hydrolysed; in dilute hydrochloric acid it readily dissolves to a green solution, soon turning blue from oxidation.

Vanadium trichloride will also take up alkylamines (from 1 to 4 molecules to every vanadium at 30° and 1 atm. pressure), if their vapour is passed over the dry halide[975]; the products are usually reddish-brown.

Cationic complexes are formed (through oxygen or nitrogen) by urea[963]; they are all of the type $[V(CO(NH_2)_2)_6]X_3$, and are all, like the ferric urea complexes, much less stable than their chromic analogues. They are bluish-green.

Anionic Complexes

Those that are formed through oxygen are practically always chelate (ato, diketone, etc.); the open-chain anions consist mainly of the complex halides, with a few cyanides and thiocyanates.

Complex Halides

These are formed by fluorine, and less readily by chlorine. Apart from a small number of derivatives of the oxyfluoride VOF, such as the

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* This reaction is common with non-metallic halides, but not with metallic.

compound $Zn[VOF_3]$, 7 H_2O described by Piccini and Giorgis,[951] they are all formed from the binary trihalides. They are of three types, with 4, 5, and 6 atoms of halogen in the anion, but there is very strong evidence to show that the co-ordination number is always made up to 6 by the addition of water molecules.

Complex Fluorides

These are numerous, and of all three types.[950-1] The salts of monovalent cations like the alkali metals are all of the type $M_3[VF_6]$ (anhydrous), or M_2VF_5, H_2O, or $MVF_4, 2H_2O$: the sum of the fluorine atoms and the water molecules always comes to 6. In the pentafluorides X-ray analysis has shown that the water molecule takes the place of one of the fluorines in the octahedral complex.[972-3] Another type which is formed by divalent metals (cobalt, nickel, zinc, and cadmium) is $M''VF_5$, 7 H_2O, one of the 7 water molecules obviously being in the anion. The ammonium, potassium, rubidium, and caesium salts of the series $M[VF_4(H_2O)_2]$ have been made; they are green, and very fairly stable; they can be recrystallized from dilute hydrofluoric acid; their solutions in water give no tests for fluorine ion. The solubility of the alkaline salts increases from potassium to caesium, which suggests that the acid $H[VF_4(H_2O)_2]$ is weak.

Aniline gives[961] two salts, $(C_6H_5NH_3)_3[VF_6]$, greenish, easily decomposed, and only stable in an atmosphere of hydrogen fluoride free from moisture, and $(C_6H_5NH_3)_2[VF_5(OH_2)]$, deeper green, soluble in water, and rather more stable.

Complex Chlorides

These are few, and so far as they are known they all seem to be of the one type $M_2[VCl_6(OH_2)]$. The rubidium salt[957] forms crimson crystals, only slightly soluble in water or alcohol; it is slowly decomposed by water. The ammonium, potassium, caesium, and magnesium salts appear to be similar, and have the same colour.

Complex Cyanides

A double cyanide $K_3V(CN)_6$ was made by Locke and Edwards[953] by precipitating the mixed solutions of vanadic chloride and potassium cyanide with alcohol. It forms large crystals, easily soluble in water but insoluble in alcohol. The aqueous solution soon decomposes and deposits the simple cyanide $V(CN)_3$ [this substance does not seem to be otherwise known], but it is more stable in presence of excess of potassium cyanide. Alkalies precipitate vanadic hydroxide $V(OH)_3$ on boiling. The free acid, and the ammonium and sodium salts, could not be isolated.

These authors point out that the stability of the salts $K_3[M(CN)_6]$ increases in the order $V < Cr < Mn < Fe < Co$.

Complex Thiocyanates

These are similar in composition to the cyanides. The potassium salt $K_3[V(CNS)_6]$,[958] 4 aq., forms dark red very soluble crystals, only stable in presence of excess of potassium thiocyanate, but much more slowly oxidized by the air than other vanadic salts. For other thiocyanates see references [955,966]. The chemical reactions and the freezing-points of the solutions indicate that the salts are completely dissociated in solution into the ions M^+, V^{+++}, and CNS^-.

These salts, even when hydrated, are soluble in ethyl acetate, and can be extracted with it.[971] They all lose the whole of their water at 100°, and become pale brown. With pyridine they will give brick-red crystals of $(pyH)[Vpy_2(CNS)_4]$, soluble in acetone and many other organic solvents, but oxidizing in air extraordinarily easily. The two pyridine molecules are obviously in the complex anion. Similar salts of the composition $M[M(NH_3)_2(CNS)_4]$ of trivalent molybdenum, chromium, and iron are known.

Complex Formates. A sodium salt $Na_3[V(HCOO)_6]$ in transparent blue plates has been obtained.[964,971]

Sulphato-Compounds. A pyridinium salt of the composition

$$(pyH)[V(SO_4)_2],\ py, 3\,H_2O$$

in emerald green plates has been made.[968]

Oxalato-compounds

These can be made[954,958] by the electrolytic reduction of a solution of vanadium pentoxide in presence of oxalic acid and an alkaline oxalate. They have the composition $M_3[V(C_2O_4)_3], 3\,H_2O$, corresponding exactly to the chromioxalates, with which they seem to be isomorphous. But they are much less stable than their chromic analogues, and the oxalate is completely precipitated from their solutions by ammonia and calcium chloride. The ammonium and potassium salts are green.

Similar complex malonates seem to occur.[970]

Salicylato-complexes

If vanadium trichloride is treated with salicylic acid and barium chloride is then added, a barium salt $Ba[HO \cdot V(OCO \cdot C_6H_4O)_2(H_2O)]$ separates in yellowish-green crystals. Similar strontium ($6\,H_2O$) and calcium ($4\,H_2O$) salts are known. This 'basic' form of complex is very unusual, but there are other examples of it, though not among the very stable ferric salicylato-complexes.

Catechol Complexes

These compounds are so extraordinarily easily oxidized that they can only be made in an atmosphere of nitrogen. If a concentrated solution of vanadium trichloride is treated with catechol, and ammonia is added, a deep green solution is produced, which turns blackish-violet with the least trace of air. On cooling, grass-green crystals of the composition

$$(NH_4)_3[V(C_6H_4O_2)_3], 2\,H_2O$$

separate out, which can scarcely be dried without turning nearly black through oxidation.

The corresponding chromic and ferric salts are known.

The very easy oxidation of these trivalent vanadium complexes is in strong contrast to the behaviour of the tetravalent vanadium catechol complexes (p. 823).

Vanadic Derivatives of β-Diketones

In presence of sodium carbonate vanadic chloride acts on acetylacetone to give the compound VA_3, which forms dark green prisms insoluble in water but easily soluble in chloroform and benzene.[944] It melts at 185–90° and can be distilled in small quantities without decomposition. In moist air it readily goes to the tetravalent compound VOA_2. Rosenheim and his colleagues[971] have confirmed this work.

DIVALENT VANADIUM

The reduction potential of divalent vanadium is so high that most of its compounds can only exist in the absence of air and water, and accordingly few have been isolated; they are almost confined to the halides, the sulphate, and the complex sulphates and cyanides. In this vanadous state the element behaves as a divalent metal, and closely resembles divalent chromium, but is even more easily oxidized. It forms quite definite salts, the vanadous ion V^{++} having a pure violet colour. This ion has a discharge potential 0·1 or 0·2 volt higher than hydrogen ion, and so decomposes water fairly rapidly in neutral solution, especially in the presence of catalysts like platinum; a vanadous salt solution on addition of a trace of chloroplatinate at once evolves hydrogen with a brisk effervescence. In acid the reaction is not quicker, but actually much slower,[991] so that a strongly acid solution can be kept for some time; the ion must be oxidized much less rapidly than the hydroxide which is formed in neutral solution by hydrolysis; the same thing happens with ferrous salts, which are, however, always much more stable than vanadous.

Vanadous Oxide VO, *and Hydroxide*, $V(OH)_2$

This oxide does not exist,[995] and the hydroxide cannot be isolated because it is so extraordinarily easily oxidized, but it must be contained

[982] A. Piccini, *Z. anorg. Chem.* 1899, **19**, 204.

[983] A. Piccini and L. Marino, ib. 1902, **32**, 55.

[984] E. Petersen, *Ber.* 1903, **36**, 1911, *Z. anorg. Chem.* 1904, **38**, 345.

[985] W. Manchot and H. Fischer, *Ann.* 1907, **357**, 129.

