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INORGANIC CHEMISTRY.
VOLUME VI. PART II.

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INORGANIC CHEMISTRY.

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J. NEWTON FRIEND, D.Sc., PH.D., F.I.C.,

Carnegie Gold Medallist.

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THE PERIODIC TABLE.*

PERIODS.		GROUP 0.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
First short period		2 He 4·002	1 H 1·0078 3 Li 6·940	4 Be 9·02	5 B 10·82	6 C 12·00	7 N 14·008	8 O 16·000	9 F 19·00	
Second short period		10 Ne 20·183	11 Na 22 997	12 Mg 24·32	13 Al 26·97	14 Si 28·06	15 P 31·02	16 S 32·06	17 Cl 35·457	
First long period	Even series	18 A 39·944	19 K 39·10	20 Ca 40·08	21 Sc 45·10	22 Ti 47·90	23 V 50·95	24 Cr 52·01	25 Mn 54·93	26 Fe 55·84 27 Co 58·94 28 Ni 58·69
	Odd ,,		29 Cu 63·57	30 Zn 65·38	31 Ga 69·72	32 Ge 72 60	33 As 74·93	34 Se 79·2	35 Br 79·916	
Second long period	Even series	36 Kr 83·7	37 Rb 85·44	38 Sr 87·63	39 Y 88·92	40 Zr 91·22	41 Nb 93·3	42 Mo 96·0	43 Ma ..	44 Ru 101·7 45 Rh 102·91 46 Pd 106·7
	Odd ,,		47 Ag 107·880	48 Cd 112·41	49 In 114·8	50 Sn 118·70	51 Sb 121·76	52 Te 127·5	53 I 126·932	
Third long period		54 Xe 131·3	55 Cs 132·81	56 Ba 137·36	57 La 138·90	58 Ce 140·13 59 Pr 140·92	60 Nd 144·27 61 Il	62 Sm 150·43 63 Eu 152·0	64 Gd 157·3 65 Tb 159·2	
Fourth long period			66 Dy 162·46 67 Ho 163·5	68 Er 167·64 69 Tm 169·4	70 Yb 173·5 71 Lu 175·0	72 Hf 178·6	73 Ta 181·4	74 W 184·0	75 Re 186·31	76 Os 191·8 77 Ir 193·1 78 Pt 195·23
Fifth long period	Even series		79 Au 197·2	80 Hg 200·61	81 Tl 204·39	82 Pb 207·22	83 Bi 209·00	84 Po [210]	85 ...	
	Odd ,,	86 Rn 222	87 ...	88 Ra 225 97	89 Ac ...	90 Th 232·12	91 Pa ...	92 U 238·14		

* The Revised International Atomic Weights for 1932 are adopted in this Table as accepted by the Council of the Chemical Society.

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J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,
CARNEGIE GOLD MEDALLIST.

VOLUME VI., PART II.

PHOSPHORUS.

BY
EDMUND B. R. PRIDEAUX,
M.A., B.Sc.(N.Z.), D.Sc.(Lond.), F.I.C.

With Frontispiece and Illustrations.

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GENERAL INTRODUCTION TO THE SERIES.

During the past few years the civilised world has begun to realise the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches: namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the elements of Group O, the general principles of Inorganic Chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern Inorganic Chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasise their application to Inorganic Chemistry, with which branch of the subject this series of text-books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed in Volume I. deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of Physical Chemistry. Yet these are subjects of supreme importance to the student of Inorganic Chemistry and are accordingly included in the Introduction.

Hydrogen and the ammonium salts are dealt with in Volume II., along with the elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV., along with the elements of Group III., as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II. and V. respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II. under ammonium, and in Volume IX. under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V. along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX. under iron, and not under ammonium in Volume II. The ferro-cyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicals and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross-referencing to the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:

Hydrogen = 1·00762.
Sodium = 22·996.
Potassium = 39·100.
Silver = 107·880.
Carbon = 12·003.
Nitrogen = 14·008.
Oxygen = 16·000.
Sulphur = 32·065.
Fluorine = 19·015.
Chlorine = 35·457.
Bromine = 79·916.
Iodine = 126·920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and moreover it renders the data for the different elements strictly comparable throughout the whole series.

Our aim has not been to make the volumes absolutely exhaustive, as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined lists, pp. xvii–xix.

The addition of the *Table of Dates of Issue of Journals* (pp. xxi–xxviii) will, it is hoped, enhance the value of this series. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr. F. W. Clifford and his staff. To these gentlemen the Editor and the Authors desire to express their deep indebtedness.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin & Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

January 1934.

PREFACE.

A GENERAL survey of Group V. of the Periodic Classification has already been given in Part I. of this Volume, Chapter I. The position of phosphorus, and its importance in the progress of pure chemistry and technology, call, however, for a further brief introduction.

Like nitrogen, phosphorus is a key element in agriculture, with the following important differences however. Nitrogen compounds are "wasting assets" which require to be vigorously supplemented by the application of manures which may be natural or artificial. A supply of phosphates in a finely divided state represents more permanent capital, which is not much drawn upon except by the actual requirements of plant life. The industry of phosphatic fertilisers is mainly concerned with supplying phosphates in a more soluble form and also in admixture with other essential materials, such as lime, potash and ammonia. Recognition of the importance of phosphatic manures dates from about the middle of the XIXth century, when they were applied in the form of bones, bone-dust, bone-ash, guano and superphosphates as a result of a sequence of operations which has developed into the present great phosphate industry.

The luminosity of phosphorus, due to its smouldering combustion, attracted much attention on the discovery of the element towards the end of the XVIIth century. Although Boyle was able to describe some of the properties of the element and to prepare the pentoxide, knowledge of this active element did not make much progress until about the end of the XVIIIth century, when Scheele discovered a more abundant source in bone-ash, and also an efficient method of preparation. From the beginning of the XIXth century, however, much research was undertaken into the numerous compounds of phosphorus, many of which are volatile without decomposition, and hence played a leading part in establishing atomic and molecular weights.

Phosphoric acid was the original of the "three water molecule type"; replacement of these molecules by basic oxides in typical phosphates, investigated by Clark, led Graham to the theory of basicity. In aqueous solutions phosphoric acid has played a no less important part as an example of successive dissociation of hydrogen ions. The theory of isomorphism, enunciated by Mitscherlich and others, was founded on the phosphates and arsenates.

An important technical development which took place from about the middle of the XIXth century was the manufacture of friction matches, which was largely due to the discovery of red phosphorus at this period.

The systematic chemistry of phosphorus was known in considerable detail by the third quarter of last century; its thermochemistry had been largely worked out by Thomsen, Berthelot and Giran, while numerous physical constants had been obtained by Gladstone, Sir Edward Thorpe and others. These data, and their references, lend a somewhat antique air to parts of this book, but are nevertheless the accepted data of to-day.

Most types of combination are shown by this most reactive element; the number and variety of its compounds with other non-metallic elements are especially noteworthy. The halide series is more complete than that of any other non-metal, including the congeners nitrogen and arsenic. In number and variety of hydrogen compounds, however, phosphorus is surpassed by nitrogen. Alkyl compounds are well developed with all three elements; there is, however, a greater variety of organic nitrogen compounds, while the extensive discovery of organo-arsenic compounds due to their importance in medicine has necessitated a special treatise in this Series, *i.e.* Volume XI., Part II.

Phosphorus is almost exclusively tervalent in its organo-compounds and lower halides, etc., and quinquevalent in the compounds PX_5, phosphonium compounds and the phosphoric acids; according to modern theory, however, this quinquevalency is really quadricovalency. Compounds showing other valencies are not common, and sometimes are of doubtful individuality.

In the Fifth Group the higher stage of oxidation appears to attain a maximum stability in the case of phosphorus, as is seen by comparing the pentoxide or phosphoric acids with the corresponding compounds of nitrogen and arsenic. Phosphoric oxide and acid are formed with the greatest decrease of total energy, and do not, like nitric and arsenic acids, behave as oxidising agents under ordinary conditions. Connected with this is the fact that the lower oxides and acids of phosphorus act as reducing agents in solution to a greater extent than nitrous and arsenious acids.

Phosphoric acids form many auto- and hetero-complexes, in which respect they are similar to the acids of vanadium and its congeners, as well as those of silicon. Three degrees of hydration, known as ortho-, pyro- and meta-, are also found, with certain differences, with other members of Group V.

In addition to the original memoirs in recognised scientific journals the writer has found it convenient to consult Mellor's *Comprehensive Treatise* and the detailed contributions by Brauner and Schenck in the third part of the third volume of Abegg's *Handbuch der anorganischen Chemie*. For special sections free use has been made of Smits' *Theory of Allotropy* and other monographs, the appropriate original papers, and the Annual Reports of the Chemical Society. The principal sources of technical information are: Parrish and Ogilvie's *Artificial Fertilisers* (Benn), Fritsch's *The Manufacture of Chemical Manures* (Scott, Greenwood and Company), the various Reports on Applied Chemistry, and articles in the technical journals.

In conclusion, it is again a pleasant duty to express my thanks to the General Editor of this Series, Dr. J. Newton Friend, for his unfailing care, and to Mr. W. E. Thorneycroft for further useful criticisms of the proofs.

E. B. R. PRIDEAUX.

UNIVERSITY COLLEGE, NOTTINGHAM,
January 1934.

CONTENTS.

PAGE
THE PERIODIC TABLE (*Frontispiece*) iv
GENERAL INTRODUCTION TO THE SERIES . . . vii
PREFACE xi
LIST OF ABBREVIATIONS xvii
TABLE OF DATES OF ISSUE OF JOURNALS . . . xxi

CHAPTER I. **Phosphorus, General** 3

Occurrence—History—Commercial Preparation of White and Red Phosphorus—Uses—Physiological Action.

CHAPTER II. **Phosphorus, The Element** 14

SOLID PHOSPHORUS:—General—Melting and Freezing of White Phosphorus—Specific Heats—Latent Heat of Fusion—Density—Compressibility—Crystalline Form—Refractivity—Electrical Conductivity—Dielectric and Magnetic Properties—Ionisation Potential—Solubility.

LIQUID PHOSPHORUS:—Density and Specific Volume—Vapour Pressure—Latent Heat of Vaporisation—Surface Tension.

PHOSPHORUS VAPOUR:—Density and Dissociation—Refractivity—Spectra of Phosphorus and its Compounds—Absorption of Radiation—Fluorescence—Mass Spectrum.

CHEMICAL REACTIONS OF PHOSPHORUS:—General—Action on Solutions of Metallic Salts—Red Phosphorus—Scarlet Phosphorus—Colloidal Phosphorus.

DETECTION AND ESTIMATION OF PHOSPHORUS.

CHAPTER III. **Allotropic Forms of Phosphorus and Conditions of Transformation** 31

RED PHOSPHORUS:—Preparation—Physical Properties.

VIOLET PHOSPHORUS:—History and Preparation—Physical Properties.

THEORY OF THE ALLOTROPIC FORMS:—Phase Diagram—"Molecular Species."

BLACK PHOSPHORUS:—General—Physical Properties.

SCARLET PHOSPHORUS, AND THE TRANSITIONS TO VIOLET PHOSPHORUS:—Preparation.

ATOMIC WEIGHT OF PHOSPHORUS:—Historical—Standard Methods and Results—General Conclusions.

CHAPTER IV. **Phosphorus in Combination** 51

PHYSICAL PROPERTIES:—Atomic Volume of Element—Molar Volumes of Compounds—Structure of Compounds—Volume of Phosphorus in Liquid Compounds under Conditions of Maximum Contraction—Parachors of Phosphorus Compounds—Atomic and Molar Refractions—Stereochemistry—Dipole Moment of Phosphine—Representation of Phosphorus Compounds by Electronic Theories of Valency.

PAGE

CHAPTER V. **The Phosphides** 60

Methods of Preparation—Alkali Phosphides—Alkaline Earth Phosphides—Copper, Silver and Gold Phosphides—Zinc Group Phosphides—Boron and Aluminium Phosphides—Titanium Group Phosphides—Tin and Lead Phosphides—Arsenic, Antimony and Bismuth Phosphides—Chromium, Molybdenum and Tungsten Phosphides—Manganese Phosphides—Iron, Cobalt and Nickel Phosphides—Platinum Phosphides.

CHAPTER VI. **Phosphorus and Hydrogen** . . . 68

PHOSPHINE:—Comparison with NH_3 and H_2S—Historical—Occurrence—Preparation—General Properties—Physical Properties—Liquid Phosphine—Chemical Properties.

PHOSPHONIUM COMPOUNDS:—Chloride—Bromide—Iodide.

LIQUID HYDROGEN PHOSPHIDE:—Composition, Properties and Preparation.

SOLID HYDROGEN PHOSPHIDE:—Preparation, Properties, Chemical Reactions.

Higher Hydrogen Phosphides—Hydroxyphosphides—Alkylphosphines, Alkylphosphine Oxides and Sulphides.

CHAPTER VII. **Phosphorus and the Halogens** . . 86

FLUORIDES:—Trifluoride — Pentafluoride — Trifluorodichloride — Trifluorodibromide—Fluophosphoric Acid.

CHLORIDES:—Dichloride — Trichloride — Pentachloride — Chlorobromides — Chloroiodides.

BROMIDES:—Tribromide—Pentabromide.

IODIDES:—Diiodide—Triiodide.

CHAPTER VIII. **Oxy- and Thio-Halides** . . . 105

OXY-HALIDES:—Oxytrifluoride—Fluophosphoric Acids—Oxytrichloride—Pyrophosphoryl Chloride—Metaphosphoryl Chloride—Phosphoryl Monochloride — Phosphoryl Dichlorobromide — Phosphoryl Chlorodibromide — Oxytribromide—Metaphosphoryl Bromide—Oxyiodides.

THIO-HALIDES:—Thiotrifluoride — Thiotrichloride — Thiotribromide — Mixed Thiotrihalides—Thioiodides.

CHAPTER IX. **The Slow Oxidation of Phosphorus** . . 116

The Glow of Phosphorus—Effect of Pressure upon Oxidation of Phosphorus—Velocity of the Reaction—Effect of Temperature—Production of Ozone—Inhibition of the Glow—Nature of the Chemiluminescence—Ionisation by the Glow—The Emission Spectrum.

CHAPTER X. **The Oxides of Phosphorus** . . . 125

Suboxides—Trioxide—Dioxide or Tetroxide—Pentoxide.

CHAPTER XI. **The Oxyacids of Phosphorus—Unsaturated** . 135

Hypophosphorous Acid—Phosphorous Acid—Hypophosphites and Phosphites, Structure and Tautomerism—Meta- and Pyro-phosphorous Acids—Detection and Estimation of Phosphites and Hypophosphites—Hypophosphoric Acid—Detection and Estimation of Hypophosphates.

CHAPTER XII. **Phosphoric Acids** 155

HISTORICAL AND GENERAL.

ORTHOPHOSPHORIC ACID:—Preparation—Physical Properties of Solid Hydrates of P_2O_5—Solubilities, Melting-points and Eutectics of the System H_3PO_4-H_2O—Densities of Aqueous Solutions—Vapour Pressures—Conductivities of Concentrated and Dilute Solutions—Viscosities—Refractive Index—Basicity and Neutralisation of the Phosphoric Acids—Constitution

PAGE

—Chemical Properties—Physiological Action—Uses—Dehydration and Production of Pyro- and Meta-acids.

Pyrophosphoric Acid—Polyphosphoric Acids—Metaphosphoric Acid—Complex Metaphosphoric Acids and their Salts—Properties and Reactions of Ortho-, Meta- and Pyro-phosphates—Common and Distinctive Reactions—Estimation of the Phosphoric Acids—Phosphorus in Alloys—Perphosphoric Acids.

CHAPTER XIII. **Phosphorus and Sulphur or Selenium** . 186

PHOSPHORUS AND SULPHUR:—Historical—Physical Mixtures—The System Phosphorus-Sulphur and Compounds—Tetraphosphorus Trisulphide—Diphosphorus Trisulphide — Tetraphosphorus Heptasulphide — Phosphorus Pentasulphide—Uses of the Sulphides of Phosphorus—Oxysulphides—Thiophosphites, Thiohypophosphates and Thiophosphates.

PHOSPHORUS AND SELENIUM:—Selenides—Selenophosphates—Sulphoselenides.

CHAPTER XIV. **Phosphorus and Nitrogen** . . . 197

Amido-derivatives of Phosphorous and Orthophosphoric Acids—Amido- and Imido-derivatives of Metaphosphoric Acid—Amides and Imides of Condensed Phosphoric Acids—Nitrilophosphoric Acids—Amido-, Imido- and Nitrilo-thiophosphoric Acids—Phosphorus Halonitrides or Amidohalides—Phosphorus Nitride.

CHAPTER XV. **Phosphatic Fertilisers** 208

OCCURRENCE AND CIRCULATION OF PHOSPHORUS:—Mineral Phosphates—Assimilation by Plants—Sources of Phosphates—The Composition of Phosphorites—The Distribution of Phosphatic Rocks—Oceanic Deposits and Guanos—The World's Production of Phosphate Rock.

BASIC SLAG:—Production—High-grade Slag—"Open-hearth" Slag—Fertiliser Action.

SUMMARY OF PHOSPHATIC FERTILISERS.