[986] T. F. Rutter, *Z. anorg. Chem.* 1907, **52**, 368.

[987] O. Ruff and H. Lickfett, *Ber.* 1911, **44**, 506.

[988] O. Ruff and L. Friedrich, *Z. anorg. Chem.* 1914, **89**, 279.

[989] J. B. Conant and A. W. Sloan, *J.A.C.S.* 1923, **45**, 2466.

[990] J. B. Conant and H. B. Cutter, ib. 1926, **48**, 1016.

[991] J. Meyer and M. Aulich, *Z. anorg. Chem.* 1930, **194**, 278.

[992] F. Ephraim and E. Ammann, *Helv. Chem. Acta*, 1933, **16**, 1273.

[993] A. Morette, *C.R.* 1938, **207**, 1218.

[994] W. Biltz and A. Köcher, *Z. anorg. Chem.* 1939, **241**, 324.

[995] E. Hoschek and W. Klemm, ib. **242**, 63.

in the brown precipitate which is formed when an alkali is added to a vanadous solution; in organic acids this gives violet vanadous solutions, but it almost immediately evolves hydrogen and goes to the trivalent state.[991]

Vanadous sulphide, VS, is a black powder obtained by heating the sesquisulphide V_2S_3 in hydrogen[994] (see also above, p. 808).

Vanadous Fluoride, VF_2

This has not been isolated, but vanadium aluminisilicide $V_8Al_2Si_{13}$ reacts violently with aqueous hydrofluoric acid to give a reddish-violet solution, which from its colour must contain the difluoride, and which in air is at once oxidized to vanadium trifluoride.[985]

Vanadous Chloride, VCl_2

This can be made by passing a mixture of hydrogen and vanadium tetrachloride vapour through a red-hot tube, or better[987] by heating the trichloride in a stream of pure dry nitrogen to 800°, when the tetrachloride distils off, and the dichloride remains behind. Above 800° the tetrachloride reacts with the glass to form the vanadyl dichloride $VOCl_2$.[988]

The dichloride forms pale green leaflets which sublime only above 1,000°; they are not wetted by water, and at first float on it, dissolving only slowly (rather like chromous chloride) to give a violet solution, which soon turns green through oxidation, with evolution of hydrogen. The dichloride forms a blue solution in alcohol and a greenish-yellow one in ether, these differences of colour being presumably due to solvation. In air the dry salt remains unaffected for some time, and then slowly takes up moisture and oxygen to form a brown solution.

Vanadous chloride is an even stronger reducing agent than chromous chloride. Conant has shown[989,990] that it will reduce various organic compounds to free radicals; thus triphenyl carbinol in hydrochloric acid is converted into triphenyl-methyl, and 9-phenyl xanthylium chloride into Gomberg and Cone's phenyl-xanthyl.

Vanadous Bromide, VBr_2

This is not formed by heating the tribromide, which sublimes unchanged, but it can be made[992] by reducing vanadic bromide with hydrogen.

It forms light reddish-brown crystals. It gives a stable compound $VBr_2, 3\,NH_3$, but the structure of this is unknown.

Vanadous Iodide, VI_2[993]

Like the chloride (but unlike the bromide and fluoride) vanadic iodide loses iodine (reversibly) on heating; after 24 hours *in vacuo* at 400° the di-iodide VI_2 remains in rose-coloured plates. It begins to oxidize in air at 125–30°; it is soluble in water. At 650° it gives with hydrogen sulphide the sesquisulphide V_2S_3 and with phosphorus the phosphide VP.

Vanadous Sulphate, $VSO_4, 7\,H_2O$

This salt, which is violet, can be made by reducing either electrolytically or with sodium amalgam or zinc, a solution of vanadium pentoxide in sulphuric acid, and leaving it *in vacuo* over phosphorus pentoxide.[982-3,986,991] It is extremely easily oxidized; it cannot be kept unchanged even in the dry state in carbon dioxide; it evolves hydrogen with water, and reduces the salts of tin, copper, silver, gold, mercury, and platinum to the metals.[983] Like ferrous and chromous sulphates its solution will absorb nitric oxide. It is rather less readily oxidized in strongly acid solution, and then does not evolve hydrogen. Otherwise it behaves as a normal divalent sulphate; it forms mixed crystals dimorphically with the chromous and ferrous salts, and behaves as a vitriol.

Complex Salts of Divalent Vanadium

Only two series of these have been prepared, the sulphates (which are very doubtfully complex) and the cyanides.

Double Sulphates. The ammonium, potassium, and rubidium salts have been made from the component solutions.[982-3,991] They are all of the schönite type, $M_2V(SO_4)_2, 6\,H_2O$ (schönite is $K_2[Mg(SO_4)_2], 6\,H_2O$). They are violet or reddish-violet in colour, and rather more stable than the simple vanadous sulphate VSO_4, especially in presence of excess of acid.[991]

Complex Vanadocyanides[984]

The potassium salt is formed when excess of potassium cyanide solution is added to the vanadous solution obtained by reducing vanadic acetate $V(OCO\cdot CH_3)_3$ with potassium amalgam; it is precipitated on addition of alcohol. It forms brownish-yellow crystals; the composition is

$$K_4[V(CN)_6], 3\,H_2O,$$

corresponding exactly to that of the ferrocyanide $K_4Fe(CN)_6, 3\,H_2O$. It gives precipitates with the heavy metals in the same way as a ferrocyanide, but differs from the latter in being very readily oxidized, so much so that all work on it must be carried out in the absence of air.

NIOBIUM (COLUMBIUM)

NIOBIUM is much more like tantalum than vanadium (it was aptly named after Niobe, the daughter of Tantalus); the two practically always occur in nature together, and in fact they were only clearly distinguished after some 50 years of very careful work, in the course of which a series of spurious elements, such as pelopium, ilmenium, neptunium, and dianium were eliminated (see Chilesotti).[1000]

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[996] F. Russ, *Z. anorg. Chem.* 1902, **31**, 42.

[997] R. F. Weinland and L. Storz, *Ber.* 1906, **39**, 3056.

[998] Id., *Z. anorg. Chem.* 1907, **54**, 223.

[999] W. v. Bolton, *Z. Elektrochem.* 1907, **13**, 145.

[999a] F. H. Horn and W. T. Ziegler, *J.A.C.S.* 1947, **69**, 2762.

[1000] Abegg, *Handbuch*, Bd. III, Abt. 3 (1907), pp. 789–92.

The main characteristics of niobium and tantalum as compared with vanadium are the increasing instability of the lower valencies, the greater weakness of the acids derived from the pentoxides (both normal relations in an A subgroup), and the fact that the binary halides, which with vanadium are far less important than the oxyhalides, are equally important with niobium and more so with tantalum.

Our knowledge of the lower valencies of niobium is very imperfect, but it is clear that they are far less stable than those of vanadium. Divalent niobium probably occurs in the oxide NbO but not elsewhere; of the trivalent and tetravalent compounds the only one that has been isolated apart from the oxides and sulphides (which are unsatisfactory evidence owing to their large and unknown molecular weights, and their ambiguous structures) is the trichloride $NbCl_3$, a black non-volatile solid, insoluble in all solvents except those which oxidize it. Niobium dioxide NbO_2, the only compound of tetravalent niobium that has been isolated, is also an insoluble black powder, which, though a definite compound, may be composed of pentavalent and trivalent niobium atoms, with no true tetravalent atoms at all.

There is, however, no doubt that niobium can assume a valency (or valencies) lower than 5; the most conclusive evidence is[1007-8] that by the electrolytic reduction of niobic acid a series of coloured solutions of strong reducing power can be obtained, in which the valency can be determined by the quantitative oxidation of the niobium.

Metallic Niobium

The pure metal is difficult to obtain, but it can be made[999] by reducing the pentoxide with aluminium thermite, and driving off the excess of aluminium by heating the product *in vacuo*. It is a grey fairly hard metal, melting at 1,950°, rather above vanadium but far below tantalum (see table, p. 804). It combines with oxygen only slowly and at a high temperature, but readily with the halogens. It dissolves in no acid but hydrofluoric, not even in aqua regia, assuming the passive state with great ease.[1001]

Niobium and Hydrogen

Metallic niobium absorbs hydrogen on heating, and if cooled in it at 1 atm. it takes up 1·12 per cent. (NbH would contain 1·07 per cent. H).[990] No definite hydride has been isolated. The solid is superconducting at low temperatures.[999a]

[1001] W. Muthmann and F. Fraunberger, *Sitz.-Ber. Bayr. Akad.* 1904, ii. 226.

[1002] G. Brauer, *Z. anorg. Chem.* 1941, **248**, i.

[1003] C. W. Balke and E. F. Smith, *J.A.C.S.* 1908, **30**, 1637.

[1004] W. M. Barr, ib., 1908, **30**, 1668.

[1005] O. Ruff and J. Zedner, *Ber.* 1909, **42**, 492.

[1006] O. Ruff and E. Schiller, *Z. anorg. Chem.* 1911, **72**, 329.

[1007] F. Ott, *Z. Elektrochem.* 1912, **18**, 349.

[1008] A. Stähler, *Ber.* 1914, **47**, 841.

Niobium and Carbon

Niobium carbide, NbC, can be made by heating a mixture of the powdered metal and carbon for half an hour at 1,700-2,100°.[1015] It is a pale yellow-brown mass, which melts at 3,500°.[1014]

Niobium Nitride, NbN

This can be made by reducing the pentoxide in hydrogen to a lower oxide, and heating a mixture of this with carbon in nitrogen,[1011] or by heating the metal in nitrogen to 1,100-1,200°.[1015]

It is a pale grey substance insoluble in hydrochloric, nitric, or sulphuric acid, or in aqua regia, even on boiling. It becomes a superconductor at 15·2° K., the highest transition temperature known for any superconductor.[999a] If it is heated in air it oxidizes easily to niobium pentoxide Nb_2O_5; if it is heated with soda-lime it evolves ammonia. It melts at 2,300° with considerable dissociation. Like VN this has a sodium chloride lattice, and is probably formed of the ions Nb^{+++} and N^{---} (see pp. 663 and 807).

A nitride Nb_2N can be made by heating NbN with an equivalent amount of niobium; X-ray powder photographs show it to have an interstitial type of structure with a close-packed hexagonal lattice; the density is 8·08.[1016]

Niobium and Sulphur

These compounds resemble the sulphides of vanadium; Biltz and Köcher[1020] have examined the system, using pure materials, by phase rule methods combined with measurements of dissociation tension and X-ray diagrams. They sum up their results by saying that 'in the language of the older chemistry' niobium forms a sulphide Nb_2S_3, which can further take up as much as 5 atoms of sulphur (giving NbS_4); it also forms a monosulphide NbS, which can dissolve as much as one atom of niobium per molecule, giving Nb_2S.

PENTAVALENT NIOBIUM

Niobium Pentoxide, Nb_2O_5

This can be made by dehydrating niobic acid (precipitated by dilute acid from a niobate solution) or by igniting the sulphide, nitride, or carbide in the air. It occurs in three forms, one of which is isomorphous with

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[1009] W. Biltz and A. Voigt, *Z. anorg. Chem.* 1921, **120**, 71.

[1010] C. Renz, *Helv. Chim. Acta*, 1921, **4**, 961.

[1011] E. Friederich and L. Sittig, *Z. anorg. Chem.* 1925, **143**, 307.

[1012] H. Funk and K. Niederländer, *Ber.* 1928, **61**, 249. [1013] Id., ib., 1385.

[1014] C. Agte and H. Alterthum, *Z. techn. Phys.* 1930, **11**, 182 (*B.C.A.* 1931, A. 170).

[1015] C. Agte and K. Moers, *Z. anorg. Chem.* 1931, **198**, 233.

[1016] G. Brauer, *Z. Elektrochem.* 1940, **46**, 397.

[1017] A. Rosenheim and E. Roehrich, *Z. anorg. Chem.* 1932, **204**, 342.

[1018] H. Funk, *Ber.* 1934, **67**, 1801.

[1019] S. J. Kiehl, R. L. Fox, and H. B. Hardt, *J.A.C.S.* 1937, **59**, 2395.

[1020] W. Biltz and A. Köcher, *Z. anorg. Chem.* 1938, **237**, 369.

tantalum pentoxide.[1002] It is a white powder, insoluble in water, but dissolving both in fused potassium bisulphate $KHSO_4$ and also in potassium hydroxide solution; this shows that it is amphoteric in character, though as an acid it is excessively weak.

It can be reduced to a lower oxide, perhaps the sesquioxide Nb_2O_3, by heating in hydrogen. Its solution can also be reduced electrolytically to give a series of solutions differing in colour, and of different valencies as determined by titration with an oxidising agent.[1007-8]

Niobic Acid

Niobium pentoxide is precipitated in a hydrated form when acid is added to a solution of a niobate; but the precipitate is colloidal, and there is no indication of any definite hydrates.[1010]

In an alkaline solution the pentoxide dissolves to form a niobate. Niobic acid is, however, extremely weak, and resembles silicic or stannic acid rather than vanadic; the solution of an alkaline niobate is decomposed even by carbon dioxide.

The niobates are of a great variety of types both single and multiple. The ratio M′:Nb can vary from 4 to 0·25, and it is difficult, even now, to get any better basis for the classification of the various types of salt than this ratio.

If the pentoxide is fused with sodium carbonate an ortho-niobate Na_3NbO_4 is formed; if this is dissolved in water a slightly soluble residue remains, which is the metaniobate $NaNbO_3, 3\,H_2O$ or $NaH_2NbO_4, 2\,H_2O$. The metaniobates (for example, Na, $3\,H_2O$; Mg, 3·5; Ag, 1; Cu″, 1·75; Cd, 1·75; Al, 6)[1003] are the most stable class of niobates. Among the more complicated are the pyroniobates $M_4Nb_2O_7$ and the hexaniobates $M_8Nb_6O_{19}$.

Peroxyniobates

When niobic acid is treated with hydrogen peroxide it has one or more of its oxygen atoms replaced by O_2 groups. As usual, the stability of the per-acids formed by elements of the subgroup rises with the atomic weight of the central atom, and the peroxide derivatives of niobium are more stable than those of vanadium. A greenish-yellow colour with hydrogen peroxide is characteristic of even the purest niobium pentoxide.[1003]

If the niobate solution is treated with hydrogen peroxide and excess of potash, and alcohol is added, the salt K_3NbO_8 or $K_3[Nb(O_2)_4]$ separates. A number of such salts have been made[1003]: Na, K, Rb, Cs, anhydrous; MgNa, $8\,H_2O$; MgK 7; CaK 4, etc. They all lose their peroxide oxygen on heating. If dilute sulphuric acid is added to the concentrated solution of one of these peroxyniobates, the free (mono-) peroxyniobic acid

$$H_3[Nb(O_2)O_3]\ \text{aq.}$$

crystallizes out as a lemon-yellow powder. This acid is remarkably stable; dilute sulphuric acid only decomposes it (to hydrogen peroxide and niobic acid) on warming.

Niobium Pentafluoride, NbF_5

This was made by Ruff[1005] by passing fluorine over niobium pentachloride in a platinum tube; the tube is heated at first, but the heat of reaction keeps the temperature up, showing that the Nb—F link has more than 3·3 k.cals. more energy of formation than the Nb—Cl (F—F 64·0, Cl—Cl 57·4). The pentafluoride can be made more easily by boiling niobium pentachloride with aqueous hydrofluoric acid.

It is a white mass, which can be purified by sublimation *in vacuo* at about 100°, and then condenses in colourless prisms. M. pt. 75·5°; b. pt. 217-20°. It is very hygroscopic; it gives a clear solution in water, from which sodium hydroxide or ammonia precipitates the pentoxide. It is a characteristic difference between the two elements that while alkalies convert niobium pentafluoride into the niobate—i.e. remove all the fluorine from the niobium—they convert tantalum pentafluoride into the fluorotantalate; in the same way with potassium fluoride niobium pentafluoride gives only traces of the double fluoride, the main product being the oxyfluoride, while tantalum pentafluoride is wholly converted into the double fluoride. Both these facts show that the fluorine is much more firmly attached (as compared with oxygen) to tantalum than to niobium.