THE SYSTEM LIME AND PHOSPHORIC ACID:—Solubility of Calcium Phosphates—Conditions of Formation of Basic and Acid Calcium Phosphates—Composition of Solutions Saturated with Calcium Hydrogen Phosphates—Equilibria between Solid Phases and Solutions at Various Temperatures—Changes during Neutralisation—The Acid Phosphates—Manufacture of Superphosphate—Retrogression—Treatment of Special Ores—Phosphoric Acid—Commercial Preparation and Extraction from Rock—The History and Technology of Superphosphate Manufacture—Mixed and Concentrated Phosphoric Fertilisers—Potassium Phosphates—Ammonium Phosphates.

NAME INDEX 229

SUBJECT INDEX 236

LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
Afhandl. Fys. Kem.	Afhandlingat i Fysik, Kemi och Mineralogi.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie (1719–1815, and 1914+).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique (Paris) (1816–1913).
Ann. Mines	Annales des Mines.
Ann. Pharm.	Annalen der Pharmacie (1832–1839).
Ann. Phys. Chem.	Annalen der Physik und Chemie (1819–1899).
Ann. Physik	Annalen der Physik (1799–1818, and 1900+).
Ann. Physik, Beibl.	Annalen der Physik, Beiblättes.
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arbeiten Kaiserl. Gesundheitsamte	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
Arch. exp. Pathol. Pharmak.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles, Genève.
Atti Acc. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia Lincei.
B.A. Reports	British Association Reports.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Akad. Ber.	See *Sitzungsber. K. Akad. Wiss. Berlin.*
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Bot. Zeit.	Botanische Zeitung.
Bul. Soc. Stünte Cluj.	Buletinul Societâtei de Stünte din Cluj.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. de Belg.	Bulletin de la Société chimique Belgique.
Bull. Sci. Pharmacol.	Bulletin des Sciences Pharmacologiques.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. min. de France	Bulletin de la Société minéralogique de France.
Bull. U.S. Geol. Survey	Bulletins of the United States Geological Survey.
Centr. Min.	Centralblatt für Mineralogie.
Chem. Ind.	Die Chemische Industrie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung (Cöthen).
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Crell's Annalen	Chemische Annalen für die Freunde der Naturlehre, von L. Crelle.
Dingl. poly. J.	Dingler's polytechnisches Journal.

Abbreviated Title.	Journal.
Drude's Annalen	Annalen der Physik (1900–1906).
Electroch. Met. Ind.	Electrochemical and Metallurgical Industry.
Eng. and Min. J.	Engineering and Mining Journal.
Gazzetta	Gazzetta chimica italiana.
Gehlen's Allg. J. Chem.	Allgemeines Journal der Chemie.
Geol. Mag.	Geological Magazine.
Gilbert's Annalen	Annalen der Physik (1799–1824).
Giorn. di Scienze Naturali ed Econ.	Giornale di Scienze Naturali ed Economiche.
Helv. Chim. Acta	Helvetica Chim. Acta.
Int. Zeitsch. Metallographie	Internationale Zeitschrift für Metallographie.
Jahrb. kk. geol. Reichsanst.	Jahrbuch der kaiserlich-koniglichen geologischen Reichsanstalt.
Jahrb. Miner.	Jahrbuch fur Mineralogie.
Jahresber.	Jahresbericht über die Fortschritte der Chemie.
Jenaische Zeitsch.	Jenaische Zeitschrift fur Naturwissenschaft.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chem. Soc.	Journal of the Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Gasbeleuchtung	Journal für Gasbeleuchtung.
J. Geology	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Metals	Journal of the Institute of Metals.
J. Miner. Soc.	Mineralogical Magazine and Journal of the Mineralogical Society.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physique	Journal de Physique.
J. prakt. Chem.	Journal fur praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (*Petrograd*).
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Jahrb.	Landwirtschaftliche Jahrbucher.
Mem. Coll. Sci. Kyōtō.	Memoirs of the College of Science, Kyōtō Imperial University.
Mém. Paris Acad.	Mémoirs présentés par divers savants à l'Académie de Sciences de l'Institut de France.
Monatsh.	Monatshefte fur Chemie und verwandte Theile anderer Wissenschaften.
Mon. scient.	Moniteur scientifique.
Münch. Med. Wochenschr.	Münchener Medizinische Wochenschrift.
Nature	Nature.
Nuovo Cim.	Il nuovo Cimento.
Oesterr. Chem. Zeit.	Oesterreichische Chemiker-Zeitung.
Öfvers. K. Vet.-Akad. Förh.	Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Post	Pharmazeutische Post.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Review	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie (1824–1877).
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Phil. Soc. Glasgow	Proceedings of the Royal Philosophical Society of Glasgow.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.

ABBREVIATED TITLE.	JOURNAL.
Rec. Trav. chim.	Recueil des Travaux chimiques des Pay-Bas et de la Belgique.
Roy. Inst. Reports	Reports of the Royal Institution.
Schweigger's J.	Journal fur Chemie und Physik.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Koniglich-Preussischen Akademie de Wissenschaften zu Berlin.
Sitzungsber. K. Akad. Wiss. Wien.	Sitzungsberichte der Koniglich-Bayerischen Akademie der Wissenschaften zu Wien.
Techn. Jahresber.	Jahresbericht uber die Leistungen der Chemischen Technologie.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trav. et Mém. du Bureau intern. des Poids et Mes.	Travaux et Mémoires du Bureau International des Poids et Mesures.
Verh. Ges. deut. Naturforsch. Aerzte.	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wied. Annalen	Wiedemann's Annalen der Physik und Chemie (1877–1899).
Wissenschaftl. Abhandl. phys.-tech. Reichsanst.	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift fur analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift fur angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift fur anorganische Chemie.
Zeitsch. Chem.	Kritische Zeitschrift fur Chemie.
Zeitsch. Chem. Ind. Kolloide	Zeitschrift fur Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift fur Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift fur Krystallographie und Mineralogie.
Zeitsch. Nahr. Genuss-m.	Zeitschrift fur Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift fur physiologische Chemie.
Zeitsch. wiss. Photochem.	Zeitschrift fur wissenschaftliche Photographie, Photophysik, und Photochemie.

TABLE OF DATES OF ISSUE OF JOURNALS.

For the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year.	Amer. J. Sci.	Ann Chim. Phys.	Ann. Min.	Arch. Pharm.	Dingl. Poly. J.	Gilbert's Annalen.	J. Pharm. Chim.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.
1800	...	(1) 32–35	...	...	...	4–6	...	5–8	90	...
1	...	36–39	...	...	...	7–9	...	8–11	91	...
2	...	40–43	...	...	...	10–12	...	11–14	92	...
3	...	44–47	...	...	...	13–15	...	14–17	93	...
4	...	48–51	...	...	...	16–18	...	17–20	94	...
1805	...	52–55	...	...	...	19–21	...	20–23	95	...
6	...	56–60	...	...	...	22–24	...	23–26	96	...
7	...	61–64	...	...	...	25–27	...	26–29	97	...
8	...	65–68	...	...	...	28–30	...	29–32	98	...
9	...	69–72	...	...	...	31–33	(1) 1*	33, 34	99	...
1810	...	73–76	...	...	...	34–36	2	35, 36	100	...
11	...	77–80	...	...	...	37–39	3	37, 38	101	...
12	...	81–84	...	...	...	40–42	4	39, 40	102	...
13	...	85–88	...	...	...	43–45	5	41, 42	103	...
14	...	89–92	...	...	...	46–48	6	43, 44	104	...
1815	...	93–96	...	...	...	49–51	(2) 1	45, 46	105	...
16	...	(2) 1–3	...	...	...	52–54	2	47, 48	106	...
17	...	4–6	1, 2	...	...	55–57	3	49, 50	107	...
18	...	7–9	3	...	...	58–60	4	51, 52	108	...
19	(1) 1	10–12	4	...	...	61–63	5	53, 54	109	...
1820	2	13–15	5	...	1–3	64–66	6	55, 56	110	...
21	3	16–18	6	...	4–6	67–69	7	57, 58	111	...
22	4, 5	19–21	7	1, 2	7–9	70–72	8	59, 60	112	...
23	6	22–24	8	3–6	10–12	73–75	9	61, 62	113	...
24	7, 8	25–27	9	7–10	13–15	76	10	63, 64	114	1, 2
1825	9	28–30	10, 11	11–14	16–18	Continued as Pogg. Annalen.	11	65, 66	115	3–5
26	10, 11	31–33	12, 13	15–19	19–22		12	67, 68	116	6–8
27	12	34–36	(2) 1, 2	20–23	23–26		13	(2) 1, 2	117	9–11
28	13, 14	37–39	3, 4	24–26	27–30		14	3, 4	118	12–14
29	15, 16	40–42	5, 6	27–30	31–34		15	5, 6	119	15–17

* First series known as *Bulletin de Pharmacie.*

Year.	Amer. J. Sci.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Bull. Soc. chim.	Compt. rend.	Dingl. poly. J.	J Pharm. Chim.	J. prakt. Chem.	Mon.* scient.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.	Proc. Roy. Soc.	Quart. J. Chem. Soc	Sitzungsber. K. Akad. Wiss. Wien.
1830	17, 18	...	43–45	7–8	31–34	...	...	35–38	16	...	...	7, 8	120	18–20	...	...	...
31	19, 20	...	46–48	...	35–39	...	...	39–42	17	...	...	9, 10	121	21–23	...	...	...
32	21, 22	1–4	49–51	(3) 1, 2	40–43	...	...	43–47	18	...	...	11 (3) 1	122	24–26	1	...	...
33	23, 24	5–8	52–55	3, 4	44–47	...	...	48–50	19	...	...	2, 3	123	27–30	2	...	...
34	25–27	9–12	56–57	5, 6	48–50	...	...	51–54	20	1–3	...	4, 5	124	31–33	...	...	...
1835	28, 29	13–16	58–60	7, 8	(2) 1–4	...	1	55–58	21	4–6	...	6, 7	125	34–36	...	...	...
36	30, 31	17–20	61–63	9, 10	5–8	...	2, 3	59–62	22	7–9	...	8, 9	126	37–39	...	...	...
37	32, 33	21–24	64–66	11, 12	9–12	...	4, 5	63–66	23	10–12	...	10, 11	127	40–42	3	...	...
38	34, 35	25–28	67–69	13, 14	13–16	...	6, 7	67–70	24	13–15	...	12, 13	128	43–45	...	...	...
39	36, 37	29–32	70–72	15, 16	17–20	...	8, 9	71–74	25	16–18	...	14, 15	129	46–48	...	...	...
1840	38, 39	33–36	73–75	17, 18	21–24	...	10, 11	75–78	26	19–21	...	16, 17	130	49–51	...	...	...
41	40, 41	37–40	(3) 1–3	19, 20	25–28	...	12, 13	79–82	27	22–24	...	18, 19	131	52–54	...	...	...
42	42, 43	41–44	4–6	(4) 1, 2	29–32	...	14, 15	83–86	(3) 1, 2	25–27	...	20, 21	132	55–57	...	...	...
43	44, 45	45–48	7–9	3, 4	33–36	...	16, 17	87–90	3, 4	28–30	...	22, 23	133	58–60	4	...	...
44	46, 47	49–52	10–12	5, 6	37–40	...	18, 19	91–94	5, 6	31–33	...	24, 25	134	61–63	...	...	...
1845	48–50	53–56	13–15	7, 8	41–44	...	20, 21	95–98	7, 8	34–36	...	26, 27	135	64–66	...	...	...
46	(2) 1, 2	57–60	16–18	9, 10	45–48	...	22, 23	99–102	9, 10	37–39	...	28, 29	136	67–69	...	...	...
47	3, 4	61–64	19–21	11, 12	49–52	...	24, 25	103–106	11, 12	40–42	...	30, 31	137	70–72	...	1	...
48	5, 6	65–68	22–24	13, 14	53–56	...	26, 27	107–110	13, 14	43–45	...	32, 33	138	73–75	...	1, 2	1
49	7, 8	69–72	25–27	15, 16	57–60	...	28, 29	111–114	15, 16	46–48	...	34, 35	139	76–78	...	2, 3	2, 3
1850	9, 10	73–76	28–30	17, 18	61–64	...	30, 31	115–118	17, 18	49–51	...	36, 37	140	79–81	...	3	4, 5
51	11, 12	77–80	31–33	19, 20	65–68	...	32, 33	119–122	19, 20	52–54	...	(4) 1, 2	141	82–84	5	4	6, 7
52	13, 14	81–84	34–36	(5) 1, 2	69–72	...	34, 35	123–126	21, 22	55–57	...	3, 4	142	85–87	...	5	8, 9
53	15, 16	85–88	37–39	3, 4	73–76	...	36, 37	127–130	23, 24	58–60	...	5, 6	143	88–90	...	6	10, 11
54	17, 18	89–92	40–42	5, 6	77–80	...	38, 39	131–134	25, 26	61–63	...	7, 8	144	91–93	6, 7	7	12–14
1855	19, 20	93–96	43–45	7, 8	81–84	...	40, 41	135–138	27, 28	64–66	...	9, 10	145	94–96	7	8	15–18
56	21, 22	97–100	46–48	9, 10	85–88	...	42, 43	139–142	29, 30	67–69	...	11, 12	146	97–99	8	9	19–22
57	23, 24	101–104	49–51	11, 12	89–92	...	44, 45	143–146	31, 32	70–72	(1) 1	13, 14	147	100–102	9	10	23–27
58	25, 26	105–108	52–54	13, 14	93–96	1	46, 47	147–150	33, 34	73–75	2	15, 16	148	103–105	9	11	28–33
59	27, 28	109–112	55–57	15, 16	97–100	1	48, 49	151–154	35, 36	76–78	3	17, 18	149	106–108	9, 10	12	34–38

* Often referred to by Series: Series 3, vols. 1–16, 1871–1886; Series 4, vols. 1–24, 1887–1910; Series 5, vols. 1–9, 1911–1919 (one vol. yearly).

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Annalen Suppl.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J	Chem. Zeit.
1860	...	29, 30	...	113–116	...	58–60	17, 18	101–104	...	2	1, 2	...	...
61	...	31, 32	...	117–120	1	61–63	19, 20	105–108	...	3	3, 4	...	...
62	...	33, 34	...	121–124	2	64–66	(6) 1, 2	109–112	...	4	5, 6	...	...
63	...	35, 36	...	125–128	2	67–69	3, 4	113–116	...	5	7, 8	...	...
64	...	37, 38	...	129–132	3	(4) 1–3	5, 6	117–120	...	(2) 1, 2	9, 10	..	...
1865	...	39, 40	...	133–136	3, 4	4–6	7, 8	121–124	...	3, 4	11, 12	...	...
66	...	41, 42	...	137–140	4	7–9	9, 10	125–128	...	5, 6	13, 14	...	...
67	...	43, 44	...	141–144	5	10–12	11, 12	129–132	...	7, 8	15, 16	...	...
68	...	45, 46	...	145–148	6	13–15	13, 14	133–136	1	9, 10	17, 18	...	...
69	...	47, 48	...	149–152	...	16–18	15, 16	137–140	2	11, 12	19, 20	...	...
1870	...	49, 50	...	153–156	7	19–21	17, 18	141–144	3	13, 14	21, 22	...	...
71	...	(3) 1, 2	...	157–160	...	22–24	19, 20	145–148	4	15, 16	23, 24	...	...
72	.	3, 4	...	161–164	8	25–27	(7) 1, 2	149–150, 201 *	5	17, 18	25, 26	...	...
73	...	5, 6	...	165–170	...	28–30	3, 4	201–203	6	19, 20	27, 28	...	...
74	...	7, 8	...	171–174	..	(5) 1–3	5, 6	204, 205	7	21, 22	29, 30	...	...
1875	...	9, 10	...	175–179	...	4–6	7, 8	206, 207	8	23, 24	31, 32	...	...
76	...	11, 12	1	180–183	...	7–9	9, 10	208, 209	9	25, 26	33, 34	...	...
77	...	13, 14	2	184–189	...	10–12	11, 12	210, 211	10	27, 28	35, 36	..	1
78	...	15, 16	3	190–194	...	13–15	13, 14	212, 213	11	29, 30	37, 38	...	2
79	1	17, 18	4	195–199	...	16–18	15, 16	214, 215	12	31, 32	39, 40	...	3
1880	1, 2	19, 20	5	200–205	...	19–21	17, 18	216, 217	13	33, 34	41, 42	...	4
81	2, 3	21, 22	6	206–210	...	22–24	19, 20	218, 219	14	35, 36	43, 44	...	5
82	3, 4	23, 24	7	211–215	...	25–27	(8) 1, 2	220	15	37, 38	45, 46	...	6
83	4, 5	25, 26	8	216–221	...	28–30	3, 4	221	16	39, 40	47, 48	...	7
84	5, 6	27, 28	9	222–226	...	(6) 1–3	5, 6	222	17	41, 42	49, 50	...	8
1885	6, 7	29, 30	10	227–231	...	4–6	7, 8	223	18	43, 44	51, 52	...	9
86	7, 8	31, 32	11	232–236	...	7–9	9, 10	224	19	45, 46	53, 54	...	10
87	9	33, 34	12	237–242	...	10–12	11, 12	225	20	47, 48	55, 56	1	11
88	10	35, 36	13	243–249	...	13–15	13, 14	226	21	49, 50	57, 58	2, 3	12
89	11	37, 38	14	250–255	...	16–18	15, 16	227	22	(3) 1, 2	59, 60	4, 5	13

* Joining Series 1 and 2 together. Also written as (3) 1, 2, 3, etc.

Year.	Compt. rend.	Dingl. poly. J.	Gazzetta.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Pharm. Chim.	J. prakt Chem.	J. Russ. Phys. Chem. Soc.	J. Soc. Chem. Ind.	Monatsh.	Mon. scient.*	Nature.	Phil Mag.
1860	50, 51	155–158	...	...	...	37, 38	79–81	...	...	...	4	...	19, 20
61	52, 53	159–162	...	...	...	39, 40	82–84	...	...	...	...	...	21, 22
62	54, 55	163–166	...	...	15	41, 42	85–87	...	...	...	...	...	23, 24
63	56, 57	167–170	...	...	16	43, 44	88–90	...	...	...	5	...	25, 26
64	58, 59	171–174	...	...	17	45, 46	91–93	...	...	...	6	...	27, 28
1865	60, 61	175–178	...	...	18	(4) 1, 2	94–96	...	...	...	7	...	29, 30
66	62, 63	179–182	...	...	19	3, 4	97–99	...	...	...	8	...	31, 32
67	64, 65	183–186	...	...	20	5, 6	100–102	...	...	...	9	...	33, 34
68	66, 67	187–190	...	...	21	7, 8	103–105	...	...	...	10	...	35, 36
69	68, 69	191–194	...	...	22	9, 10	106–108	1	...	..	11	1	37, 38
1870	70, 71	195–198	...	...	23	11, 12	(2) 1, 2	2	...	...	12	1, 2, 3	39, 40
71	72, 73	199–202	1	...	24	13, 14	3, 4	3	...	..	13	3, 4, 5	41, 42
72	74, 75	203–206	2	...	25	15, 16	5, 6	4	...	...	14	5, 6, 7	43, 44
73	76, 77	207–210	3	...	26	17, 18	7, 8	5	...	...	15	7, 8, 9	45, 46
74	78, 79	211–214	4	...	27	19, 20	9, 10	6	...	...	16	9, 10, 11	47, 48
1875	80, 81	215–218	5	...	28	21, 22	11, 12	7	...	...	17	11, 12, 13	49, 50
76	82, 83	219–222	6	...	29, 30	23, 24	13, 14	8	...	.	18	13, 14, 15	(5) 1, 2
77	84, 85	223–226	7	..	31, 32	25, 26	15, 16	9	...	...	19	15, 16, 17	3, 4
78	86, 87	227–230	8	...	33, 34	27, 28	17, 18	10	...	...	20	17, 18, 19	5, 6
79	88, 89	231–234	9	1	35, 36	29, 30	19, 20	11	...	..	21	19, 20, 21	7, 8
1880	90, 91	235–238	10	2	37, 38	(5) 1, 2	21, 22	12	...	1	22	21, 22, 23	9, 10
81	92, 93	239–242	11	3	39, 40	3, 4	23, 24	13	...	2	23	23, 24, 25	11, 12
82	94, 95	243–246	12	4	41, 42	5, 6	25, 26	14	1	3	24	25, 26, 27	13, 14
83	96, 97	247–250	13	5	43, 44	7, 8	27, 28	15	2	4	25	27, 28, 29	15, 16
84	98, 99	251–254	14	6	45, 46	9, 10	29, 30	16	3	5	26	29, 30, 31	17, 18
1885	100, 101	255–258	15	7	47, 48	11, 12	31, 32	17	4	6	27	31, 32, 33	19, 20
86	102, 103	259–262	16	8	49, 50	13, 14	33, 34	18	5	7	28	33, 34, 35	21, 22
87	104, 105	263–266	17	9	51, 52	15, 16	35, 36	19	6	8	29, 30	35, 36, 37	23, 24
88	106, 107	267–270	18	10	53, 54	17, 18	37, 38	20	7	9	31, 32	37, 38, 39	25, 26
89	108, 109	271–274	19	11	55, 56	19, 20	39, 40	21	8	10	33, 34	39, 40, 41	27, 28

* See footnote, p. xxii.

Year.	Phil. Trans.	Pogg. Annalen.	Proc. Chem. Soc.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Rec Trav. Chim.	Sitzungsber K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem.
1860	150	109–111	...	10, 11	13	...	39–42	...	...	...	...	...	...
61	151	112–114	...	11	14	...	43, 44	...	...	...	...	...	...
62	152	115–117	...	11, 12	Continued as J. Chem. Soc	...	45, 46	...	...	1	...	...	...
63	153	118–120	...	12, 13		...	47, 48	...	...	2	...	...	...
64	154	121–123	...	13		...	49, 50	...	...	3	...	...	...
1865	155	124–126	...	14	...	...	51, 52	...	...	4	...	...	...
66	156	127–129	...	15	...	...	53, 54	...	...	5	...	...	...
67	157	130–132	...	15, 16	...	...	55, 56	...	...	6	...	...	...
68	158	133–135	...	16, 17	...	...	57, 58	...	...	7	...	...	...
69	159	136–138	...	17, 18	...	...	59, 60	...	...	8	...	...	...
1870	160	139–141	...	18, 19	...	...	61, 62	...	...	9	...	...	...
71	161	142–144	...	19, 20	...	...	63, 64	...	...	10	...	...	...
72	162	145–147	...	20, 21	...	...	65, 66	...	...	11	...	...	...
73	163	148–150	...	21, 22	...	...	67, 68	...	...	12	...	...	...
74	164	151–153	...	22, 23	...	...	69, 70	...	...	13	...	...	...
1875	165	154–156	...	23, 24	...	...	71, 72	...	...	14	...	...	...
76	166	157–159	...	24, 25	...	...	73, 74	...	...	15	...	...	...
77	167	160	...	25, 26	...	...	75, 76	...	1, 2	16	...	1, 2	...
78	168, 169	Continued as Wied. Annalen.	...	27, 28	...	...	77, 78	...	3–5	17	...	2, 3	...
79	170		...	28, 29, 30	...	...	79, 80	...	6–8	18	...	3, 4	...
1880	171	...	...	30, 31	...	...	81, 82	...	9–11	19	...	4, 5	...
81	172	...	...	31, 32, 33	...	...	83, 84	1	12–14	20	...	5, 6	...
82	173	...	...	33, 34	...	1	85, 86	2	15–17	21	...	6, 7	...
83	174	...	...	34, 35, 36	...	2	87, 88	3	18–20	22	...	7, 8	...
84	175	...	...	36, 37, 38	...	3	89, 90	4	21–23	23	...	8, 9, 10	...
1885	176	...	1	38, 39	...	4	91, 92	5	24–26	24	...	10, 11	...
86	177	...	2	40, 41	...	5	93, 94	6	27–29	25	...	11, 12	...
87	A. 178	...	3	42, 43	...	6	95, 96	7	30–32	26	...	12, 13	1
88	179	...	4	43, 44, 45	...	7	97	8	33–35	27	1	13, 14, 15	2
89	180	...	5	45, 46, 47	...	8	98	9	36–38	28	2	15	3, 4

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Week-blad.	Chem. Zeit.	Compt. rend.
1890	12	39, 40	15	256–260	19–21	17, 18	228	23	3, 4	61, 62	6, 7	...	14	110, 111
91	13	41, 42	16	261–266	22–24	19, 20	229	24	5, 6	63, 64	8, 9	...	15	112, 113
92	14	43, 44	17	267–271	25–27	(9) 1, 2	230	25	7, 8	65, 66	10, 11	...	16	114, 115
93	15	45, 46	18	272–277	28–30	3, 4	231	26	9, 10	67, 68	12, 13	...	17	116, 117
94	16	47, 48	19	278–283	(7) 1–3	5, 6	232	27	11, 12	69, 70	14, 15	...	18	118, 119
1895	17	49, 50	20	284–288	4–6	7, 8	233	28	13, 14	71, 72	16, 17	...	19	120, 121
96	18	(4) 1, 2	21	289–293	7–9	9, 10	234	29	15, 16	73, 74	18, 19	...	20	122, 123
97	19	3, 4	22	294–298	10–12	11, 12	235	30	17, 18	75, 76	20, 21	...	21	124, 125
98	20	5, 6	23	299–303	13–15	13, 14	236	31	19, 20	77, 78	22, 23	...	22	126, 127
99	21, 22	7, 8	24	304–309	16–18	15, 16	237	32	21, 22	79, 80	24, 25	...	23	128, 129
1900	23, 24	9, 10	25	310–313	19–21	17, 18	238	33	23, 24	81, 82	26, 27	...	24	130, 131
1	25, 26	11, 12	26	314–319	22–24	19, 20	239	34	25, 26	83, 84	28, 29	..	25	132, 133
2	27, 28	13, 14	27	320–325	25–27	(10) 1, 2	240	35	27, 28	85, 86	30, 31	...	26	134, 135
3	29, 30	15, 16	28	326–329	28–30	3, 4	241	36	29, 30	87, 88	32, 33	...	27	136, 137
4	31, 32	17, 18	29	330–337	(8) 1–3	5, 6	242	37	31, 32	89, 90	34, 35	...	28	138, 139
1905	33, 34	19, 20	30	338–343	4–6	7, 8	243	38	33, 34	91, 92	36, 37	..	29	140, 141
6	35, 36	21, 22	31	344–350	7–9	9, 10	244	39	35, 36	93, 94	38, 39	...	30	142, 143
7	37, 38	23, 24	32	351–357	10–12	11, 12	245	40	(4) 1, 2	95, 96	40, 41	4	31	144, 145
8	39, 40	25, 26	33	358–363	13–15	13, 14	246	41	3, 4	97, 98	42, 43	5	32	146, 147
9	41, 42	27, 28	34	364–371	16–18	15, 16	247	42	5, 6	99, 100	44, 45	6	33	148, 149
1910	43, 44	29, 30	35	372–377	19–21	17, 18	248	43	7, 8	101, 102	46, 47	7	34	150, 151
11	45, 46	31, 32	36	378–385	22–24	19, 20	249	44	9, 10	103, 104	48, 49	8	35	152, 153
12	47, 48	33, 34	37	386–394	25–27	(11) 1, 2	250	45	11, 12	105, 106	50, 51	9	36	154, 155
13	49, 50	35, 36	38	395–401	28–30	3, 4	251	46	13, 14	107, 108	52, 53	10	37	156, 157
14	Publication ceased	37, 38	39	...	...	5, 6	252	47	15, 16	109, 110	54, 55	11	38	158, 159
1915		39, 40	40	...	...	...	253	48	17, 18	111, 112	56, 57	12	39	160, 161
16	...	41, 42	41	...	...	...	254	49	19, 20	113, 114	58, 59	13	40	162, 163
17	...	43, 44	42	...	...	...	255	50	21, 22	115, 116	60, 61	14	41	164, 165
18	...	45, 46	43	...	...	...	...	51	23, 24	117	62, 63	15	42	166, 167
19	...	47, 48	44	...	...	...	...	52	25, 26	118, 119	64, 65	16	43	168, 169

Year.	Dingl. poly. J.	Gazzetta.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Ind. Eng. Chem.	J. Pharm. Chim.	J. Physical Chem.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc.	J. Soc. Chem. Ind.	Monatsh.	Mon.* scient.	Nature.	Phil. Mag.
1890	275–278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41, 42, 43	29, 30
91	279–282	21	13	59, 60	...	23, 24	...	43, 44	23	10	12	37, 38	43, 44, 45	31, 32
92	283–286	22	14	61, 62	...	25, 26	...	45, 46	24	11	13	39, 40	45, 46, 47	33, 34
93	287–290	23	15	63, 64	...	27, 28	...	47, 48	25	12	14	41, 42	47, 48, 49	35, 36
94	291–294	24	16	65, 66	...	29, 30	...	49, 50	26	13	15	43, 44	49, 50, 51	37, 38
1895	295–298	25	17	67, 68	...	(6) 1, 2	. .	51, 52	27	14	16	45, 46	51, 52, 53	39, 40
96	299–302	26	18	69, 70	...	3, 4	...	53, 54	28	15	17	47, 48	53, 54, 55	41, 42
97	303–306	27	19	71, 72	...	5, 6	...	55, 56	29	16	18	49, 50	55, 56, 57	43, 44
98	307–310	28	20	73, 74	...	7, 8	...	57, 58	30	17	19	51, 52	57, 58, 59	45, 46
99	311–314	29	21	75, 76	...	9, 10	...	59, 60	31	18	20	53, 54	59, 60, 61	47, 48
1900	315	30	22	77, 78	...	11, 12	4	61, 62	32	19	21	55, 56	61, 62, 63	49, 50
1	316	31	23	79, 80	...	13, 14	5	63, 64	33	20	22	57	63, 64, 65	(6) 1, 2
2	317	32	24	81, 82	...	15, 16	6	65, 66	34	21	23	58	65, 66, 67	3, 4
3	318	33	25	83, 84	...	17, 18	7	67, 68	35	22	24	59	67, 68, 69	5, 6
4	319	34	26	85, 86	...	19, 20	8	69, 70	36	23	25	60, 61	69, 70, 71	7, 8
1905	320	35	27	87, 88	...	21, 22	9	71, 72	37	24	26	62, 63	71, 72, 73	9, 10
6	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73, 74, 75	11, 12
7	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75, 76, 77	13, 14
8	323	38	30	93, 94	...	27, 28	12	77, 78	40	27	29	68, 69	77, 78, 79	15, 16
9	324	39	31	95, 96	1	29, 30	13	79, 80	41	28	30	70, 71	79–82	17, 18
1910	325	40	32	97, 98	2	(7) 1, 2	14	81, 82	42	29	31	72, 73	82–85	19, 20
11	326	41	33	99, 100	3	3, 4	15	83, 84	43	30	32	74, 75	85–88	21, 22
12	327	42	34	101, 102	4	5, 6	16	85, 86	44	31	33	76, 77	88, 89, 90	23, 24
13	328	43	35	103, 104	5	7, 8	17	87, 88	45	32	34	78, 79	90, 91, 92	25, 26
14	329	44	36	105, 106	6	9, 10	18	89 90	46	33	35	80, 81	92, 93, 94	27, 28
1915	...	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94, 95, 96	29, 30
16	...	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96, 97, 98	31, 32
17	...	47	39	111, 112	9	15, 16	21	95, 96	...	36	38	84	98, 99, 100	33, 34
18	...	48	40	113, 114	10	17, 18	22	97, 98	...	37	39	85	100–102	35, 36
19	...	49	41	115, 116	11	19, 20	23	99, 100	...	38	40	86	102–104	37, 38

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* See footnote, p. xxii.

Year.	Phil. Trans.	Physikal. Zeitsch.	Proc. Chem. Soc.	Proc. Roy. Soc.	Rec. Trav. Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. anorg. Chem.	Zeitsch. Elektro-chem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem.
1890	A. 181	...	6	47, 48, 49	9	99	10	39–41	29	3	...	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42–44	30	4	...	...	19, 20	7, 8
92	183	...	8	50, 51, 52	11	101	12	45–47	31	5	1, 2	...	20, 21	9, 10
93	184	...	9	52, 53, 54	12	102	13	48–50	32	6	3, 4, 5	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51–53	33	7	5–7	1	23, 24	13–15
1895	186	...	11	57, 58, 59	14	104	15	54–56	34	8	8–10	1, 2	24, 25	16–18
96	187, 188	...	12	59, 60	15	105	16	57–59	35	9	11, 12, 13	2, 3	26–28	19–21
97	189, 190	...	13	60, 61, 62	16	106	17	60–63	36	10	13–15	3, 4	28, 29	22–24
98	191	...	14	62, 63, 64	17	107	18	64–66	37	11	16–19	4, 5	29–31	25–27
99	192, 193	...	15	64, 65, 66	18	108	19	67–69	38	12	19–22	5, 6	31, 32	28–31
1900	194, 195	1	16	66, 67	19	109	20	Continued as Annalen der Physik.	39	13	22–25	6, 7	32–34	32–35
1	196, 197	2	17	68, 69	20	110	21		40	14	26–29	7	34–36	36–38
2	198, 199	3	18	69, 70	21	111	22		41	15	29–33	8	36, 37	39–42
3	200–202	4	19	71, 72	22	112	23		42	16	33–37	9	37–39	43–46
4	203	5	20	72, 73, 74	23	113	24		43	17	38–42	10	39, 40	47–49
1905	204, 205	6	21	74–76	24	114	25		44	18	43–48	11	40–42	50–53
6	206	7	22	A. 77, 78	25	115	26		45	19	48–52	12	42, 43	54–57
7	207	8	23	78, 79, 80	26	116	27		46	20	52–56	13	43, 44	58–60
8	207–209	9	24	80, 81	27	117	28		47	21	56–60	14	44–46	61–64
9	209, 210	10	25	82, 83	28	118	29		48	22	61–65	15	46, 47	65–69
1910	210	11	26	83, 84	29	119	30		49	23	65–69	16	48, 49	70–74
11	210, 211	12	27	84, 85, 86	30	120	31		50	24	69–73	17	49, 50	75–77
12	211, 212	13	28	86, 87	31	121	32		51	25	73–79	18	50–52	78–80
13	212, 213	14	29	88, 89	32	122	33		52	26	79–83	19	52, 53	81–86
14	213, 214	15	30	89, 90	33	123	34		53	27	84–90	20	54	86–88
1915	215, 216	16	Publication of matter of scientific interest now abandoned.	...	34	...	35		54	28	90–93	21	55	89, 90
16	216, 217	17		...	35	...	36		55	29	94–98	22	..	91, 92
17	217	18		...	36, 37	...	37		56	30	99–101	23	...	92
18	217	...		...	37	...	38		57	31	102–104	24	No issue*	92
19	...	...		...	38	...	39		58	32	105–109	25	...	...

* Remainder of vol. 55 appeared in 1920.

A TEXT-BOOK OF

INORGANIC CHEMISTRY.

VOLUME VI. PART II.

A TEXT-BOOK OF
INORGANIC CHEMISTRY.