Niobium Pentachloride, $NbCl_5$

This is formed by the action of chlorine on the heated metal; or, less easily, when niobium pentoxide is heated in the vapour of carbon tetrachloride, a reaction which goes so much more slowly with tantalum than with niobium that it can be used for separating the two; this is a marked instance of the greater ease of reaction of niobium as compared with tantalum compounds. It is best made from chlorine and niobium sulphide at 250°.[1009]

Niobium pentachloride is a pale yellow solid which melts at 194° to a raspberry-coloured liquid and boils at 241°[1003] to give a yellow vapour, which is monomeric at 275-300°. Electron diffraction has shown[1027] that $NbCl_5$ and $NbBr_5$ are trigonal bipyramids, with Nb—Cl 2·29 and Nb—Br 2·46 (theory 2·33, 2·48). The specific conductivity of the pentachloride at temperatures from 220° to 235° is $0·22 \times 10^{-6}$.[1009] It is soluble without decomposition in alcohol, ether, chloroform, carbon tetrachloride, and sulphur monochloride S_2Cl_2; water decomposes it into niobium pentoxide which is precipitated, and hydrochloric acid, but it dissolves in concentrated acids. Unlike niobium pentafluoride it forms no double salts. For its organic compounds with phenols and aromatic hydrocarbons see references [1012–13].

[1021] J. L. Hoard, *J.A.C.S.* 1939, **61**, 1252.

[1022] P. Süe, *C.R.* 1939, **208**, 814.

[1023] Id., ib., 1088.

[1024] Id., *Bull. Soc. Chim.* 1939, [v] **6**, 828.

[1025] Id., ib. 830.

[1026] Id., *C.R.* 1939, **208**, 440.

[1027] H. A. Skinner and L. E. Sutton, *Trans. Far. Soc.* 1940, **36**, 668.

Niobium Pentabromide, $NbBr_5$

This can be made by passing bromine vapour over metallic niobium.[1004] It is a red crystalline powder, looking like red phosphorus; after fusion it forms garnet-red prisms. Electron diffraction shows that the molecules in the vapour are trigonal bipyramids.[1027] It melts at 150° and distils in a stream of carbon dioxide at 270° without decomposition. It fumes in air, and is very hygroscopic, being converted by moisture first into the oxybromide $NbOBr_3$ and then into the pentoxide.

Niobium Pentaiodide, NbI_5. Barr[1004] made this from the pentabromide, and states that it is very stable; but he could not get it free from the pentabromide.

Niobium Oxyfluoride, $NbOF_3$, is formed by the action of gaseous hydrogen fluoride on a fused mixture of niobium pentoxide and calcium fluoride at a red heat. It forms small colourless crystals (Joly, 1870).

Niobium Oxychloride, $NbOCl_3$, can be prepared by the action of chlorine on a heated mixture of niobium pentoxide and carbon, or, along with niobium pentachloride, by passing the vapour of carbon tetrachloride over the heated pentoxide.

It forms pure white crystals (whereas the pentachloride is yellow[1009]); at very high temperatures it is converted into a mixture of niobium pentoxide and pentachloride; if its vapour mixed with chlorine is passed over carbon at 700°, it is converted into the pentachloride.[1022] When heated in air at 500° it is oxidised to the pentoxide.[1025]

Niobium Oxybromide, $NbOBr_3$,[1004] can be made by heating the pentoxide mixed with carbon in bromine vapour. It is a voluminous yellow solid, which on heating sublimes without melting, but at the same time is converted to a small extent into the pentoxide and the pentabromide. It fumes in air, going over into the pentoxide.

Pentavalent Niobium Complexes

These are not numerous, and are practically all either neutral (chelate β-diketone derivatives) or anionic, including halides (probably only fluorides), oxyhalides (fluorides, chlorides, and bromides), and a few ato-compounds (oxalic and catechol derivatives).

Complex Fluorides

These are few. The simpler compounds are of two types, $MNbF_6$ and M_2NbF_7, the latter being the most easily made. No compound M_3NbF_8 is known, though there is a salt Na_3TaF_8.[1028-9] The potassium heptafluoride can be got by recrystallizing the oxyfluoride from hydrofluoric acid,[1003] or by fusing potassium hydrogen fluoride (but not potassium fluoride) with niobium pentafluoride.[1006] It is a colourless salt. Its crystal structure shows that it is a true 7-covalent complex, but quite different

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[1028] J. L. Hoard and W. J. Martin, *J.A.C.S.* 1941, **63**, 11.

[1029] A. W. Laubengayer and C. G. Polzer, ib. 3264.

from the heptafluorides of zirconium, M_3ZrF_7[1021]; this is curious because the electronic structures (not the charges) of the central atoms are the same in both series. The salt K_2NbF_7 is stable in the dry state up to 100°, but hot water reconverts it into the oxyfluoride. More complicated 'polynuclear' fluorides are also known.

No complex chlorides or bromides have yet been described, and a supposed complex iodide has been shown[998] to contain no niobium (vanadium gives no complex halides at all, other than the oxyhalides).

Complex Oxyhalides[1003]

These are more numerous, and are formed with fluorine, chlorine, and bromine.

Oxyfluorides

There are three main types, M_2NbOF_5, M_3NbOF_6, and M_4NbOF_7, in addition to a good many complicated forms. Hoard has shown by X-ray analysis that $K_2[NbOF_5]$, H_2O has octahedral $[NbOF_5]$ ions,[1028] and that K_3NbOF_6 is made up of K^+ and $[NbOF_6]^{---}$ ions, the latter of the same type as $[ZrF_7]$ (not NbF_7).[1030] The M_2NbOF_5 type is the commonest (K, H_2O; Rb, Cs, Tl′ anhydrous), and the others are converted into it by recrystallization from water, while recrystallization from concentrated hydrofluoric acid converts them all into double fluorides.

The hydrated salts lose their water at 100°, and can then be heated to redness without decomposition. In solution they are decomposed by alkali.

Complex Oxychlorides[997-8]

There are two series of these, $M[NbOCl_4]$ and $M_2[NbOCl_5]$, made by treating the pentoxide, the oxytrichloride, or the pentachloride with very concentrated hydrochloric acid and the alkaline or other chloride.

The salts are colourless or pale greenish-yellow; they are only stable in dry air; in moist air they evolve hydrochloric acid, and water at once decomposes them with precipitation of niobium pentoxide.

Oxybromides.[997-8] These were made in the same way as the chlorides; they are even more readily decomposed than the latter.

No *oxy-iodides* have been described.

Oxalato-complexes

These can be made[996] by treating a niobate with oxalic acid and precipitating with acetone or alcohol. They are all of the type $M_3[NbO(C_2O_4)_3]$, and are hydrated (Na, 4 H_2O:K, 2: Rb, 2:NH_4, 1·5), but the water may well be attached to the oxalato-group. It should be noticed that the covalency maximum for vanadium is 6 and for niobium is 8: and that the oxalato-compounds of pentavalent vanadium are all of the type

$$M_3[VO_2(C_2O_4)_2],$$

and so 6-covalent, whilst the pentavalent niobium salts are necessarily at least 7-covalent, and obviously in fact 8. (The oxalato-group in such complexes is always chelate, and never an open-chain, as the sulphato sometimes is.)

These salts, which are colourless, are hydrolysed by water with the precipitation of niobium pentoxide, and are stable in solution only in presence of excess of the oxalate ion (Rosenheim).[1017]

It is to be noticed that no simple oxalates of pentavalent niobium, either as such or in the niobyl form, are known.

Catechol Complexes

Freshly precipitated niobium pentoxide is very easily soluble in a boiling alkaline solution of catechol (in an atmosphere of nitrogen to avoid oxidation). From this deep yellow solution a series of salts can be made, many containing more or less 'catechol of crystallization' (as with the catechol derivatives of pentavalent vanadium, and others). Thus the potassium salt is $K_2H[NbO(C_6H_4O_2)_3]$, 2 $C_6H_6O_2$, 3 H_2O (again a covalency of more than 6): the ammonium salt is the same, except that it has only half a molecule of catechol. Other salts have none, and some have all 3 H atoms replaced, as in $(NH_4)_3[NbO(cat)_3]$, 9 H_2O. The salts are all reddish or yellow; they are partly hydrolysed in water with separation of the pentoxide, but are soluble in acetone without change.

β-Diketone Derivatives

Acetyl and benzoyl acetone react[1018] with niobium pentachloride (and with tantalum pentachloride also) if the halide is first dissolved in alcohol, which undoubtedly replaces some of the halogen atoms by alkoxy groups. The products are always $NbCl_2(OAlk)_2A$. Their colours and melting-points are:

Alk	A	*Colour*	*M. pt.*
CH_3	Acetylacetone	Yellow	128-9°
C_2H_5	,,	Yellow	75°
CH_3	Benzoylacetone	Deep yellow	144-5°
C_2H_5	,,	Pale yellow	111°

See also Rosenheim.[1017]

TETRAVALENT NIOBIUM

The only compound isolated in which niobium seems to have this valency is the dioxide NbO_2 (often, and perhaps rightly, written Nb_2O_4 and called the tetroxide); by the reduction of niobates, solutions can be got whose state of oxidation indicates that they contain either tetravalent niobium or equal amounts of pentavalent and trivalent. The latter view seems the more probable on the whole, since there is definite evidence for it with tantalum.

[1030] M. B. Williams and J. L. Hoard, *J.A.C.S.* 1942, **64**, 1139.

[1031] G. Brauer, *Naturwiss.* 1940, **28**, 30.

[1032] G. Grube, O. Kubaschewski, and K. Zwiauer, *Z. Elektrochem.* 1939, **45**, 885.

[1033] O. Kubaschewski, ib. 1940, **46**, 284.

Niobium Dioxide, NbO_2

The behaviour of the pentoxide on reduction with hydrogen has been disputed. Recent work[1031-3] indicates that even at 1,300° it is not reduced beyond NbO_2, but above this it may[1032-3] go to Nb_2O; the Debye-Scherrer diagrams show the existence of Nb_2O, NbO, NbO_2, and Nb_2O_5, but not Nb_2O_3.[1032] The dioxide is a black insoluble powder with a bluish reflex,[1023-4] unaffected in the cold by acids, bromine water, hydrogen peroxide, permanganate, or alkaline solutions,[1024] but when heated a powerful reducing agent. It is oxidized to the niobate by heating with sodium hydroxide, carbonate, sulphate, sulphite, or nitrite.[1026] In the same way it will reduce carbon dioxide to the monoxide at 900–50°, sulphur dioxide to sulphur at 320-65°, and nitric oxide to nitrous oxide at 210°.[1024]

TRIVALENT NIOBIUM

This valency appears to occur in a non-volatile trichloride, and in certain reduced niobate solutions; the supposed sesquioxide Nb_2O_3 does not seem to exist.[1032]

Niobium Trichloride, $NbCl_3$

This compound is formed when the vapour of niobium pentachloride is passed through a red-hot tube (Roscoe); it is best made[1025] by passing a mixture of the vapour with hydrogen through a tube at 400-50°. It forms black crystals looking like iodine. It is non-volatile, not deliquescent, and not decomposed by water (so it can scarcely be a simple salt). It can be oxidized to the pentoxide with nitric acid, and converted into the pentavalent oxychloride $NbOCl_3$ by burning in air, or by carbon dioxide (which is reduced to the monoxide) at a red heat.

Trivalent Niobium in Solution

A solution of niobium pentoxide in sulphuric acid can be reduced with a lead platinum or mercury cathode to the trivalent stage, as determined by the titration of the solution with an oxidizing agent; this solution, if it is aqueous, is pure blue, but if the solvent used is alcohol it is red-brown.[1007,1034] A red salt is said to have been got from the solution,[1007] but this has not been confirmed.[1008] The trivalent niobium in this solution is oxidized by water in the presence of acid[1019] with evolution of hydrogen, but very slowly unless a catalyst such as platinum black is present.

DIVALENT NIOBIUM

The monoxide NbO, in which the metal is presumably divalent, has been obtained by Braumer[1031] as a cubic grey metallic powder by heating the dioxide in argon at 1,750°; its existence is confirmed by the Debye X-ray diagram.[1032]

[1034] G. Grube and H. L. Grube, *Z. Elektrochem.* 1938, 44, 771.

MONOVALENT NIOBIUM

This again rests solely on an oxide Nb_2O of unknown structure, got[1032] by reducing the pentoxide with hydrogen in the presence of moisture, and likewise confirmed by the Debye-Scherrer diagram.[1032]

TANTALUM

TANTALUM: GENERAL

TANTALUM always occurs in nature along with niobium. Its chief ores are the tantalites, which mainly have the composition (Fe″, Mn″) $[TaO_3]$.

Tantalum was named after Tantalus, because the pentoxide, when suspended in excess even of the strongest acids, is unable to take any up. This, however, is due to the high valency, and is not peculiar to tantalum, but is shared by vanadium and niobium, though not by protoactinium.

The lower valencies of tantalum show the same kind of instability as those of niobium, but speaking generally are even less stable; they cannot be produced in solution by reduction, as those of niobium can.

There is no evidence of the real existence of the tetravalent state with tantalum, but rather the opposite. But it is curious that though the trivalent state is on the whole less stable than it is with niobium, there is better evidence of the existence of the divalent form with tantalum. One main difference between the two elements is the relative instability of the 'tantalyl' radical TaO in the halides. The best method of separation depends on the fact that under the same conditions niobium pentoxide is converted into the oxyfluoride K_2NbOF_5 and tantalum pentoxide into the much less soluble heptafluoride K_2TaF_7.

There are also signs that tantalum and its compounds are slower to react than those of niobium; they have a greater heat of activation, which is perhaps connected with the much greater mass of the tantalum atom. For example, when tantalum pentoxide is heated in the vapour of carbon tetrachloride, or in hydrogen fluoride, chloride, or bromide, it reacts much more slowly than niobium pentoxide, although the pentahalides of tantalum are the more stable; moreover, tantalum pentafluoride, the product of the reaction of hydrogen fluoride on tantalum pentoxide, is in general, though it is more slowly produced, less reactive than the niobium compound.

[1035] P. Melikov and M. Pissarjewsky, *Z. anorg. Chem.* 1899, **20**, 344.

[1036] C. W. Balke, *J.A.C.S.* 1905, **27**, 1140.

[1037] W. v. Bolton, *Z. Elektrochem.* 1905, **11**, 45.

[1038] M. v. Pirani, ib. 555.

[1039] R. F. Weinland and L. Storz, *Z. anorg. Chem.* 1907, **54**, 223.

[1040] C. W. Balke and E. F. Smith, *J.A.C.S.* 1908, **30**, 1666.

[1041] O. Ruff and E. Schiller, *Z. anorg. Chem.* 1911, **72**, 329.

[1042] K. Lindner and H. Feit, *Ber.* 1922, **55**, 1458.

[1043] O. Ruff and F. Thomas, ib. 1466.

[1044] W. Biltz and A. Voigt, *Z. anorg. Chem.* 1922, **120**, 71.

[1045] O. Hahn and K. E. Putter, ib. **127**, 153.

[1046] K. Lindner and H. Feit, ib. 1924, **132**, 10.

A curious difference is that if the pentoxides are dissolved in ammonium oxalate, and ammonia added and then tannin, and the liquid boiled, all the tantalum is found in the precipitate with scarcely any of the niobium.[1065]

Metallic Tantalum

Metallic tantalum (like metallic niobium) is extremely difficult to purify. It is best prepared by reducing a fluorotantalate (such as K_2TaF_7) with an alkali metal, and can then be purified by heating *in vacuo* in the electric arc, when the impurities, being more volatile, evaporate away.[1037]

It is a heavy grey, very hard metal, which especially when pure, can readily be drawn into fine wires; m. pt. 2,800°. It is extraordinarily resistant to chemical attack. Acids other than hydrofluoric, even aqua regia, have no action on it; aqueous alkalies do not attack it, and even fused alkalies only very slowly. Fluorine, chlorine, and oxygen only react with it on heating, but at high temperatures it absorbs hydrogen and combines with nitrogen and carbon. It is used for various purposes for which its resistance to corrosion is important, as for surgical instruments, and for the tips of fountain pens. It was formerly used for incandescent lamps, but is now replaced by wires made of single crystals of the even more infusible tungsten, of m. pt. 3,400°.

Tantalum and Hydrogen

At a red heat tantalum will absorb at atmospheric pressure 0·3 per cent. of hydrogen (TaH would contain 0·55 per cent. H).[1038] The solid becomes a superconductor at low temperatures.[999a]

Tantalum and Carbon

The carbide TaC can be made[1058] like NbC by heating the metal with carbon powder for half an hour to 1,700-2,100°. It is a dark yellow crystalline mass, melting at 3,880° C.[1057]

[1047] K. Linder and H. Feit, *Z. anorg. Chem.* 1924, **137**, 66.

[1048] E. Friederich and L. Sittig, ib. 1925, **143**, 308.