VOL. VI. PART II.
PHOSPHORUS.

CHAPTER I.

PHOSPHORUS, GENERAL.

Symbol, P. Atomic number, 15. Atomic weight, 31·02 (O = 16).

Occurrence.—Phosphorus does not appear to occur in the free state in nature. If it were produced by the reduction of phosphatic minerals at high temperatures it would be liberated as vapour, which would condense to liquid or solid white phosphorus, and would again be oxidised rapidly under most conditions. Sulphur, which resembles phosphorus in so many respects, does, however, occur as element in considerable quantities, because it is produced in many reactions which take place at comparatively low temperatures (such as that between H_2S and SO_2), and, when once produced, is far less easily oxidised than phosphorus. Phosphorus (0·142) is actually more abundant than sulphur (0·093), the numbers in brackets referring to the percentage of the earth's 10-mile crust, with atmosphere and hydrosphere,[1] constituted by the element. Phosphorus is thus twelfth in the order of abundance, coming below chlorine but above carbon. In the 10-mile crust composed of the lithosphere only, phosphorus is present to the extent of 0·157 per cent., being now in the tenth place, since hydrogen and chlorine in the rocks occupy a position below phosphorus, although they are still above carbon. The average proportion in igneous rocks is 0·13 per cent., whilst the element is also common in sedimentary rocks, chiefly as phosphate of lime, and to a less extent as phosphates of iron and alumina. These secondary deposits are by far the most important sources of phosphates. They are derived probably from the widely but sparsely diffused ingredients of igneous rocks and from the well-crystallised but more stable minerals such as *apatite* (calcium fluo- or chloro-phosphate), which gradually disintegrate,[2] pass into the soil, and are concentrated in plant tissues and in the bones of animals, which eventually yield deposits of phosphate of lime. The compositions of the principal phosphatic rocks are detailed in Chapter XV.

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[1] Clark and Washington, *Proc. Nat. Acad. Sci. U.S.A.*, 1922, 8, 108. See also Harkins, *J. Amer. Chem. Soc.*, 1917, 39, 856; Tammann, *Zeitsch. anorg. Chem.*, 1923, 131, 96.

[2] Lindgren, *Econ. Geol.*, 1923, 18, 419; also Blackwelder, *Amer. J. Sci.*, 1916, [4], 42, 285.

Phosphorus is present to the extent of about 0·1 per cent. in ordinary soils. From this source plants draw the supplies which are essential to their growth—the phosphorus is found mainly in the seeds, and is more concentrated in the germ of these. It is estimated that 100 lbs. of corn contain nearly $\frac{1}{2}$ lb. of phosphorus. Phosphorus is also present in the bodies of animals, and although a minor constituent of the soft parts, is absolutely necessary to life. It is present as soluble phosphate in the blood, milk and other fluids, as a constituent of organic compounds in the brain, spinal cord, and other parts, and as calcium phosphate in the bones. The proportions vary considerably in different parts of the body. Ox brain has been found to contain nearly 2 per cent., human liver 1 per cent. In animal fats phosphorus occurs combined in the "lipoid" form—for example, as lecithin. Bones contain over 40 per cent. of calcium and magnesium phosphates. The human skeleton, weighing about 14 lbs., contains about 5 lbs. of calcium phosphate, or 1 lb. of phosphorus. Since the bones form about 10 per cent. of the total weight of the body, and the rest of the body, exclusive of the bones, contains of the order of 0·1 per cent. of phosphorus, it will be seen that there is slightly over 1 lb., or about 500 grams, of this element in the body. Analysis of certain parts of the body shows that about 90 per cent. of the phosphorus is present in the bones, 8 per cent. in the muscles, and a total of 2 per cent. in the brain, liver, lungs, and blood.[1]

While plants use phosphorus very sparingly, animals require a greater proportion for their metabolism.

The continual secretion of phosphorus necessitates a constant supply. About 1 gram a day for the adult is required to maintain the body equilibrium.* An adequate supply is also one of the factors which control growth. The milk of the cow contains about 0·2 per cent. of P_2O_5, that of the rabbit nearly 1 per cent. In other cases also there is a relation between the percentage of phosphorus in the milk and the reciprocal of the number of days required to double the weight at birth.

History.—As just explained, phosphorus is concentrated in plant and animal products. These are not only more widely distributed than the rich phosphatic minerals, but they also form a more interesting and attractive object of experiment, and, what is perhaps more important, they contain their own reducing agents. It is not surprising, therefore, that the element was first discovered in its organic sources by the doctors and pharmacists who formed the majority of the experimentalists in the iatro-chemical and succeeding periods of chemical history. By distillation of the residue from the evaporation of urine (which contains phosphates and organic matter) the alchemist Brand in 1669 obtained a substance which glowed without any noticeable evolution of heat.[2] Brand's process was described by Kirchmaier in 1676 and discovered independently by Kunkel in 1678, who designated the product " noctiluca " and " phosphorus mirabilis " respectively, by which names it was distinguished from Bolognese phosphorus (" lapis bononiensis ") and Baldwin's phosphorus (" phosphorus hermeticus "), which are phosphorescent sulphides of the alkaline earths.

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[1] "*Die Phosphortherapie vom Standpunkte des Sauerstoffwechsels aus betrachtet,*" Weber, *Arzt. Rdsch.*, 1905, 15, 398, Munich.

* 1·26 grams per each 100 kilograms body-weight.

[2] Peters, *Arch. Geschichte Naturwiss.*, 1912, 4, 206; 1916, 7, 92.

Brand's secret was bought by Krafft, who exhibited " das kalte Feuer " at various Courts, and in 1677 at that of King Charles II., where it was seen by Boyle, who, being informed that it was prepared from an animal source, worked out the method of preparation and described this in a sealed paper which was deposited with the Royal Society in 1680 and published in 1693.[1] The urine was evaporated down to a syrup, which was mixed with three times its weight of clean sand and distilled at the highest available temperature from a retort, the neck of which almost touched the surface of some water. White fumes given off at first were followed by a vapour which condensed and fell to the bottom of the water. At the beginning of the eighteenth century the " noctiluca " was made and sold by Boyle's assistant Hanckewitz, and consequently it became known as " Boyle's phosphorus or English phosphorus."

Phosphorus was detected also in mustard seed by Albinus in 1688.[2] The existence of large supplies in minerals had been established by Gahn towards the end of the eighteenth century, who also recognised it in *bone-ash* (1769) and in the mineral *pyromorphite* (1779).

Phosphorus was prepared in various European countries during the eighteenth century, but it remained an expensive chemical curiosity until Gahn, about 1770, discovered in bone-ash a more suitable source of phosphorus, and Scheele developed a method of preparing the element which was described in several communications.[3] According to this method the acid liberated from bone-ash by means of nitric acid and freed from lime by precipitation with sulphuric acid, was distilled with charcoal, phosphorus being collected under water. This method has the advantage of yielding the phosphorus at a comparatively low temperature, but the metaphosphoric acid liberated by the nitric acid is partly volatilised and so partly escapes reduction. The present method of preparation proceeds by the following stages :—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4 \qquad . \qquad . \qquad (1)$$

The calcium sulphate is filtered off and the phosphoric acid concentrated to a syrup and strongly heated in order to convert it into metaphosphoric acid—

$$H_3PO_4 = HPO_3 + H_2O \qquad . \qquad . \qquad . \qquad (2)$$

This acid is mixed into a paste with charcoal or ground coke and distilled, finishing at a yellow heat—

$$4HPO_3 + 12C = P_4 + 2H_2 + 12CO \qquad . \qquad . \qquad . \qquad (3)$$

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[1] Boyle, *Phil. Trans.*, 1680, 13, 196, 428; *ibid.*, 1693, 17, 583; "*Aerial Noctiluca,*" London, 1680; "*Icy Noctiluca,*" London, 1680.

[2] Albinus, "*Dissert. de phosphoro liquido et solido,*" Francofurti, 1688.

[3] Scheele, *Svenska Akad. Handl.*, 1771, 33, 120; "*Gazette Salutaire de Bouillon,*" 1775; see also "*Chem. Abh. von der Luft und Feuer,*" 1771.

COMMERCIAL PREPARATION OF PHOSPHORUS.

Preparation of White Phosphorus.

(a) **By Reduction of Phosphoric Acid.**—The world's supplies of phosphorus were for nearly a century obtained by a method substantially identical with that of Scheele. Scheele's raw material bone-ash, containing as it does from 34 to nearly 40 per cent. of P_2O_5 and decomposed easily by sulphuric acid, is still the best which can be used. Precipitated phosphate of lime obtained as a by-product in the manufacture of glue from bones also contains nearly 40 per cent. of P_2O_5 and is otherwise suitable. If phosphatic minerals are used for the preparation they must contain less than 10 to 12 per cent. of calcium carbonate, with only small quantities of the oxides of iron, aluminium, magnesium and the alkali metals, since these dissolve in the acid and reappear in the retorts with undesirable effects. The aqueous phosphoric acid liberated by the sulphuric acid is concentrated by evaporation in lead-lined wooden tanks heated by lead pipes through which passes superheated steam. Evaporation is continued with stirring until the density of the liquor is raised to 1·325 or to 1·50, according to the nature of the next process. After the removal of any gypsum, $CaSO_4.2H_2O$, or anhydrite, $CaSO_4$, the concentrated acid is mixed with saw-dust or charcoal, the former of which is suitably mixed with an acid of lower density, or the latter with syrupy acid. The mixture is evaporated in a cast-iron pot to expel any sulphuric acid which may remain. The charred mass is then introduced into fireclay bottles, a number of which, say 24, are placed back to back in a galley furnace similar to that used in the distillation of zinc by the Belgian process. The necks of these bottles are luted to malleable iron pipes, which dip beneath water in closed troughs. Gases which are evolved during the distillation are trapped and led away to be burnt. Finally the retorts are raised to a white heat. The phosphorus vapour is completely distilled over in about 16 hours. The liquid which collects under water in the sloping troughs is ladled occasionally into boxes made of malleable iron for transport to the refinery. Here the crude product, which may be buff to brick-red or nearly black, is agitated under water with sulphuric acid and dichromate of potash or soda. The liquid is afterwards siphoned and filtered through a canvas bag, then being remelted and run into tin moulds, where it solidifies in the form of sticks or wedges. The yield is slightly less than 70 per cent., or about two-thirds of the weight of combined phosphorus present in the charge, the loss being due in part to the fact that metaphosphoric acid is volatile above a red heat, and therefore escapes the reduction which is symbolised by equation (3), p. 5. Consequently the original procedure of Scheele was modified by the addition of only so much sulphuric acid as would form monocalcium phosphate, $CaH_4(PO_4)_2$, which, on ignition, yields the metaphosphate. When this metaphosphate is strongly heated it loses two-thirds of its phosphoric anhydride, which as it is liberated is reduced by the carbon as follows :—

$$3Ca(PO_3)_2 = Ca_3(PO_4)_2 + 2P_2O_5$$
$$2P_2O_5 + 10C = P_4 + 10CO$$

The yield in this process is diminished by the production of phosphide, in addition to carbide, thus—

$$Ca_3(PO_4)_2 + 14C = 3CaC_2 + 2P + 8CO$$
$$Ca_3(PO_4)_2 + 8C = Ca_3P_2 + 8CO\ ^1$$

It is stated that phosphorus can be made in the ordinary blast furnace at 1300° C., but it rapidly oxidises to the pentoxide, the production of 1 ton of which requires about 4 tons of coke.[2]

(b) **Electric Furnace Processes.**—The intermediate preparation of phosphoric acid and acid phosphates can be avoided by taking advantage of the fact that the less volatile silica can expel the more volatile phosphoric anhydride, which can be reduced by carbon.[3] High temperatures are required for these reactions, and these are best attained by electrical heating, although gas-fired furnaces lined with carborundum have also been employed.

The more acid phosphates of lime melt below 1500° C.—$CaO.P_2O_5$ at 970° to 980° and $2CaO.P_2O_5$ at 1230° [4]—while tribasic and more basic calcium phosphates melt above 1550° C., $3CaO.P_2O_5$ at 1670°. This last compound combines with silica at about 1150° C. to form compounds such as $3CaO.3SiO_2.P_2O_5$ (m.pt. 1760° C.), which are rather more easily reduced by carbon than the original phosphate, on account of the increase in vapour pressure of the P_2O_5, which also combines with excess of silica to form completely reducible compounds such as $2SiO_2.P_2O_5$ and $3SiO_2.P_2O_5$. The whole process may be summarised by the equation :

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 6CaSiO_3 + 10CO + P_4$$

The mixture of bone-ash or ground phosphate rock, sand and coal dust or wood charcoal is introduced continuously into a furnace heated by the electric current, passing between carbon electrodes (see p. 8). The reaction begins at about 1100° C., but a much higher temperature is required to melt the charge and slag of calcium silicate which is drawn off continuously, while the phosphorus distils at about 1300° C. The yield is said to be about 92 per cent. of the theoretical.

The first proposals for the employment of electrical heating in the production of phosphorus were made by Readman, Parker and Robinson.[5] The simultaneous production of an alkali silicate by heating alkali phosphate, silica and carbon in a regenerative furnace was patented by Folie-Desjardins.[6] In the Readman-Parker-Robinson process, as worked later, the phosphate, carbon and fluxes, previously heated to a high temperature, are introduced into the upper part of an electric furnace made of iron lined with refractory bricks and fitted with condensing pipes in its upper part. The gases pass through a series of copper condensers, the first of which contains hot water, the others cold water (or see p. 9). It has been found advisable to replace

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[1] Hilbert and Frank, *German Patent* (1895), 92838.

[2] Royster and Turrentine, *Ind. Eng. Chem.*, 1932, 24, 223.

[3] Readman, *J. Soc. Chem. Ind.*, 1890, 9, 163, 473; 1891, 10, 445.

[4] Dieckman and Houdremont, *Zeitsch. anorg. Chem.*, 1921, 120, 129.

[5] Readman, *English Patent* (1888), 14962; Parker and Robinson, *English Patent* (1888), 17719.

[6] Folie-Desjardins, *English Patent* (1890), 13240.

the electric arc originally employed by an electrically heated resister,[1] shown in fig. 1. The current is carried by the graphite rod R, which is packed into the walls of the furnace with blocks of carbon. The rod radiates heat on to a charge C which consists of 100 parts of calcium phosphate and 50 parts of sand and carbon. This charge is introduced through D, is melted on the hearth, and the slag flows away through E. The phosphorus vapour and the gases are drawn off through the pipe P.

The product is said to be more free from impurities than that made by the reduction of the free acid. The phosphorus vapour, in an atmosphere of carbon monoxide, is condensed in a slanting tube, which is connected by a set of vertical tubes with another slanting tube which conducts the gases to a condensing tower containing flat plates wetted with a solution of a copper salt or other reagent which will remove the last suspended globules of phosphorus. The issuing gas containing carbon monoxide is burnt, and supplies heat for the distillation of the crude condensed phosphorus. The second distillate is condensed in a box under water and may be purified as described later.

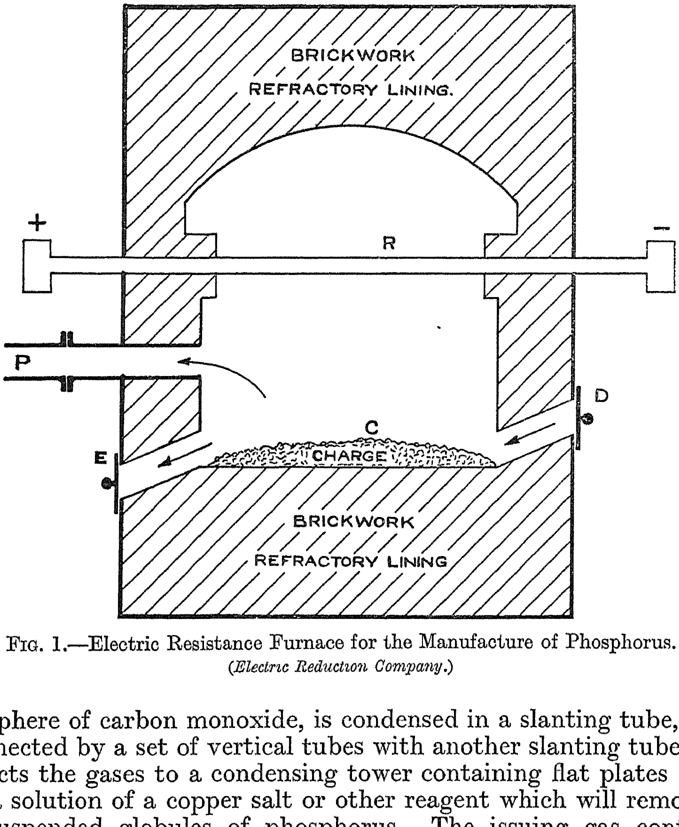

Fig. 1.—Electric Resistance Furnace for the Manufacture of Phosphorus. (*Electric Reduction Company.*)

An experimental study of the reaction in a graphite tube resistance led to the following conclusions.[2] The mixture was still solid at 1500°. The phosphorus volatilised ranged from 60 to 99·8 per cent. of that present. Volatilisation of phosphorus from mixtures of tricalcium phosphate and carbon begins at 1150° C., and under favourable conditions the reaction is complete in one hour at 1325° C., or in 10 minutes at 1500° C. Less than 0·2 per cent. of the phosphorus is converted into phosphide at such temperatures. The reaction, in the presence of excess of carbon, is unimolecular between 1250° and 1400° C.

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[1] Electric Reduction Co., *English Patent* (1898), 5796. See also Hempel, *Zeitsch. angew. Chem.*, 1905, 18, 132, 401; Neumann, *ibid.*, 1905, 18, 289.

[2] Jacob and Reynolds, *Ind. Eng. Chem.*, 1928, 20, 1204.

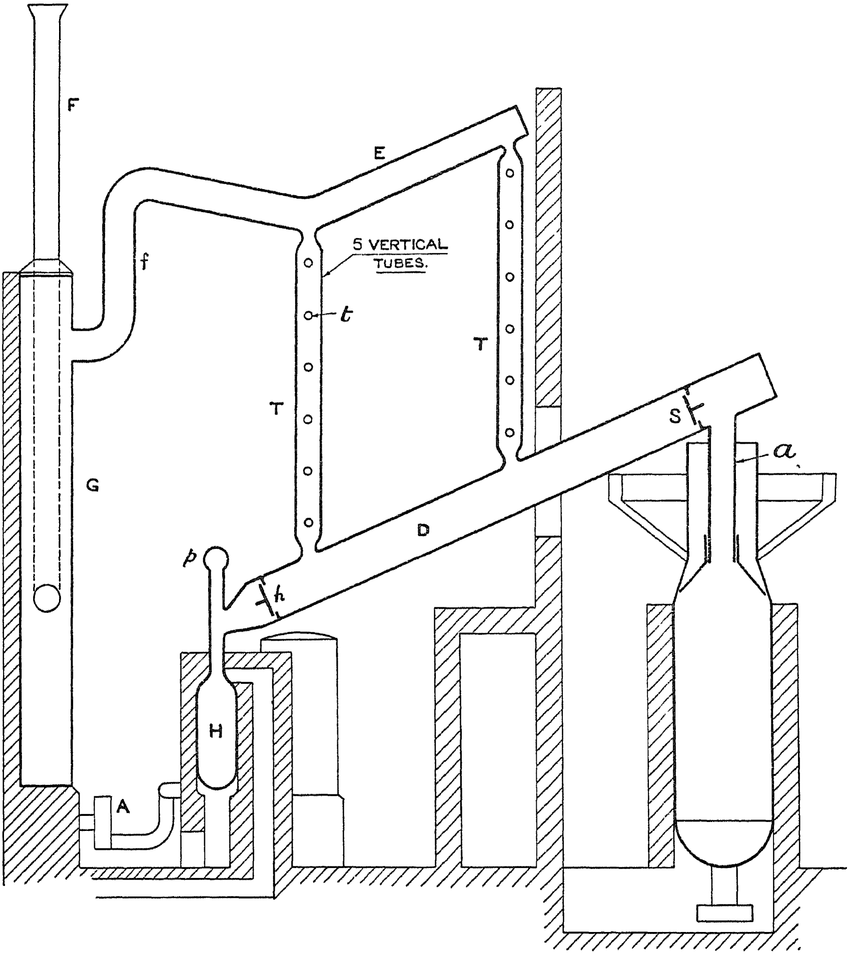

Fig. 2.—Distillation of Phosphorus.

Condensation and Redistillation.—The condensation of the phosphorus vapour, mixed as it is with dust and furnace gases, presents special difficulties. The sketch (fig. 2) shows, diagrammatically only, how these have been overcome in the patent of Billandot et Cie.[1]

The phosphorus vapour, escaping from the furnace, passes up a vertical tube which can be cleared of obstructions from time to time by a movable weight. It then passes down an inclined tube D, which is connected with another tube E by a set of vertical tubes T. Both the lower and the upper end of D can be closed by valves. The phosphorus vapour condenses in droplets at about 50° C. Its flow can be further regulated by the introduction of gases from a compressor through the holes in the vertical tubes. The semi-fluid mixture is thus pushed through the valve *h* into a mixing chamber, and then into one of two distillation retorts H. These are built into the wall and heated by carbon monoxide from the escaping gases. The distillate drops into a double lead-lined and water-cooled box, which is inclined at an angle to the horizontal and furnished with an outflow cock. This condenser is not shown in the elevation (fig. 2).

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[1] *German Patent* (1929), 106408.

The gases escape through *f* and a valve into one of three plate-condensing towers G, and through a fan A which delivers them where required, or through a flue F. The plate towers are supplied with a solution of a copper or other metallic salt, which absorbs the last traces of phosphorus vapour.

Purification is effected mainly by the methods already described. Crude phosphorus may be melted under dilute solutions of chromic acid, nitric acid or chlorine. Arsenic may be removed by distilling in a current of steam and carbon dioxide, and condensing under water. Phosphorus can be granulated if desired by melting under water and shaking until cold.

Preparation of Red Phosphorus.

For many of the purposes to which phosphorus is applied the red form is equally suitable, and when this is the case this form is greatly to be preferred on account of its non-poisonous and non-inflammable character (see p. 28). The conditions of transformation are now accurately known (see Chap. III.).

On the large scale white phosphorus is heated in an iron pot embedded in a sand-bath which is contained in an external iron vessel with double walls, the space between which is filled with an alloy of tin and lead. The pot containing the phosphorus is lined with porcelain and is provided with a tight cover bearing a bent tube of iron or copper which can be closed by a tap. The end of this tube, which acts as a safety valve against too high a pressure, dips under water or mercury. The external metal pot is heated to 220–250°, and not above 260° C., for about ten days. Transformation proceeds more quickly if the operation is conducted in an autoclave at higher temperatures. The product, a purplish-red mass, is ground and boiled with caustic soda to remove any unchanged white phosphorus, then washed and dried at a steam heat.

USES OF PHOSPHORUS.

Pyrotechnic Uses.—The quantity of phosphorus consumed in the match industry exceeds by far that required for all other purposes. The total consumption exceeds 1000 tons per annum, the greater part of which is worked up for matches, hundreds of millions of which are made per annum in factories in all parts of the world. The phosphorus is now applied in the red or scarlet form or as one of the sulphides (*q.v.*). The materials used in friction matches have varied greatly at different periods.

The first chemical matches are attributed to Chancel of Paris (1805) and were manufactured from 1812. They contained no phosphorus, but consisted of sticks of wood tipped with melted sulphur and then coated with a mixture of sugar and chlorate of potash. They were ignited by dipping in a bottle containing asbestos moistened with concentrated sulphuric acid. Similar applications of phosphorus have been described. Phosphoric tapers were made of wax coated with phosphorus, and were enclosed in sealed glass tubes. These were warmed and then opened, when the phosphorus burst into flame.

Friction matches, invented in England in 1827, were tipped with a mixture of antimony trisulphide, potassium chlorate and gum, and ignited by rubbing on sand-paper. The recognition of the superior properties of phosphorus as an ingredient of these miniature explosives dates from about 1833, when wooden matches, the heads of which contained phosphorus, appeared simultaneously in several countries. Attempts to prepare matches from yellow phosphorus had been made from about 1816 by Dérosne and others, but it was only later discovered that the heads must be coated first with another combustible material such as sulphur to transmit the flame of the phosphorus-chlorate mixture. The first matches were both explosive and dangerous. Chlorate was later replaced by lead peroxide, then by red lead and manganese dioxide in 1837.[1] The first safety matches, prepared by Böttger in 1848,[1] were tipped with gum, sulphur and chlorates or chromates, and a similar process was patented by May in 1865. From about 1855 great quantities of safety matches were made in Sweden. These were struck by rubbing on a surface containing red phosphorus worked up with gum and antimony sulphide. The red phosphorus is often replaced by scarlet phosphorus [2] or the sulphide. The ingredients are worked up with glue and powdered glass or emery and mechanically painted on the sides of the boxes. The match sticks are well soaked in paraffin wax or sulphur, and the ends then dipped in a warm mixture of chlorate, dichromate, red lead and antimony sulphide.

Recipes for matches have been the subject of numerous patents. The following is an example of the complexity of the mixtures :—

Potassium chlorate 450 parts, potassium dichromate 110 parts, glass powder 75 parts, sulphur 60 parts, iron oxide 25 parts, red phosphorus 7–8 parts, tragacanth 30 parts, gum arabic 110 parts.

The heads of lucifer matches, which will ignite on any rough surface, contain phosphorus in addition to the ingredients of the heads of safety matches. Accounts of the history and manufacture of matches may be obtained from the following sources :—

"*An Account of the Invention of Friction Matches*," John Walker, Stockton-on-Tees, 1909 ; "*The True History of the Invention of the Lucifer Match*," John Walker, Heavisides, Stockton-on-Tees, 1927 ; see also Clayton, *Chem. News*, 1911, **104**, 223 ; "*The Match Industry*," Dixon, London, 1925 ; "*Guide to Bryant and May's Museum*," Simpkin and Marshall, London ; see also Gore, *Chem. News*, 1861, **4**, 16, 31, etc.

Allied to the match industry is the use of phosphorus as a constituent of fireworks, thus :—

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[1] Böttger, *Annalen*, 1843, 47, 337.

[2] Muir and Bell, *United States Patent* (1903), 724411.

White Fire.—Potassium nitrate 100 parts, amorphous phosphorus 10 parts.

Blue Fire.—Potassium nitrate 500 parts, barium carbonate 300 parts, aluminium powder 200 parts, amorphous phosphorus 5 parts.

Red Fire.—Strontium nitrate 500 parts, strontium carbonate 300 parts, aluminium powder 200 parts, amorphous phosphorus 5 parts.

Firework and match materials are all potentially explosive, and should be mixed with care and in small quantities only.

Alloys.—Phosphorus as a constituent of bronzes is chiefly valued for its deoxidising effect, which confers a great toughness on the metal. The principal alloys are those containing copper, tin, zinc, nickel, lead and antimony. The phosphorus is usually added in the form of phosphor-tin. Phosphor-coppers may be made by heating copper phosphate or copper turnings and phosphorus in crucibles at 600–800°.[1, 2] Phosphor-bronze may contain Cu 89, Sn 11 and P 0·3 per cent.[3] The phosphorus should not exceed 0·6 per cent.

Miscellaneous Uses.—Calcium phosphide is used in marine signal lights, which are so constructed that they evolve spontaneously inflammable phosphine when thrown into water.

Phosphides have been used to give a conducting surface to plaster moulds for electroplating. The mould is dipped in a solution of copper sulphate, then, after drying, in a solution containing caustic potash and phosphorus from which phosphine is being evolved. Copper phosphide is precipitated on or below the surface of the plaster.[4] In silver plating a slightly different procedure is employed. The plaster mould is first covered with wax, then dipped in a solution of phosphorus in four times its weight of carbon disulphide. It is then exposed to the air until fuming begins, whereupon it is dipped in a solution of silver nitrate containing about 100 grams of silver to the litre.

In the manufacture of tungsten lamps the tungstic oxide may be reduced by heating with yellow or red phosphorus in an atmosphere of hydrogen. The tungsten powder containing phosphide which results is suitable for drawing into the filaments.

Physiological Action.—Phosphorus in oil or emulsified in fat and chalk has been used in medicine, but appears to have no particular value. However, a preparation made by exposing finely divided iron to the vapours of smouldering phosphorus is useful as an application to wounds caused by corrosive concentrated carbolic acid.

The small doses of phosphorus which have occasionally been prescribed have the effect of thickening the spongy tissue of bone by the deposition of true bone. Another effect is to stimulate metabolism, leading to increased secretion of nitrogen as ammonium salts of lactic and ketonic acids, which result from the incomplete oxidation of fats and glycogen. Some of the unoxidised fat is deposited in the liver and muscles and leads to degeneration of these.

When taken internally in quantities from 1½ grains upwards, white phosphorus is an acute poison, producing at first symptoms of nausea and pain, which subside for a while, and are then succeeded by jaundice

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[1] Weekhorst, *J. Amer. Chem. Soc.*, 1897, 19, 393.

[2] Heyn and Bauer, *Zeitsch. anorg. Chem.*, 1907, 52, 129.

[3] Philip, *Brass World*, 1910, 6, 77.

[4] Osann, *J. prakt. Chem.*, 1854, 66, 254.

and finally coma.[1, 2] This action is due to the fact that phosphorus prevents the complete oxidation of glycogen and fat. In cases of violent internal poisoning the stomach-pump is used, followed by copper sulphate in amounts sufficient to cause vomiting, then oil of turpentine. Black coffee is also recommended, and also the application of mustard plasters.

The poisonous action of the vapour of phosphorus, or that of its lower oxide, is probably due to attack on exposed bone, *e.g.* in decayed teeth. It produces necrosis, which spreads inwards and gives rise to the disease known as "phossy jaw," which has been found among workers in factories where phosphorus was made or used. Apart from the effect on bones, the vapour does not appear to be poisonous in small amounts.

Hypophosphites and phosphates, *e.g.* calcium hypophosphite and glycerophosphate, are used in considerable quantities as "patent medicines" and in medicine generally as accessory foods. Acid phosphates are used extensively in baking powders and various manufactured foods. The phosphorus requirements of the animal body are stated on p. 4, and also the supply of the element in certain vegetable products, while the probable rôle of phosphates in some biological processes is indicated on p. 169. From their intimate connection with life it will be gathered that by far the most important use of phosphorus compounds is in the manufacture of fertilisers (see Chap. XV.).

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[1] Tardieu, "*Etude médico-légale et clinique sur l'empoisonnement,*" Paris, 1875.

[2] Wohlgemuth, *Zeitsch. physiol. Chem.*, 1905, 44, 74, 428.

CHAPTER II.

PHOSPHORUS, THE ELEMENT.

Solid Phosphorus.

Phosphorus exhibits allotropy, and formerly was thought to exist in two forms, yellow and red. In addition, several other varieties, scarlet, violet, metallic and black phosphorus, were discovered later, some of which are perhaps not to be regarded as true allotropes. Their properties will be considered partly in the present chapter, and partly in Chapter III.

General.—White or yellow phosphorus * is a colourless or pale yellow, translucent, lustrous solid of waxy appearance, soft at ordinary temperatures and brittle when cold (*e.g.* at 0° C.). It melts at about 44° C., giving a transparent liquid which can be supercooled many degrees below the melting-point without solidifying. The liquid catches fire in the air at about 60° C. and boils at about 280° C. in an indifferent atmosphere, giving a vapour which contains complex molecules (P_4). On long heating at temperatures slightly below its boiling-point it is transformed into red phosphorus. White phosphorus is almost insoluble in water, but is volatile with steam, to which it imparts a luminosity; this serves as a delicate test for the element. It is soluble in carbon disulphide and in most organic solvents.

It is one of the most easily oxidised of the non-metals, having a low ignition-point and burning in the air with great evolution of heat and the production of the pentoxide and some red phosphorus. It also combines vigorously with the halogens, and gives a more complete series of halides than any other non-metallic element.

The Melting and Freezing of White Phosphorus.—Pure white phosphorus when slowly heated melts very sharply at 44·0° C. Under these conditions it behaves as a "unary" substance, *i.e.* one whose molecules are all the same, physically as well as chemically. But, in the account of the transformations which is given later, the theory is put forward that the liquid contains at least two kinds of molecules, which may be called $P\alpha$ and $P\beta$. There will be a definite concentration of each in equilibrium at any one temperature, and if the temperature is lowered slowly, these relative concentrations will alter down to the melting-point, 44·0° C., at which the solid is in equilibrium with a particular mixture of $P\alpha$ and $P\beta$. The solid is not necessarily in equilibrium at this melting-point with those proportions of $P\alpha$ and $P\beta$ which are found at a higher temperature. The expected alteration in the freezing-point was realised experimentally by cooling phosphorus very rapidly from 100° C. to temperatures just below or just above 44·0° in a capillary tube, then inoculating with solid phosphorus. Temperatures were read on a resistance thermometer which had a negligible heat capacity and lag, and hence took up the temperature of its surroundings practically instantaneously. After a slight fall, the temperature rose to 44·1, 44·25 and even above 45·0°, an extreme range of 1·8° being observed. The pseudo-binary character of the pure white form was thus revealed.

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* *Note.*—The terms as generally used are almost synonymous. We have preferred "white" in this volume, as the most carefully purified element is very pale in colour.

The degree of supercooling to which liquid phosphorus can be subjected without solidification also depends on its previous history. If the cooling be slow, pure liquid phosphorus may be kept for days at 18° C. If the liquid be heated to 100° C. and suddenly cooled to ordinary temperatures it crystallises spontaneously in a few seconds without inoculation.[1, 2, 3]

As the fusion of phosphorus is accompanied by an increase of volume (see p. 16), the melting-point is raised by increase of pressure. The experimental results are expressed by the formula

$$t_{\mathrm{m}} = 43{\cdot}93 + 0{\cdot}0275p - 0{\cdot}0_{6}50p^2$$

in which the pressure p is expressed in kilograms per square centimetre.[4]

Specific Heats.—The mean specific heat of solid white phosphorus has been determined by several investigators with moderately concordant results :—

Temperature Interval (° C.).	Specific Heat.	Investigator.
(1) − 78° to +10°	0·170–0·174	Regnault.[5]
(2) + 7° „ +30°	0·185	„
(3) + 13° „ +36°	0·202	Kopp.[6]
(4) − 21° „ + 7°	0·1788	Person.[7]
(5) −188° „ +20°	0·169	Richards and Jackson.[8]

The atomic heats are therefore 5·33, 5·74 and 6·26 over the three ranges of temperature (1), (2), (3). There is a slight deviation from Dulong and Petit's law [9] at the lower temperatures, in the same sense as that met with in the case of the elements carbon, boron and silicon. But although phosphorus has a relatively low atomic weight, it also has a low melting-point, and the atomic heat as usual assumes the normal value at temperatures near the melting-point.