[1049] O. Ruff and F. Thomas, ib. 1925, **148**, 1.

[1050] Id., ib. 19.

[1051] K. Lindner, ib. 1927, **160**, 57.

[1052] H. Funk and K. Niederländer, *Ber.* 1928, **61**, 249.

[1053] Id., ib. 1385.

[1054] Id., ib. 1929, **62**, 1688.

[1055] G. F. Hüttig and A. König, *Z. anorg. Chem.* 1930, **193**, 93.

[1056] K. R. Krishnaswami, *J.C.S.* 1930, 1277.

[1057] C. Agte and H. Alterthum, *Z. techn. Phys.* 1930, **11**, 182 (*B.C.A.* 1931, A. 170).

[1058] C. Agte and K. Moers, *Z. anorg. Chem.* 1931, **198**, 233.

[1059] A. Rosenheim and E. Roehrich, ib. 1932, **204**, 342.

[1060] H. Funk, *Ber.* 1934, **67**, 1801.

[1061] W. Biltz and A. Köcher, *Z. anorg. Chem.* 1938, **238**, 81.

[1062] F. Körösy, *Techn. Kurir*, 1938, **9**, 81 (*B.C.A.* 1939, A. 36).

[1063] J. L. Hoard, *J.A.C.S.* 1939, **61**, 1252.

[1064] G. C. Hampson, *Ann. Rep. Chem. Soc. for 1939*, **36**, pp. 169, 170.

[1065] H. Wirtz, *Z. analyt. Chem.* 1939, **117**, 6.

Tantalum and Nitrogen

TaN is obtained as a black or grey mass when the pentachloride is heated with ammonia and the product raised to a white heat (Rose, 1857; Joly, 1876); or when a mixture of the pentoxide and carbon[1048] or the metal[1058] is heated in nitrogen to 1,200°. Unlike NbN it does not become superconducting even at 1·88° K.[999a] It melts at 3,100°, and is not attacked by acids other than hydrofluoric. It is an interstitial compound.[999a]

Tantalum and Sulphur

The relations here, as with vanadium and niobium, are very difficult to make out, owing to the solubility of the elements and the products in one another in the solid state. A recent examination of the system[1061] by the methods of the phase rule, by the determination of the dissociation tensions, and the use of X-ray diagrams, shows that the two elements form at least two compounds, TaS_3 and TaS_2, and probably TaS as well. It must be remembered that owing to the strong tendency of sulphur to form chains, the valency of the metal cannot be inferred from the composition of the sulphide without the help of crystal data.

TaS_3 forms a black fibrous mass.

TaS_2 is a black powder, the larger crystals having a yellow reflex. It can be heated above 1,000° without sublimation or decomposition.

Both these compounds can form solid solutions with sulphur, and TaS can do this also with the metal (up to about Ta_2S).

It is to be noticed that while TaS_2 and TaS_3 are definite compounds, with their own crystal lattices, niobium can form no such sulphides, the highest being the sesquisulphide Nb_2S_3, though this can form solid solutions with more sulphur.

Tantalum Pentoxide

The pentoxide is the product of heating the metal or almost any of its compounds in air; it is best made by igniting the metal in oxygen.

It is a white powder, insoluble in all acids except hydrofluoric, and not attacked on ignition by air, chlorine, hydrogen, sulphide, or sulphur. Unlike niobium pentoxide it is not attacked on heating with hydrochloric or hydrobromic acid, but at a white heat it breaks up into the metal and oxygen. It is definitely more stable than niobium pentoxide: it is not changed when heated in hydrogen to 1,250°,[1048] which reduces niobium pentoxide to the trioxide, and it is much less readily attacked by carbon tetrachloride vapour than the niobium compound.

The hydrated oxide, the so-called tantalic acid, which is precipitated by acids from a tantalate solution, is gelatinous and colloidal; its dehydration curve[1055] shows no definite hydrate. When it is heated it loses water, and then suddenly glows, owing to the heat evolved when the colloidal pentoxide goes over to the crystalline state; niobium pentoxide and titanium dioxide behave in the same way. The freshly precipitated acid will dissolve in excess of concentrated mineral acids, just as niobic does, probably owing to the formation of complex acids.

The supposed loss of tantalum when the pentoxide is evaporated with hydrofluoric acid does not occur when the oxide is pure[1055]; but if alkali is present the heptafluoride M_2TaF_7 is formed, which gives some volatile pentafluoride on ignition.

Tantalic Acid and the Tantalates

Tantalic acid, like niobic, is very weak. The tantalates in general resemble the niobates, but have an even greater tendency to form condensed ions. The salts can be made by fusing the pentoxide with an alkaline hydroxide or carbonate; when the hydroxide is used there seems to be scarcely any limit to the amount of tantalum pentoxide which can be taken up; but if the pentoxide is fused with sodium carbonate a fairly definite ortho-tantalate Na_3TaO_4 is formed. Another fairly well-marked series of salts is that of the hexa-tantalates, with the general formula, $M'_8[Ta_6O_{19}]$ aq.; it is remarkable that the alkaline salts of this type are the only readily soluble tantalates known.

Owing to the weakness of the acid, the salts are highly hydrolysed by water, but some acids, such as arsenic and especially tartaric and citric, will not precipitate the pentoxide from the tantalate solution, owing to the formation of complexes. Tantalic acid can also form a series of hetero-poly-acids.

Peroxytantalates[1038,1040]

Tantalum, like the rest of the group, can form a peroxide compound when the solution of a tantalate is treated with hydrogen peroxide. The basicity of the acids, that is, practically speaking, the tendency to form salts with the less condensed forms, rises with the atomic number: vanadium and niobium mainly form pyro-salts such as $M_4V_2O_{11}$ or $M_4Nb_2O_{11}$, and tantalum mainly the simple ortho-per-acids M_3TaO_8.[1035]

Of these per-salts the best marked are of the type of $K_3[TaO_8]$: for example, Na_3, $14H_2O$; K_3, Rb_3, Cs_3 anhydrous; Mg Na 8; Mg K 7; Mg Rb 9; Ca Na 4·5 H_2O per cent. They must contain the ion $[Ta(—O—O)_4]$. If the potassium salt is treated with sulphuric acid a free acid $H[TaO_4]$ aq., with one active oxygen, crystallizes out. It can be warmed to 100° for some time without decomposition, showing that it is more stable than the corresponding niobium compound.

Tantalum Pentafluoride, TaF_5

This was obtained by Ruff and Schiller[1041] by the action of liquid anhydrous hydrogen fluoride at its boiling-point (20°) on tantalum pentachloride. The reaction goes less readily than with niobium pentafluoride; the product can be purified by distillation. It can also be made by heating the complex fluoride $Ba_3[TaF_8]_2$ to 1,000° in platinum vessels.

It is a colourless substance melting at 96·8° and boiling at 229·4°.[1041]

It is less reactive than niobium pentafluoride (see p. 838). It is slightly soluble in carbon disulphide, and more so in carbon tetrachloride, chloroform, etc., but not in hydrocarbons. It dissolves in water with a hissing sound (like aluminium chloride) to give a clear solution, from which on boiling all the fluorine atoms come off as hydrogen fluoride; but if alkalies are present they remain as complex tantalifluorides. Potassium hydrogen fluoride KHF_2 combines at once on melting with the pentafluoride to give potassium heptafluoride K_2TaF_7, but from potassium fluoride KF itself the heptafluoride can only be got by long heating at 220-30°. Potassium chloride does not react with tantalum pentafluoride at all.[1041]

Tantalum Pentachloride, $TaCl_5$

This compound is formed when tantalum or its carbide, nitride, or sulphide is heated in chlorine. It is best made[1049] by heating the pentoxide in a stream of chlorine saturated with carbon tetrachloride vapour. At 270° carbon tetrachloride scarcely reacts with tantalum pentoxide at all, while it converts niobium pentoxide almost completely into the pentachloride.

Tantalum pentachloride forms yellow crystals which melt at 211° and boil at 241·6°, the same temperature as niobium pentachloride (241°), and only 12·2° higher than tantalum pentafluoride. Its vapour density at 360° is normal; the electrical conductivity of the liquid at 240° is $0{\cdot}30 \times 10^{-6}$.[1044] It is slightly soluble in ethyl bromide, chloroform, and carbon tetrachloride, and more so in carbon disulphide. It hydrolyses slowly in concentrated hydrochloric acid, and rapidly in dilute.[1046,1066] It burns in air to the pentoxide, but neither in this reaction, nor in its hydrolysis by water, is there any sign that an oxychloride is formed as an intermediate product.