Latent Heat of Fusion.—The latent heat of solidification at the melting-point, +44·2° C., is 5·034 calories per gram or 0·16 Calories

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[1] Smits, *Zeitsch. physikal. Chem.*, 1911, 76, 421.

[2] Smits, *ibid.*, 1911, 77, 367.

[3] Smits and Leeuw, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 822. See also Cohen and Olie, *Zeitsch. physikal. Chem.*, 1910, 71, 1.

[4] Tammann, "*Krystallisieren und Schmelzen*," Leipzig, 1903.

[5] Regnault, *Ann. Chim. Phys.*, 1849, [3], 26, 286; 1853, [3], 38, 129.

[6] Kopp, *Annalen Suppl.*, 1865, 3, 290.

[7] Person, *Ann. Chim. Phys.*, 1847, [3], 21, 295.

[8] Richards and Jackson, *Zeitsch. physikal. Chem.*, 1910, 70, 445.

[9] See Vol. I., this Series, or "*Text-book of Physical Chemistry*," Vol. I., J. Newton Friend (Griffin).

per gram-atom [1]—a very low value, which may be compared with that of sulphur, namely, 0·30 Calories per gram-atom. The latent heat, as usual, diminishes with fall of temperature. The following values were obtained on allowing the supercooled liquid to crystallise :—

t° C. . .	27·35	29·73	40·05
l . . .	4·744	4·744	4·970 calories per gram.[2]

The latent heat increases at the higher melting-points which are obtained at higher pressures ; thus at $t = 50·03$° C. and $p = 220$ kg./sq. cm. l was 4·94, while at 69·98° C. and 959 kg. it was 5·28.[3] At still higher pressures the increase in l continues, as is shown by the following results, which refer to white phosphorus :—

p . .	1	2000	4000	6000	6000
t . .	44·2	99·3	148·2	191·9	−2·4
l . .	2·09	2·41	2·63	2·78	18·61 *

Pressure and temperature are expressed in the units given above, and latent heats in kilogram-metres per gram. The last value refers to black phosphorus.[4]

If the latent heat of fusion is taken as 5·0 calories absorbed per gram of phosphorus at the melting-point ($T_{\mathrm{m}} = 317·5$° C. (abs.)), the high value of 40·4 is obtained as the cryoscopic constant for 1 mol of a solute in 1000 grams of phosphorus. The experimental value obtained by dissolving naphthalene in phosphorus was 33·2.[5]

Density.—The density of solid white phosphorus is nearly twice as great as that of water. The following table is compiled from the results of different investigators :—

THE DENSITIES OF SOLID WHITE PHOSPHORUS AND OF LIQUID PHOSPHORUS AT THE MELTING-POINT.

t° C.	0	18	20	40	44	44
D	1·8368 [6] 1·82 [7]	1·828 [8] . .	1·8232 [6] . .	1·8068 [6] . .	1·805 [9] . .	1·745 (liquid) [9] 1·748 (liquid) [6]

Hence the coefficient of expansion of solid phosphorus at ordinary temperatures is 0·0037 c.c. per degree Centigrade. The solid expands by about 3 per cent. on fusion; the ratio of the density of the solid to that of the liquid at this temperature is 1·035 [1] or 1·0345 [2] to 1.

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[1] Person, *loc. cit.*
[2] Petterson, *J. prakt. Chem.*, 1881, [2], 24, 129, 293.
[3] Tammann, "*Kryst. und Schmelz.*," Leipzig, 1903.
* *Note.*—The factor for conversion into calories is 0·4268.
[4] Bridgman, *Phys. Review*, 1914, [2], 3, 153.
[5] Schenck and Buck, *Ber.*, 1904, 37, 915.
[6] Pisati and de Franchis, *Ber.*, 1875, 8, 70.
[7] Jolibois, *Thèse*, Paris, 1920.
[8] Boeseken, *Rec. Trav. chim.*, 1907, 26, 289.
[9] Hess, *Physikal. Zeitsch.*, 1905, 6, 1862.

Compressibility.—The coefficient of compressibility is defined as the fractional change of volume produced by a change of pressure amounting to 1 megabar (10^6 dynes per square centimetre). The range of pressure investigated was 100 to 500 megabars, and the compressibilities at room temperatures were 20·3 for white phosphorus and 9·2 for the red or violet variety.[3] Thus, as usual, a high compressibility was found for an element of high atomic volume, and the more condensed form had the lower compressibility.

Crystalline Form.—It was shown by the earlier investigators that phosphorus crystallised from the liquid state in octahedra and dodecahedra, from carbon disulphide in octahedra, and that, when prepared by sublimation, the crystals had about 200 distinct faces.[4] Well-shaped crystals of white phosphorus may be obtained by solidification of the liquid, by slow sublimation, or by evaporation of solutions in organic solvents. They belong to the regular system, and have a columnar shape if obtained from one set of solvents, *e.g.* carbon disulphide, benzene, alcohol, ether, petroleum, while they have shapes derived from the cube and dodecahedron if obtained from turpentine, oil of almonds, etc.[5] By slow sublimation various forms of the regular system are obtained which may have every possible number of faces (except 48) up to 200.[6] According to Bridgman [7] white phosphorus crystallises both in the regular and in the hexagonal system, the transition temperature being raised by increase of pressure. Thus under 12,000 atmospheres the conversion occurs at $+64·4°$ C., under atmospheric pressure at $-76·9°$, and under the pressure of its own vapour at $-80°$, which therefore appears to be the transition point between this β-form and the ordinary or α-form of white phosphorus. The β-form, stable under high pressures, is produced with a volume contraction of about 2 per cent. The density is 2·699.[8]

Refractivity.—As is to be expected from the brilliant gem-like appearance of the crystals and drops of liquid white phosphorus, the refractive index is high. At the ordinary temperature the refractive index for the D line ($\lambda=589·0$ to $589·6$ mμ) was found to be 2·144 [9] or 2·14.[10] The differences between the refractive indices of the solid and the liquid are shown in the table overleaf.

Electrical Conductivity.—Phosphorus is an electrical insulator. The conductivity of the solid element was found to be of the order of 10^{-11} mhos per centimetre cube and that of the liquid 10^{-6} mhos per centimetre cube.[11] Black phosphorus, which must be considered the

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[1] Hess, *Physikal. Zeitsch.*, 1905, 6, 1862.

[2] Leduc, *Compt. rend.*, 1891, 113, 259.

[3] Richards, *Zeitsch. Elektrochem.*, 1907, 13, 519; *J. Amer. Chem. Soc.*, 1915, 37, 1643.

[4] See Dammar, "*Handbuch der anorganischen Chemie*," vol. ii., pt. i.

[5] Retgers, *Zeitsch. anorg. Chem.*, 1894, 5, 218. See also Bokorny, *Chem. Zeit.*, 1896, 20, 1022; Christomanos, *Zeitsch. anorg. Chem.*, 1905, 45, 132.

[6] Retgers, *loc. cit.*

[7] Bridgman, *J. Amer. Chem. Soc.*, 1914, 36, 1344.

[8] Bridgman, *J. Amer. Chem. Soc.*, 1914, 36, 1344; *ibid.*, 1916, 38, 609.

[9] Damien, *Compt. rend.*, 1880, 91, 323. Also "*Récherches sur le pouvoir réfringent des liquides*," Paris, 1881.

[10] Retgers, *Zeitsch. anorg. Chem.*, 1893, 3, 399. See also Gladstone and Dale, *Annalen*, 1859, 108, 632; Gladstone, *Chem. News*, 1887, 55, 300.

[11] Foussereau, *Compt. rend.*, 1883, 97, 996. See also Faraday, *Phil. Trans.*, 1833, 123, 507; Matthiessen, *Annalen*, 1858, 103, 512; Matthiessen, *Phil. Trans.*, 1858, 148, 383.

REFRACTIVE INDICES OF SOLID AND LIQUID PHOSPHORUS.[1]

State.	Temp. °C.	Line and λ in mμ.			
		D 589·0–589·6.	Hα 656·3.	Hβ 486·15.	Hγ 434·07.
Solid .	25·0	2·144	. .	. .	. .
,, .	37·5	. .	2·08873	2·15388	2·1946
Liquid .	37·5	. .	2·05370	2·11675	2·15634
,, .	44·0	. .	2·05010	2·11311	2·15274

most metallic form of the element, is a relatively good conductor, the specific resistance being slightly less than 1 ohm per centimetre cube but diminishing with rise of temperature.[2]

The **dielectric constant** of solid white phosphorus was found to be 4·1 at 20° C., and that of liquid phosphorus 3·85 at 45°.[3] The **electrochemical potential** is said to lie between those of arsenic and tellurium.[4] Phosphorus is **diamagnetic.**[5] The **magnetic susceptibility** of the solid white element is about $0{\cdot}9 \times 10^{-6}$ mass units, that of the red variety rather less.[6]

Ionisation Potential, V_A.—This may be defined as the smallest difference of potential through which an electron must fall in an electric field in order that its kinetic energy, $mv^2/2$, $=eV_A$ (e is the electronic charge), may be sufficient to raise an atom after collision from state (1) with energy E_1 to another possible quantum state (2) with energy E_2. In changing back from quantum state (2) to (1) the atom will emit radiation of a frequency ν_A given by :

$eV_A = h\nu$ (h = Planck's constant ; ν = wave number in waves per cm.)

The wavelength λ_A of this radiation is calculated from :

$\lambda_A = c/\nu$ (c is the velocity of light)

In the case of phosphorus, $V_A = 5{\cdot}80 \pm 0{\cdot}1$ and $\lambda_A = 2130$ Å.[7]

The ionisation potential has also been determined by the method of electronic collisions. Free electrons, from a heated platinum wire, are introduced into the vapour of an element under low pressure. By the application of increasing potentials increasing kinetic energies are imparted to the electrons. After a certain threshold value has been passed, the electrons strike the atoms in inelastic collisions, and monochromatic radiation is emitted by the atoms. When this method was applied to phosphorus vapour the value of the potential E was found to be 10·3 volts.[1]

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[1] Damien, *loc. cit.*

[2] Bridgman, *Proc. Amer. Acad.*, 1921, 56, 126; Linck and Jung, *Zeitsch. anorg. Chem.*, 1925, 147, 288.

[3] Schlundt, *J. Physical Chem.*, 1904, 8, 122.

[4] Schenck, *Ber.*, 1903, 36, 995.

[5] Faraday, *Phil. Trans.*, 1846, 136, 41.

[6] Quincke, *Wied. Annalen*, 1885, 24, 347; P. Curie, *Compt. rend.*, 1892, 115, 1292; Pascal, *Ann. Chim. Phys.*, 1910, [8], 19, 5; Honda, *Ann. Physik*, 1910, [4], 32, 1027; Meyer, *ibid.*, 1900, [4], 1, 664.

[7] Foote and Mohler, *Phys. Review*, 1920, [2], 15, 555.

Solubility.—White phosphorus is almost insoluble in water. It dissolves easily in liquid ammonia, sulphur dioxide and cyanogen, also in such compounds as phosphorus trichloride which mix with typical organic solvents. It is moderately soluble in fatty oils, also in hydrocarbons, alcohols, ethers, halogenated hydrocarbons such as chloroform and especially methylene iodide. One of the best solvents for phosphorus, as for sulphur, is carbon disulphide, which seems to dissolve it in all proportions at ordinary temperatures; a solution has even

SOLUBILITY OF WHITE PHOSPHORUS IN AQUEOUS SOLVENTS AND OILS.

Solvent.	Water.[2]	Acetic Acid,[2] 96 per cent.	Paraffin.[2]	Oleic Acid.[2]	Almond Oil.[2]
Grams Phosphorus in 100 grams Solution . .	0·0003	0·105	1·45	1·06	1·25
Solvent.	Alcohol[3] (absolute).	Glycerol (density 1·256).[4]			
Grams Phosphorus in 100 grams Solvent . .	0·208	0·25	..	..	..

SOLUBILITY IN BENZENE.[5]

t° C.	0	5	8	10	15	18	20	23	25
Solubility in grams per 100 grams Solvent . .	1·513	1·99	2·31	2·4	2·7	3·1	3·2	3·4	3·7
Density of Solution . .	..	..	0·899	0·8985	0·894	0·892	0·890	0·8875	0·8861

t° C.	30	35	40	45	50	55	60	65	70	75	81
Solubility in grams per 100 grams Solvent . .	4·60	5·17	5·75	6·11	6·80	7·32	7·90	8·40	8·90	9·40	10·03

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[1] Compton and Mohler, "*Ionisierungs und Anregungsspounungen,*" übersetzt von R. Suhrmann, Berlin, 1925. See also Mohler and Foote, "*Ionisation and Resonance Potentials of some Non-metallic Elements,*" Washington, 1920.

[2] Stich, *Pharm. Zeit.*, 1903, 48, 343; see *Chem. Zentr.*, 1903, 1291.

[3] Schacht, *Pharm. J.*, 1880, [3], II, 464.

[4] Ossendowsky, *J. Pharm. Chim.*, 1907, [6], 26, 162.

[5] Christomanos, *Zeitsch. anorg. Chem.*, 1905, 45, 136.

SOLUBILITY IN ETHER.[1]

t° C.	0	5	8	10	15	18	20	23	25	28	30	33	35
Grams Phosphorus in 100 grams Solution . .	0·434	0·62	0·79	0·85	0·90	1·01	1·04	1·12	1·39	1·60	1·75	1·80	2·00
Density of Solution	..	..	..	0·729	0·723	0·719	0·718	0·722	0·728				

SOLUBILITY IN CARBON DISULPHIDE.[2]

t° C.	−10	−7·5	−5·0	−3·5	−3·2	−2·5	0·0	+5·0	+10·0
Grams Phosphorus in 100 grams Solution . .	31·40	35·85	41·95	66·14	71·72	75·0	81·27	86·3	89·8

been prepared containing 20 parts of phosphorus in 1 part of carbon disulphide. These solutions are dangerous; the volatile and endothermic disulphide forms an explosive mixture with air at ordinary temperatures, and the finely divided phosphorus which is left on evaporation ignites spontaneously. This is illustrated in the well-known lecture experiment in which the solution is allowed to evaporate on filter-paper.

LIQUID PHOSPHORUS.

Values of the **densities** and **specific volumes** up to the boiling-point have been determined and are as follows :—

DENSITIES AND SPECIFIC VOLUMES OF LIQUID PHOSPHORUS.[3]

t° C. . .	30	40	56·5	100	200	280	290
Density . .	1·7684	1·74924	1·7444	1·6949	1·6027	1·52867	1·4850
Specific Volume	0·5654	0·5719	0·5733	0·5899	0·6238	0·6544	0·6733

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[1] Christomanos, *Zeitsch. anorg. Chem.*, 1905, 45, 136.

[2] Cohen and Inouye, *Zeitsch. physikal. Chem.*, 1910, 72, 418; Cohen and Inouye, *Chem. Weekblad*, 1910, 7, 277. *Cf.* Giran, *J. Physique*, 1903, [4], 2, 807.

[3] Pisati and de Franchis, *Ber.*, 1880, 13, 2147.

Hence the expansion of the liquid is expressed by the formula

$$v_t = v_{50}[1 + 0{\cdot}0_3 5167(t-50) + 0{\cdot}0_6 370(t-50)^2]$$

In another investigation, on 0·7669 gram of phosphorus contained in an evacuated glass dilatometer, the increase of volume between 50° and 235° C. was found to be expressed by :[1]

$$v_t = 0{\cdot}5733[1 + 0{\cdot}0_3 505(t-50) + 0{\cdot}0_6 118(t-50)^2]$$

The agreement between the two expressions is good at the lower temperatures, and the differences at higher temperatures are about the same value as the coefficient of expansion of glass. Thus at 200° C. the second equation gives the specific volume as 0·6180 c.c. per gram. Without the correction for expansion of glass the apparent specific volume becomes 0·621 c.c.

The specific volume at the boiling-point, determined by the method of Ramsay,[2] was 0·6744 c.c. The corresponding atomic volume[2] is $20{\cdot}9 \pm 0{\cdot}4$. This constant thus lies between 20 and 21,* with a tendency to diminish on keeping the phosphorus at this boiling temperature, owing to the formation of the denser $P\beta$ molecules, which are shown by the cherry-red colour of the liquid.

Vapour Pressures.—The vapour pressures of liquid phosphorus are tabulated overpage in three sections, namely—

(*a*) Commencing below the triple point, which is practically the same as the melting-point, and up to about 150° C.[3, 4]

(*b*) From about 150° C. to nearly 360° C. Over this range three sets of measurements are available.[5, 6, 7]

(*c*) From about 500° C. to the melting-point of violet phosphorus the pressures of the metastable or supercooled liquid are known,[6] and the pressure curve of liquid violet phosphorus has been followed up to over 600° C.[6]

These results have been expressed by various interpolation formulæ. That originally proposed by Smits and Bokhorst was

$$\log p \text{ (mm.)} = -\frac{3585{\cdot}96}{T} - 3{\cdot}59 \log T + 19{\cdot}2189$$

This was found to give pressures lower than those experimentally determined between 44° and 150° C. by MacRae and Voorhis, who have altered the constants to fit this range also, as follows :—

$$\log p \text{ (mm.)} = -\frac{2898}{T} - 1{\cdot}2566 \log T + 11{\cdot}5694$$

These formulæ express the pressures of the liquid from 44° C. to 634° C.

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[1] Prideaux, *Trans. Chem. Soc.*, 1906, 91, 1713.

[2] Ramsay and Masson, *Trans. Chem. Soc.*, 1881, 39, 50.

* The probability of maximum positive error is low.

[3] Centnerszwer, *Zeitsch. physikal. Chem.*, 1913, 85, 99.

[4] Duncan, MacRae and van Voorhis, *J. Amer. Chem. Soc.*, 1921, 43, 547.

[5] Jolibois, *Compt. rend.*, 1909, 149, 287; 1910, 151, 382.

[6] Preuner and Brockmöller, *Zeitsch. physikal. Chem.*, 1912–3, 81, 129.

[7] Smits and Bokhorst, *Zeitsch. physikal. Chem.*, 1914, 88, 608 ; 1916, 91, 249.

THE VAPOUR PRESSURES OF LIQUID PHOSPHORUS.

(*a*) Liquid White Phosphorus.

t° C. .	20	30	40	44·1	69·92	100·11	119·85	150·0
p (mm.)	0·025$_3$	0·072$_4$	0·122$_1$[1]	0·173[2]	0·823	3·66	8·60	27·20[2]

(*b*) Liquid White Phosphorus.

(From about 150° to above the boiling-point (Jolibois).)

Jolibois.[3]

t° C. .	145	173	184	192	200	205	219	235	239	244
p (atm.)	0·017	0·064	0·093	0·124	0·157	0·178	0·253	0·366	0·418	0·464
t° C. .	247	250	254	257	259	262	268	273	275	279
p (atm.)	0·499	0·543	0·591	0·633	0·675	0·705	0·797	0·850	0·925	0·990
t° C. .	281	283	285	295	299	307	312	..	..	..
p (atm.)	1·034	1·071	1·122	1·329	1·437	1·650	1·817	..	..	..

Preuner and Brockmöller.[4]

t° C. .	130	140	150	160	165	170	180	190	200
p (atm.)	0·0145	0·0197	0·0263	0·0355	0·0421	0·0486	0·0684	0·100	0·145
t° C. .	209	219	226	230	250	270	290	..	..
p (atm.)	0·245	0·271	0·332	0·382	0·561	0·776	1·030	..	..

Smits and Bokhorst.[5]

t° C. .	169·0	181·3	185·3	206·9	210·0	229·8	237·9
p (atm.) .	0·04	0·07	0·09	0·18	0·20	0·32	0·42
t° C. .	252·0	261·4	265·5	280·5	298·6	331·8	332·9
p (atm.) .	0·54	0·69	0·74	1·00	1·38	2·47	2·61
t° C. .	342·0	355·7	..	..	..	..	..
p (atm.) .	2·95	3·88	..	..	..	..	..

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[1] Centnerszwer, *loc. cit.*

[2] [redacted], MacRae and van Voorhis, *loc. cit.*

[3] Jolibois, *Compt. rend.*, 1909, 149, 287 ; 1910, 151, 382.

[4] Preuner and Brockmöller, *Zeitsch. physikal. Chem.*, 1912–3, 81, 129.

[5] Smits and Bokhorst, *Zeitsch. physikal. Chem.*, 1914, 88, 608 ; 1916, 91, 249.

(c) Liquid Violet Phosphorus,~~[1]~~ 5

t° C.	504	550	581	589·5	593	608	634	695 *
p (atm.)	23·2	33·0	41·1	43·1	44·2	49·0	58·6	82·2 *

The **latent heat of vaporisation** of liquid yellow phosphorus at its boiling-point has been given as 4 Cals.[2] or 3·89 Cals.[3] This subject is further developed on p. 36, under "Violet Phosphorus."

Surface Tension.—The values of the surface tension σ and density D at two temperatures were determined with the object of calculating the molar surface energy $\sigma(M/D)^{\frac{2}{3}}$, and its change with temperature.[4]

Then, by comparison with the normal temperature coefficient, the molar weight in the liquid state can be deduced.[5]

t° C.	D.	σ.	$\sigma(M/D)^{\frac{2}{3}}$.	Δ(Molar surface energy)/Δt.
78·3	1·714	43·09	748·2	2·205 [4]
132·1	1·664	35·56	629·6	

The molar weight M used in this calculation corresponded to a molecule P_4, and since the temperature coefficient calculated on this assumption is normal, the molar weight in the liquid state is thus found to be the same as in the gaseous state. The molar weight in the dissolved state at the boiling-point of carbon disulphide,[6] and at the freezing-point of benzene, also corresponds very closely to P_4.[7]

PHOSPHORUS VAPOUR.

The Densities of Phosphorus Vapour.—That phosphorus, in common with other non-metals, forms complex molecules in the gaseous state was established early in the nineteenth century by determinations of vapour density. At a temperature of 500° C. the relative density (air $=1$) is 4·35 ; [8] at higher temperatures it falls, being 3·632 at 1484° C. and 3·226 at 1677° C.[9] The molecule P_4 requires a density of 4·294. The molecular complexity thus revealed is confirmed by the low value of the ratio of the specific heats, namely, 1·175 at 300° C.[10]

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[1] Smits and Bokhorst, *Zeitsch. physikal. Chem.*, 1916, 91, 248.

* *Note.*—Critical temperature and pressure.

[2] de Forcrand, *Compt. rend.*, 1901, 132, 878.

[3] Giran, *Compt. rend.*, 1903, 136, 550, 677; Giran, "*Récherches sur le phosphere et les acides phosphoriques,*" Paris, 1903.

[4] Aston and Ramsay, *Trans. Chem. Soc.*, 1894, 65, 173.

[5] See "*A Text-book of Physical Chemistry,*" Vol. I., J. Newton Friend (Griffin), 1933.

[6] Beckmann, *Zeitsch. physikal. Chem.*, 1890, 5, 76.

[7] Hertz, *Zeitsch. physikal. Chem.*, 1890, 6, 358.

[8] Deville and Troost, *Compt. rend.*, 1863, 56, 891.

[9] Meyer and Biltz, *Ber.*, 1889, 22, 725; see also Mensching and Meyer, *Annalen*, 1887, 240, 317.

[10] de Lucchi, *Nuovo Cim.*, 1882, [3], 11, 11. See also "*A Text-book of Physical Chemistry,*" Vol. I., J. Newton Friend (Griffin).

Many determinations at the higher temperatures have been made by measuring the pressures of a known weight of gaseous phosphorus enclosed in a fixed volume.[1] The phosphorus was vaporised by means of an electric furnace in a completely closed vessel, the pressures being read on a quartz spiral manometer, which obviated the necessity of having any manometric fluid. From measurements of pressure, temperature and volume, the apparent molecular weight, or mean relative weight of the kinds of molecules which are present, can be calculated by the usual applications of the gas laws.[1] Different amounts of phosphorus confined in the same volume exert different pressures, and a comparison of these with the relative densities indicates the effect of pressure upon dissociation for the particular temperature. From about 500° C. to 600° C. densities show the presence of P_4 molecules only. Between 600° C. (at which the density is 61·5 to 61·9 independently of the pressure) and 1200° C. dissociation takes place progressively, possibly in the stages

$$P_4 \rightleftharpoons 2P_2 \rightleftharpoons 4P$$

An attempt was made to calculate equilibrium constants for the separate dissociations, the heats of which could thus be determined :—

$$\begin{aligned} P_4 &\rightarrow 2P_2 - 31{\cdot}5 \text{ Cals.} \\ P_2 &\rightarrow 2P \;\; - 45{\cdot}5 \text{ Cals.} \end{aligned}$$

By means of the simpler assumption that each kind of dissociation is complete before the next begins, the degrees of dissociation α at each temperature and pressure can be calculated directly from the densities, as in the following table.[2]

DENSITY AND DEGREE OF DISSOCIATION OF PHOSPHORUS VAPOUR.

t° C.	P (mm.).	D.	α.	t° C.	P (mm.).	D.	α.
800	542	60·9	0·01	1200	950	46·0	0·34
,,	218	60·7	0·01	,,	699	44·8	0·38
,,	88	59·0	0·04	,,	412	41·7	0·48
900	608	59·7	0·04	,,	175	38·3	0·61
,,	99	55·0	0·12	1300	760	..	0·60 (calc.)
1000	694	55·9	0·10	,,	380	..	0·69 ,,
,,	119	50·0	0·23	,,	190	..	0·81 ,,
1100	810	51·3	0·20	,,	100	..	0·89 ,,
,,	145	43·6	0·41				

The mean **heat of dissociation**, calculated from the variations in the dissociation constant between 1100° and 1200° C., is 49·2 Cals. per mol (P_4). From this the constant, K, was calculated at 1300° C., and the percentage dissociations at this temperature. At low pressures and above this temperature, the dissociation into P_2 being now complete, it is probable that single atoms, P, will begin to appear. On the assumption that P_4, P_2 and P are all present at an early stage, it is calculated that at 1200° C. and low pressures there is already a considerable percentage of P.[1, 2]

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[1] Preuner and Brockmöller, *Zeitsch. physikal. Chem.*, 1912, 81, 161.
[2] Stock, Gibson and Stamm, *Ber.*, 1912, 45, 3527.

The dissociation constants K_4 ($P_4 \rightleftharpoons 2P_2$) and K_2 ($P_2 \rightleftharpoons 2P$) are calculated to be :

t° C. . .	800	1000	1200
K_4 . .	350	40·0	2·11
K_2 . .	7·4	9·0	36·0

The atomicity of phosphorus vapour under the critical conditions may be calculated from the van der Waals coefficient b, which represents the actual volume occupied by the molecules and is given by the equation[3]

$$b = \frac{1}{8p_c}\,\frac{T_c}{273} = \frac{1}{8 \times 82{\cdot}2} \times \frac{968}{273} = 0{\cdot}005392$$

The value of b for phosphorus in combination is obtained additively from the critical data of phosphine. For the compound b is 0·00233, and for three hydrogen atoms $3b$ is 0·001086, whence b for combined phosphorus (1 atom) is 0·001244. The ratio of this to b for the free element gives the atomicity, 4·33, of the latter.

Refractivity.—The refractivity at three wavelengths was determined by means of the Jamin refractometer, a weighed quantity of phosphorus being gradually vaporised in an evacuated tube of fused silica with transparent plane parallel ends.[4]

λ . . .	6800 Å	5893 Å	5100 Å
$(n-1)10^6$.	1200	1212	1230

The equation giving $n-1$ as a function of λ is

$$n - 1 = 0{\cdot}001162\left(1 + \frac{1{\cdot}53}{\lambda^2 10^{10}}\right)$$

From this the value of $n-1$ at $\lambda = 5893$ is about 0·0012.

Spectra of Phosphorus and Its Compounds.—When the element or some of its compounds are introduced into a flame, or when hydrogen containing a little phosphorus vapour is burned, a green colour is observed which has been resolved into bands in the orange, yellow and green.[5] The passing of an electric discharge through a tube containing phosphorus vapour at low pressures also showed a green colour which was resolved into similar bands.[6] Other observations

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[1] Stock, Gibson and Stamm, *Ber.*, 1912, 45, 3527.

[2] Preuner and Brockmöller, *loc. cit.*

[3] Smits and Bokhorst, *loc. cit.*, p. 276.

[4] Cuthbertson and Metcalfe, *Proc. Roy. Soc.*, 1908, 80 (A), 411.

[5] Dusart, *Compt. rend.*, 1856, 43, 1126.

[6] Plücker and Hittorf, *Phil. Trans.*, 1865, 155, 1; Hartley, *Phil. Trans.*, 1894, 185 (A), 161.

are summarised in the appropriate works of reference[1] and comprehensive papers.[2]

It has now been established that the emission spectrum of the element lies in the ultraviolet. Prominent lines in the arc and spark spectra are found at $\lambda = 2555{\cdot}7$, 2554·0, 2536·4, 2534·75 Å. These are also seen in the spectra from the vapour in a Geissler tube, and in addition other lines at 2497·3 and 2484·1.[3] A photographic record of the condensed spark spectrum showed lines at 2555·0, 2553·3, 2535·6, 2534 Å.[4]

When phosphoric acid or its salts are introduced into a carbon arc they give a mixed line and band spectrum. There is a band at 3286 to 3246 Å and others are found at 2635, 2625, 2611, 2597, 2588 and 2571 Å. Sharp lines are seen at 2555·0 to 2553·37 Å, which represent the double line of the element at 2535·74 to 2534·12 Å. There are several faint streaks at 2477 to 2385 Å.[5] The arc spectrum obtained by introducing phosphorus pentoxide into a copper arc contains at least 35 lines of wavelengths ranging from 2550 to 1672 Å. Many of these are connected together as systems of constant frequency difference, and some of these series are due to doubly and trebly ionised phosphorus.[6] The low-voltage arc spectrum also shows lines and bands.[7]

The spectrum of the electrodeless discharge shows, in the spectral region transmitted by fluorite (CaF_2), 12 lines between 1859·4 and 1671·5 Å.[7] These also depend upon the degrees of ionisation of the phosphorus atom.[8]

From the foregoing data it is evident that these spectra are similar to those which proceed from the slow combustion of phosphorus (p. 124).

Absorption of Radiation.—Neither phosphorus vapour nor the compounds of phosphorus with colourless elements show selective absorption in the visible region. The vapour shows general absorption in the ultraviolet from a wavelength of about 2500 Å at 150° C., 2820 Å at 190° and 2960 Å at 220°. Phosphine transmits rays down to about 2230 Å, and phosphorus trichloride down to about 2590 Å.[9] The infra-red absorption by PH_3 is described under that compound.

Fluorescence.—When the vapour of phosphorus at 600° to 700° C. and 1 mm. pressure (therefore containing a considerable proportion of diatomic molecules) is confined in a sealed quartz tube and exposed to the spark lines 2195 and 2144 Å of cadmium, 2100 and 2062 Å of zinc or 1990 and 1935 Å of aluminium, it gives a fluorescent emission consisting of a resonance series in the region 3500 to 1900 Å.[10]

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[1] Kayser, "*Handbuch der Spektroscopie,*" 6, 239, Leipzig, 1912; Hicks, "*A Treatise on the Analysis of Spectra,*" Cambridge, 1922.

[2] de Gramont, *Bull. Soc. chim.*, 1898, [3], 19, 54.

[3] Kayser, "*Hauptlinien der Linien-Spektra der Elemente,*" J. Springer, Berlin, 1926.

[4] de Gramont, *Compt. rend.*, 1920, 172, 1106.

[5] "*Atlas Typischer Spektren,*" Eder and Valenta, 1928, *Verleger d. Akad. d. Wiss. Wien.*

[6] Saltmarsh, *Phil. Mag.*, 1924, 47, 874; Sur, *Nature*, 1925, 116, 542.

[7] Duffendack and Huthsteiner, *Phys. Review*, 1925, [2], 25, 110, 501.

[8] Millikan and Bowen, *Phys. Review*, 1925, [2], 25, 591, etc.; Déjardins, *Compt. rend.*, 1927, 185, 1453.

[9] Purvis, *Proc. Camb. Phil. Soc.*, 1923, 21, 566; Dobbie and Fox, *Proc. Roy. Soc.*, 1920, 98 (A), 147.

[10] Jakovlev and Terenin, *Nature*, 1929, 337. See also Geuther, *Zeitsch. wiss. Photochem.*, 1907, 7, 1.

Mass Spectrum.—The analysis of phosphorus by positive rays shows that it is a pure element, consisting of atoms which all have the same mass.[1]

CHEMICAL REACTIONS OF PHOSPHORUS.

Phosphorus unites directly with many of the more electronegative elements, forming oxides, halides, sulphides and selenides. The conditions of formation are described under the respective sections in this volume. The energies of combination with oxygen and the halogens are great. The oxidation probably always proceeds in stages, as described under "Oxides." The combustion proceeds not only in air and in oxygen, but also in many compounds containing oxygen, such as oxides of nitrogen and sulphur. Halogenation also proceeds in stages in those cases where both a higher and a lower halide are formed (see "Halides"). Phosphorus combines with nitrogen only under special conditions, and under the influence of the electric discharge nitrogen is absorbed by phosphorus.[2] A mixture of phosphorus vapour with nitrogen under the influence of the electric discharge forms a solid nitride.[3]

Phosphorus also unites directly with many metals giving phosphides (see p. 60), which are described under the respective metals in the volumes of this Series.

Phosphorus does not, like nitrogen, combine directly with hydrogen.* In this respect it resembles the succeeding members of the Group.

Phosphorus is readily oxidised by strong oxidising agents such as nitric acid to phosphorous and phosphoric acids, eventually the latter. Hydrogen peroxide of concentration greater than 6 per cent. reacts violently when warmed with red phosphorus, less violently with white phosphorus, giving phosphine, phosphorous and phosphoric acids.[4]

The reaction of phosphorus with the alkalies is described under "Phosphine." It is really a case of hydrolysis. This can also be effected by boiling water in the presence of certain metallic salts, which probably act by the intermediate formation of phosphides. Superheated steam at 238° to 260° C. and under a pressure of 57 to 360 atmospheres gives phosphine and orthophosphoric acid, thus :—[5]

$$4P_2 + 12H_2O = 5PH_3 + 3H_3PO_4$$

The simplest reaction will be represented by the equation

$$2P + 3H_2O = PH_3 + H_3PO_3$$

The phosphorous acid then decomposes, as it is known to do, giving more phosphine.