Like niobium pentachloride it reacts with organic, and especially with hydroxylic, compounds with replacement of its chlorine atoms (Funk and Niederländer).[1052-4]

Tantalum Pentabromide, $TaBr_5$

This can be made by igniting a mixture of tantalum pentoxide and carbon in bromine vapour (Rose, 1856), or by passing bromine vapour over metallic tantalum at 300° in an atmosphere of nitrogen or argon.[1056] It forms pale yellow crystals, which are decomposed by water.

Tantalum Pentaiodide, TaI_5

Rose (1856) and Moissan (1902) could not prepare this, but it is said[1062] to be formed by the action of iodine vapour on the metal, as a brownish-black powder melting at 365°, hydrolysed in moist air, oxidized vigorously by oxygen at 100°, and insoluble in organic solvents.

[1062] O. Hönigschmid and R. Schlee, *Z. anorg. Chem.* 1935, **225**, 64.

Oxyhalides of Tantalum

In marked contrast to niobium, and still more to vanadium, tantalum forms scarcely any (if any) oxyhalides. Ruff and Thomas,[1049] on resubliming the pentachloride made from the pentoxide, got a trace of residue analysing for TaO_2Cl: but this was not further investigated. No other (non-complex) oxyhalide has been described. Some derivatives are, however, known. When the pentachloride is dissolved in acetone, hydrogen chloride is evolved, and on adding pyridine a pale yellow, fairly stable compound separates of the composition 4 TaO_2Cl, 7 py.[1045]

Complex salts derived from oxyfluorides and oxychlorides of tantalum are described below.

Complexes of Pentavalent Tantalum

A few apparent ammines of the pentahalides have been described, but their nature has not been confirmed.[1046] The established complexes are either anionic or neutral, and the most important are the fluorides.

Complex Fluorides, Fluorotantalates

These were investigated by Marignac in 1866, and subsequently by E. F. Smith and C. W. Balke.[1035] They are of three types, $M[TaF_6]$, $M_2[TaF_7]$, and $M_3[TaF_8]$, of which the second is the commonest, and the third the rarest.

The free acid of the first type $H[TaF_6], 6\,H_2O$ (colourless crystals melting at 15°) was made[1045] by dissolving tantalum pentoxide in hydrofluoric acid.

The heptafluoride K_2TaF_7 is formed at once on fusing tantalum pentafluoride with potassium hydrogen fluoride (but not with potassium fluoride KF). Being slightly soluble in cold water but more in hot, it can be used to separate tantalum from niobium, which under the same conditions gives the much more soluble K_2NbOF_5. It is stable when dry, and at a high temperature melts without decomposition; at a still higher temperature it gives off tantalum pentafluoride. It is hydrolysed by water, but less readily than the niobium salt; it can be recrystallized from dilute hydrofluoric acid. Other salts of this type are[1036]: Na, H_2O: K, Rb, Cs, anhydrous: the solubility increases from potassium to caesium, which is a sign that H_2TaF_7 is a weak acid.

The crystal structure of the potassium salt K_2TaF_7 has been determined by Hoard[1063]; the structure of the anion is the same as in the niobium compound, but different from that in the zirconium salt K_3ZrF_7; pictures of these structures are given in the *Ann. Rep. Chem. Soc.* for 1939.[1064]

All attempts to obtain chlorotantalates have failed; tantalum pentafluoride will not react with potassium chloride at all.[1041]

Complex Oxyhalides (Tantalyl Complexes)

Complex oxyfluorides of tantalum are known (though there is no simple oxyfluoride), and also, though they seem less easy to make, complex oxychlorides.

Oxyfluorides

They are apparently all derived from an (unknown) oxyfluoride $TaOF_3$. They cannot be made with hydrofluoric acid at all, because this at once converts them into the much more stable fluorotantalates, but only from tantalum pentoxide and a neutral fluoride. They are very unstable, and change in solution in the cold or at any rate on warming into tantalum pentoxide and a fluorotantalate: they do this the more rapidly, the less the solution is hydrolysed, the potassium salt quicker than the ammonium.

Most are of the type $M_3[TaOF_6]$; the ammonium salt, which can be made from tantalum pentoxide and ammonium fluoride, is isomorphous with the heptafluorides $M_3[AF_7]$, where A = Zr, Si, or Ti.

Oxychlorides

These have been made[1039] from tantalum pentachloride and various chlorides in alcoholic solution; examples are $(pyH)_2[TaOCl_5], 2\,EtOH$ and $(quin.H)_2[TaOCl_5], 2\,EtOH$. They form colourless needles.

Catechol Complexes

It is very singular that while all the known catechol derivatives of niobium (see p. 841) have only one niobium atom in the molecule, all the tantalum compounds have two atoms of tantalum[1059]: for example, $K_3H[Ta_2O(C_6H_4O_2)_6], 3\,C_6H_4(OH)_2, 10\,H_2O$.

β-Diketone Complexes

These correspond exactly to the niobium compounds, all being of the type $TaCl_2(O\cdot R)_2A$,[1060] (p. 841). They are rather paler than the niobium compounds, and melt about 10° lower:

R	A	*M. pt.* Ta	*M. pt.* Nb	
CH_3	Acetylacetone	113–15°	128°: Diff.	−14°
C_2H_5	,,	63–5°	75°	−11°
CH_3	Benzoylacetone	138–9°	144–5°:	−6°
C_2H_5	,,	114–16°	111°	+4°

TETRAVALENT TANTALUM

The evidence for this valency is the existence of an oxide TaO_2 and a chloride $TaCl_4$. Their molecular weights are unknown, and either or both of them may consist of complex molecules containing trivalent and pentavalent tantalum.

Tantalum Dioxide, TaO_2

This is made by igniting the pentoxide in a carbon crucible. It is a hard dark grey mass, which gives a dark brown powder; it is not attacked by acids, but burns when heated in air to the pentoxide, and dissolves in sodium hydroxide to give a tantalate. It is a good conductor of electricity, and was therefore used by v. Bolton to prepare the metal. A hydrate,

$TaO_2, 2H_2O$, has been obtained[1067] by the action of water on the tribromide $TaBr_3$; it slowly oxidizes to the pentoxide.

[*Tantalum Disulphide*, TaS_2

This has already been described (p. 845); for the reasons there given its existence is no evidence for the tetravalency of the tantalum.]

Tantalum Tetrachloride, $TaCl_4$

If the product of heating tantalum pentachloride with aluminium and aluminium chloride is further heated under a pressure of 2–3 mm., the aluminium chloride comes off between 120° and 200°. By 250° the residue has the approximate composition $TaCl_4$. If the temperature is raised more chlorine comes off, always in the form of tantalum pentachloride. At 350-400° the residue is the trichloride $TaCl_3$, and at 600° only the dichloride $TaCl_2$ is left.

Tantalum tetrachloride, the product at 250°, is of unknown molecular weight and structure. With water it behaves like a mixture of the trichloride and the pentachloride: the trichloride goes into solution with a bright green colour, as tantalum trichloride itself does, while the pentachloride is hydrolysed and forms a dark precipitate of impure pentoxide. The reaction is:

$$2\,TaCl_4 + 5\,H_2O = TaCl_3 + Ta(OH)_5 + 5\,HCl.$$

As we have no X-ray data, we cannot discuss the constitution of the solid; but it obviously breaks up very easily into the tri- and pentachlorides, and the solid may contain an equal number of tri- and pentavalent tantalum atoms. It is also possible that this is a true tetravalent compound, and that this valency is confined to the solid state and breaks up into a mixture of atoms of the other two valencies on going into solution. We have other examples of molecules which change their atomic groupings on fusion (such as phosphorus pentachloride, sulphur tetrachloride, and aluminium chloride), though none of this particular kind.

TRIVALENT TANTALUM

The evidence for this valency is the existence of a trichloride, a tribromide, and a complex oxychloride.

Tantalum Trichloride, $TaCl_3$

As already mentioned, if the product of heating tantalum pentachloride with aluminium and aluminium chloride is further heated under 2–3 mm. pressure to 350–400°, the residue is $TaCl_3$.[1048,1049] This is a green solid, which dissolves readily in water to form a green solution. The solution is fairly stable in the cold, but on heating the chloride is oxidized, and on boiling it is completely converted into tantalum pentoxide and hydrogen. The reaction is quicker in presence of alkali.

[1067] R. C. Young and T. J. Hastings, *J.A.C.S.* 1942, 64, 1740.

If the aqueous solution of the trichloride is evaporated *in vacuo* in the cold, a very stable basic complex $Ta_3Cl_7O, 3H_2O$ remains. (The earlier incorrect formula for this[1042,1047,1051] was corrected by Ruff.[1050]

This compound is remarkably resistant to oxidation and to hydrolysis, no doubt on account of its complex structure, whatever that may be. In some ways it resembles the polymerized chlorides of divalent molybdenum and tungsten such as Mo_3Cl_6. It retains one molecule of water till it decomposes at 230°; its alcoholic solution gives no reaction for chlorine ion, while in water it seems to produce two chlorine ions per Ta_3.

Tantalum Tribromide, $TaBr_3$

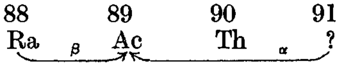
Young and Hastings[1067] find that $TaBr_5$ is reduced by hydrogen at 700° to a grey-green solid tribromide, which is slowly oxidized by water and alkali to the hydrated dioxide $TaO_2, 2H_2O$ and hydrogen.

DIVALENT TANTALUM

The evidence for this is the dichloride $TaCl_2$.[1043,1049] If the trichloride produced by heating the product of the reduction of tantalum pentachloride to 400° with aluminium is further heated, pentachloride distills away, and at 600° $TaCl_2$ remains. At 500° the residue is a mixture of tri- and dichlorides; with water the tantalum trichloride dissolves to form a deep green solution, while the dichloride remains as a greenish-black mass. Tantalum dichloride is insoluble in water, but very soon attacks it with liberation of hydrogen, and then goes into solution as a green trivalent tantalic salt.

PROTOACTINIUM 91

THIS element is of great interest, both from its chemical and from its nuclear properties. It was discovered in 1918 independently by Soddy and Cranston,[1068] and by Hahn and Meitner.[1069] Actinium had been shown, by the diffusion work of Hevesy and by the chemical investigation of Fleck, to be a trivalent element of Group III with the atomic number 89, and its parent must therefore be either no. 88 by a β-ray or no. 91 by an α-ray change. If the parent was 88, it would be an



isotope of radium, and since both radium and actinium are ultimately derived from uranium, it must be present in ordinary radium, which was not the case (see however, below, p. 852). Hence actinium must be produced by an α-ray change from element no. 91, in the fifth group, a homologue of tantalum; it should therefore be possible to isolate this from the pitchblende residues by adding tantalum and removing it, and this was effected. As the parent of actinium it was called protoactinium.

[1068] F. Soddy and J. A. Cranston, *Proc. Roy. Soc.* 1918, 94, 384.
[1069] O. Hahn and L. Meitner, *Phys. Z.* 1918, 19, 208.

Of the three radioactive series, uranium, thorium, and actinium, the members of the last have by far the shortest lives; for example, the half-lives of the three emanations are Ra Em. 3·825 days; Th Em. 54·5″; Ac Em. 3·92″. The only member of the actinium series which lives long enough to be obtained in weighable quantities is protoactinium, and so our knowledge of the atomic weight of every member of the series depends on that of Pa. An indirect determination of the value was obtained by Aston from the study of the isotopes of lead. All three series end ultimately in lead, the relations being

$$\begin{aligned} \text{U } 238-8\,\alpha &= \text{Pb } 206 \\ \text{Th } 232-6\,\alpha &= \text{Pb } 208 \\ \text{AcU ?} \longrightarrow \text{Pa ?} -6\alpha &= \text{Pb ?} \end{aligned}$$

Aston showed[1070] that the main isotopes of ordinary lead are 206, 207, and 208, roughly in the proportions 4:3:7. Lead from a uranium mineral was found[1071] to be mainly Pb 206, as we should expect, but to contain 9 per cent. of Pb 207 and 4 per cent. of Pb 208. Now since ordinary lead contains more than twice as much 208 as 207, the 9 per cent. of 207 in the uranium lead could not have come from an admixture of ordinary lead, but must have been the end-product of the only other known radio-active series, that of actinium. Hence the atomic weight of protoactinium must be $207+24 = 231$. It was, however, very important to check this conclusion by a direct determination of the atomic weight of protoactinium, the only member of the series that could be got in sufficient quantity. This was done by v. Grosse in 1934,[1072] and he obtained the value $230{\cdot}6\pm0{\cdot}5$, in agreement with Aston's conclusion. This fixes the mass-numbers of the whole actinium series, for example, Ac 227, Ac Em 219.

This affords a fourth (and the strongest) example of the atomic weights not being in the same order as the atomic numbers:

18 A	39·94	27 Co	58·94	52 Te	127·61	90 Th	232·1
19 K	*39·10*	28 Ni	*58·69*	53 I	*126·92*	91 Pa	*230·6*
Diff.	0·84		0·25		0·69		1·5
Diff. %	2·2		0·43		0·54		0·65

Protoactinium is derived ultimately from the uranium isotope ^{235}U (actino-uranium, AcU), present to about 0·7 per cent. (1/140) in ordinary uranium, which must go by an α-ray change $^{231}_{90}$UY, and this by a β-change to $^{231}_{91}$Pa. This ^{235}U has become famous from its use in the atomic bomb (see under Uranium VI. 1088).

Chemical Properties of Protoactinium

These bear on the question where the 'Second Rare Earth Group' begins, i.e. when the fifth quantum group of 18 electrons begins to expand

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[1070] F. W. Aston, *Nature*, 1927, **120**, 224.

[1071] Id., ib. 1929, **123**, 313.

[1072] A. v. Grosse, *J.A.C.S.* 1934, **56**, 2501.

as the fourth does with cerium. This is discussed in detail under uranium (VI. 1091). Here it may be said that protoactinium, so far as its chemical properties are known, gives no sign of any valency lower than 5.

The separation of protoactinium from the residues of pitchblende is very difficult owing to its close similarity to tantalum. It can be separated (1) by the addition and precipitation of Ta_2O_5: the separation is very complete, and shows the similarity of the two elements; but it is not at all easy to separate the protoactinium from the tantalum, especially as both have the undesirable properties (from the analytical point of view) of V A elements, of being easily hydrolysed, and forming colloidal solutions. The second method of separation is to add zirconium salts and precipitate ZrO_2, which brings down the protoactinium with it: titanium can be used in the place of zirconium[1073–5]; this is a good example of the 'diagonal relationship', the increase in valency being balanced by the increase in radius. From the zirconium mixture the zirconium is then separated as the oxychloride $ZrOCl_2$, to which protoactinium has no analogue. Finally, the latter can be separated from admixed tantalum by treatment with concentrated sulphuric acid and hydrogen peroxide: the tantalum remains in solution (as a peracid) while the Pa_2O_5 is insoluble.[1076–7] For the determination of the atomic weight the protoactinium was converted[1078] into the heptafluoride K_2PaF_7; this was decomposed with excess of sulphuric acid, the mixed potassium and protoactinium sulphates dissolved in water, the protoactinium precipitated as Pa_2O_5 with ammonia, and weighed after ignition as Pa_2O_5. The value 230·6±0·5 was thus obtained.

The properties of protoactinium, so far as they are known, are those to be expected in the heaviest member of subgroup V A. The pentoxide is basic and differs from those of V, Nb, and Ta in having no acidic properties: it is not dissolved by fused K_2CO_3. It forms a colourless pentachloride, which melts at 301°, and has a considerable vapour pressure at this temperature. The metal has been prepared by v. Grosse[1077] by bombarding the oxide with high speed electrons: it forms a shiny metallic, mass, which unlike radium does not oxidize in the air: this is what we should expect.

[1073] Cheng Da-Chang, *J. Chinese Chem. Soc.* 1935, 3, 381.
[1074] Mme H. Emmanuel-Zavizziano, *C.R.* 1936, 202, 1052.
[1075] Mme H. Emmanuel-Zavizziano and H. Raissinsky, ib. 203, 161.
[1076] A. v. Grosse, *J.A.C.S.* 1930, 52, 1742.
[1077] A. v. Grosse and M. S. Agruss, ib. 1934, 56, 2200.
[1078] A. v. Grosse, *Proc. Roy. Soc.* 1935, 150, 363.