The Action of Phosphorus on Solutions of Metallic Salts.—When white phosphorus is placed in solutions of the salts of the more "noble" metals the metals are deposited and oxy-acids of phosphorus are found in the solution. The ratios of metal deposited to phosphorus oxidised are not constant except under certain carefully regulated conditions. It is stated that in the case of copper sulphate the ratio was 5Cu : 2P when only that phosphorus was included which was present as phosphoric acid.[1] The ratio 2Cu : P (total phosphorus) has also been found when air was excluded.[2] The reaction proceeds in stages.[3] When the copper has been completely precipitated from decinormal copper sulphate about 13 per cent. is present as phosphide, but this phosphorus is oxidised later to oxy-acids. During the later part of the reaction the ratio is 2Cu : P, or 4 equivalents of copper are deposited to 1 atom of phosphorus oxidised.[4] The metals which are deposited from neutral or slightly acid solution are those which react with phosphine, *i.e.* Cu, Hg, Ag, Pd, Pt, Au ; those above copper in the electrochemical series are not deposited. In ammoniacal solution deposits are also obtained from salts of Pb, Ni, Tl, Sn, Co, Cd, Zn.[5, 6]

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[1] Aston, "*Isotopes*," Churchill, 1923.

[2] Newman, *Proc. Phys. Soc.*, 1921, 33, 73.

[3] Kohlschutter and Frumkin, *Zeitsch. Elektrochem.*, 1914, 20, 110.

* *Note.*—Under special conditions a certain degree of combination was detected (see p. 68).

[4] Weyl, *Zeitsch. phys. Chem. Unterricht*, 1906, 39, 1307.

[5] Ipatieff and Nikolaieff, *Ber.*, 1926, 59, B, 595.

The reaction with silver nitrate has been thoroughly investigated at different stages.[4, 6] The deposit is dark at first, of a bright crystalline appearance later, and finally grey and spongy. The ratio Ag : P may be more than 5 : 1 at the beginning and 3·6 : 1 or less at the end of the reaction. During the middle part the ratio is 4 : 1. Both the phosphorous and phosphoric acids were determined, and it was suggested that these were produced in equimolecular amounts after the first deposition of phosphide had ceased.

The metal may be deposited on a piece of platinum, gold or carbon at some distance from the stick of phosphorus with which this is in contact. The silver phosphide which was first produced had the formula Ag_3P and phosphorous acid was formed simultaneously. The following equations were suggested as representing the various stages :—

$$2P + 3H_2O = PH_3 + H_3PO_3$$
$$PH_3 + 3AgNO_3 = Ag_3P + 3HNO_3$$
$$Ag_3P + 5AgNO_3 + 4H_2O = 8Ag + 5HNO_3 + H_3PO_4$$

These equations perhaps give a general representation of the reactions which occur between phosphorus and solutions containing salts of the "noble" metals.

Further references to the action of phosphorus on metallic salts are: Senderens, *Compt. rend*., 1887, **104**, 175 ; Böttger, *Repert. Pharm.*, 1875, 24, 725 ; Philipp, *Ber.*, 1883, **16**, 749; Rosenstein, *J. Amer. Chem. Soc.*, 1920, 42, 883 ; Poleck and Thummel, *Ber.*, 1883, **16**, 2442.

Red Phosphorus.—The chief chemical properties of red or amorphous phosphorus were determined by the discoverer and other early investigators. As compared with white phosphorus, both red and scarlet phosphorus are relatively inert, except in respect to certain reactions which depend largely on the extent of surface exposed to aqueous reagents.

Red phosphorus does not glow in the air, but shows a faint luminescence in ozone. When heated in the air or moist oxygen it does not ignite below about 260° C., at which temperature the vapour pressure has become appreciable (p. 33).[1, 2] In warm moist air it is gradually oxidised to phosphorous and phosphoric acids.[2, 3]

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[1] Bird and Diggs, *J. Amer. Chem. Soc.*, 1914, 36, 1382.
[2] Straub, *Zeitsch. anorg. Chem.*, 1903, 35, 460.
[3] Tauchert, *Zeitsch. anorg. Chem.*, 1913, 79, 350.
[4] Walker, *Trans. Chem. Soc.*, 1926, 128, 1370.
[5] Kulisch, *Annalen*, 1885, 231, 327.
[6] Moser and Brukl, *Zeitsch. anorg. Chem.*, 1922, 121, 73; Brukl, *ibid.*, 1922, 125, 252.

It is even more readily oxidised by concentrated nitric acid than is white phosphorus, the product in both cases being a phosphoric acid (*q.v.*). It is not affected by concentrated sulphuric acid in the cold, but on heating SO_2 is evolved and oxidation of the phosphorus takes place. It is not affected by aqueous alkalies but dissolves in alcoholic potash,[4] giving a deep red solution from which acids reprecipitate the red element containing a suboxide.

It combines with halogens, although not so violently as white phosphorus; with chlorine, either gaseous or in aqueous solution; with bromine in the cold; and with iodine on warming.

Red phosphorus is less soluble than white in all solvents. In water and alcohol it is almost insoluble. It is somewhat soluble in ether and in hot acetic acid, from which it is reprecipitated by water. It is slightly soluble in phosphorus trichloride. These solubilities refer to the ordinary preparation, which, as shown on p. 32, usually contains residual quantities of the white form. Red phosphorus is able to reduce salts, especially those of the "noble" metals, in aqueous solution on boiling. Salts of mercury are reduced to the metal; those of gold and silver give insoluble phosphides; while ferric and stannic salts are reduced to ferrous and stannous respectively.[5]

Scarlet Phosphorus, sometimes called "Schenck's phosphorus,"[6] can be prepared by boiling a 10 per cent. solution of phosphorus in phosphorus tribromide. It appears to be an intermediate form between the white and the red. The conditions of its formation and its physical properties, so far as these are known, are more fully described under "Scarlet Phosphorus," p. 42.

The chemical properties partly resemble those of white, partly those of red, phosphorus. It does not glow in the air, but does so in ozone. It is rapidly attacked by alkalies, giving hypophosphite and phosphine which is not spontaneously inflammable. It is coloured intensely black by ammonia. It dissolves in aqueous alcoholic potash giving red solutions from which acids precipitate a mixture of phosphorus and solid hydride. It dissolves in phosphorus tribromide to the extent of about 0·5 gram in 100 grams of the solvent at about 200° C. It is said to be non-poisonous; its physiological properties probably resemble those of red phosphorus (*q.v.*).

Colloidal Phosphorus.—An aqueous collosol has been prepared by boiling commercial red phosphorus with water to which has been added stabilising substances such as gelatin, dextrin or sucrose, etc. Contrary to the usual order, the last-named substances seem to have the strongest effect in protecting the phosphorus against coagulation by salts.[7] When an alcoholic solution of white phosphorus is poured into water a colloidal solution is obtained.[8] A colloidal solution in

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[1] Hittorf, *Annalen*, 1865, 126, 193; *Chem. News*, 1866, 13, 133; Schrötter, *J. prakt. Chem.*, 1853, [1], 58, 158.

[2] Baker and Dixon, *Proc. Roy. Soc.*, 1889, 45, 1.

[3] Personne, *Compt. rend.*, 1857, 45, 113.

[4] Michaelis and Arendt, *Annalen*, 1902, 325, 361.

[5] Rosenstein, *loc. cit.*

[6] Schenck, *Ber.*, 1902, 35, 351; *ibid.*, 1903, 36, 979, 4202.

[7] Müller, *Ber.*, 1904, 37, 11.

[8] von Weimarn, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 453.

*iso*butyl alcohol was made by passing arcs between red phosphorus suspended in this medium.[1]

DETECTION AND ESTIMATION OF PHOSPHORUS.

White phosphorus is easily detected by its well-marked property of glowing in the dark as well as by its peculiar smell and reducing properties (*q.v.* pp. 27, 28). Smaller quantities may be detected by the well-known Mitscherlich test. The material is boiled with water in a flask furnished with a long glass reflux condenser cooled by air. A luminous band is seen (in the dark) at the point where the steam is condensed. The phosphorus may be distilled with steam and collected under water in small globules. The distillate will reduce ammoniacal silver nitrate and mercuric salts. The presence of phosphorus in the steam may also be demonstrated by allowing the latter to impinge upon a piece of paper wetted with silver nitrate, which is at once blackened. Other vapours and gases (such as AsH_3) which have the same effect are not likely to be produced under the conditions. Traces of white phosphorus in matches may be found by extraction with benzene. Strips of filter paper soaked in this extract, suspended in a glass tube and exposed to a current of air at 40–50° C. become luminescent if 0·01 milligram or more of phosphorus is present.[2]

Small quantities of red phosphorus are best detected after oxidation by the tests given under "Phosphoric Acid," pp. 179, 180.

Phosphorus combined in organic compounds, or as phosphide in metals, is also estimated after oxidation by precipitation as ammonium phosphomolybdate or magnesium ammonium phosphate, with the subsequent treatment which is described on pp. 181–183. The methods by which the phosphorus is brought into solution vary with the nature of the material which is being analysed. Organic compounds are oxidised in a sealed tube with fuming nitric acid or in a flask by a mixture of concentrated sulphuric and nitric acids.

Alloys of copper and tin such as the phosphor bronzes are dissolved in nitric acid of density 1·5, and the metastannic acid, which contains all the phosphoric oxide, after ignition and weighing is fused with KCN. The aqueous solution of the melt is freed from tin globules by filtration and from traces of soluble copper and tin by H_2S, then containing all the phosphorus as potassium phosphate, which is determined as described below.

Iron and steel are dissolved in 1 : 1 nitric acid, the solution evaporated to dryness and the residue taken up with concentrated hydrochloric acid until all the silica is rendered insoluble. The solution containing the phosphoric and hydrochloric acids is evaporated to dryness once more to get rid of the latter acid, and the residue then taken up with nitric acid and ammonium nitrate solution and precipitated with ammonium molybdate.

Small quantities of phosphorus may be estimated quickly by the molybdate method, the amount of phosphomolybdate being estimated colorimetrically by comparison in Nessler glasses or test-tubes with a standard prepared under conditions which are made identical as far as possible. An account of this estimation is given under "Phosphoric Acid," p. 182.

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[1] Svedberg, *Ber.*, 1906, 39, 1714.

[2] Schroder, *Arbeiten Kaiserl. Gesundheitsamte*, 1913, 44, 1.

CHAPTER III.

ALLOTROPIC FORMS OF PHOSPHORUS AND CONDITIONS OF TRANSFORMATION.

General.—Although the allotropic forms of phosphorus are not so numerous as those of sulphur, they are better defined ; the differences between them are more striking. Apart from plastic sulphur, which is really a supercooled liquid, the forms of sulphur are obviously varieties of the same element ; the differences are found chiefly in the crystalline form, the other physical properties not differing much. The contrast in the appearance and obvious properties of ordinary white phosphorus and the other varieties is so great that a casual observer would hardly suppose that they were the same element. If the allotropic forms of phosphorus are classified by means of their striking properties, then at least five will be recognised, namely—White, Scarlet, Red, Violet and Black, which show great differences in other physical properties besides colour, and also in chemical properties. These forms will now be discussed from the view-points of their histories, preparation and physical properties, the conditions of their transformation and the evidence as to their molecular complexity. The chemical reactions and some physical properties of all the forms are given in Chapter II.

RED PHOSPHORUS.

Preparation.—The production of this form can hardly escape observation, since it is present in the residue from the combustion of white phosphorus in the air.

When liquid phosphorus is heated in a closed vessel or in a non-oxidising atmosphere, such as one of carbon dioxide, the liquid gradually turns red and is then converted into a red solid. The change is rapid at 240° C. and very rapid just below the boiling-point, 280·5° C., of the white form. Red phosphorus was first prepared in this way by Schrötter [1] in 1845, and its chief properties were then investigated.

The red form is chiefly amorphous, and of vitreous appearance and fracture. On prolonged heating it gradually turns violet and exhibits double refraction.[2]

The transformation is greatly accelerated, and takes place at lower temperatures, in the presence of small quantities of iodine,[3] and also of selenium. In the presence of $AlCl_3$ the transformation occurs in evacuated tubes below 100° C.[4]

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[1] Schrötter, *Annalen*, 1850, 81, 276.

[2] Hittorf, *Annalen*, 1865, 126, 193.

[3] Brodie, *Quart. J. Chem. Soc.*, 1853, 5, 289.

[4] Boeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1907, 9, 613.

When white phosphorus is treated with liquid ammonia it is converted into red phosphorus with simultaneous formation of amide and nitride.[1] White phosphorus, when dissolved in turpentine, phosphorus tribromide and certain other solvents, is converted into red phosphorus by heating for several hours at 290° C.[2] Red phosphorus may be deposited when phosphorus vapour is suddenly cooled (see p. 10), and it was early shown that on account of its small vapour pressure this form might be condensed in the hotter part of a tube (at 300° C.) from vapour derived from white phosphorus in the cooler part of the tube.[3] All varieties of phosphorus when strongly heated in sealed tubes may be converted into yellow liquids which deposit red crystals at about 550° C.

A survey of the forms of phosphorus is given by Linck, *Zeitsch. anorg. Chem.*, 1908, **56**, 393.

The red phosphorus prepared by moderate heating may be ground up with a solution of sodium hydroxide as in the technical preparation (see p. 10) and may also be extracted with carbon disulphide until the extract is free from white phosphorus. The resulting preparation is considered to be the purest red phosphorus.[4]

Physical Properties.—*Density.*—There is considerable variation in the values given by different investigators. A preparation which would answer most closely to the description of "pure" red phosphorus and prepared as described above has a density which varies only within the comparatively narrow limits of 2·18 and 2·23, and the value remains practically constant after long heating at 357° C. The density of ordinary red phosphorus may be taken then as $2{\cdot}20 \pm 0{\cdot}02$. Cohen and Olie,[4] to whom these results are due, regard red phosphorus as a solid solution of the white in the violet form. On long heating at 450° C. the density increased to a maximum, which was held to correspond with the maximum proportion of the violet form, at a value of about 2·30. Heating to higher temperatures, between 500° and 600° C., so that the phosphorus became liquid, in some cases increased the density to 2·34, but in others the density diminished, *e.g.* to 2·24. The increase in the density on heating above 360° C. was considered by Jolibois [5] to be due to the production of the form which he called "pyromorphic" phosphorus, which was stable below 450° C., but he also considered that red phosphorus was a distinct allotropic form, with an interval of stability from 450° to 610° C.

Vapour Pressure.—The vapour pressures of red phosphorus are much lower than those of liquid phosphorus or of solid white phosphorus at all temperatures within the experimental range.[6] The latter are therefore unstable forms, or are monotropic with respect to red phosphorus (and equally of course to the violet form).

Thus at 279° C. the vapour pressure of liquid phosphorus is 753 mm., while at 289° C. that of red phosphorus is 23 mm.[5] The pressures of red phosphorus are not in equilibrium, but fall slowly as the solid changes into the more stable "pyromorphic" (violet) form.

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[1] Stock and Johannsen, *Ber.*, 1908, 41, 1593.

[2] Colson, *Compt. rend.*, 1907, 145, 1167; *ibid.*, 1908, 146, 71.

[3] Troost and Hautefeuille, *Ann. Chim. Phys.*, 1874, [5], 2, 145.

[4] Cohen and Olie, *Zeitsch. physikal. Chem.*, 1910, 71, 1.

[5] Jolibois, *Compt. rend.*, 1910, 151, 383.

[6] Hittorf, *Annalen*, 1865, 126, 193.

The pressure of the latter, however, appears to increase more rapidly with rise of temperature than that of red phosphorus, as is seen from the following table, on account of which 400° C. was given as the transition temperature [1] by Jolibois.

Red Phosphorus.[1]		"Pyromorphic" Phosphorus.[1]	
t° C.	p (mm.).	t° C.	p (mm.).
289	23	345	20
398	755	422	710
400	798	430	1045

These measurements agree fairly well with those of Hittorf [2] and of v. Schrötter.[3]

Melting-point.—According to Chapman [4] the melting-point of red phosphorus is 610° C.; according to Stock and Gomolka [5] 620° to 625° C. It is not far removed from that of violet phosphorus. The variability in the melting-point, vapour pressure and density is explained if red phosphorus is a mixture of various forms and is not itself a modification of phosphorus. [A " modification " is a state of aggregation which can exist in inner equilibrium, and which therefore is able to behave in a unary manner.[6]] (See p. 39.)

The *Specific Heat* of red phosphorus is less than that of white phosphorus, being 0·1698 to 0·1705 between 15° C. and 98° C.[7]

The specific heats determined over other ranges of temperature are— [8]

t ° C. . . .	0–51° C.	0–134° C.	0–199° C.
Specific heat .	0·1829	0·2121	0·2162

Hardness.—This is greater than that of white phosphorus, being 3·5 on Moh's scale.

VIOLET PHOSPHORUS.

History and Preparation.—The incipient crystallisation of red phosphorus, which has been noted already, can be carried to completion by a procedure due to Hittorf,[9] who dissolved red phosphorus in molten lead, and on cooling obtained yellowish-red translucent plates which had a density of 2·34 and belonged to the hexagonal system of crystals. Later investigators have obtained curved rectangular leaflets which were transparent, had a steely blue lustre and belonged to the monoclinic system. The form prepared in this manner is known as "Hittorf's" or violet phosphorus, with reference to its appearance *en masse* (see below). The preparation was repeated by Stock and Gomolka.[1] Red phosphorus was heated with lead in a sealed tube at 800° C. for 48 hours. After purification from lead and glass (the former was not completely removed, however), the phosphorus appeared as brown transparent plates, the density of which, corrected for the lead present, was 2·31 to 2·33. This form has also been crystallised from molten bismuth in which, however, phosphorus is less soluble.

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[1] Jolibois, *loc. cit.*

[2] Hittorf, *loc. cit.*

[3] v. Schrötter, *Annalen*, 1850, 81, 276.

[4] Chapman, *Trans. Chem. Soc.*, 1899, 75, 734.

[5] Stock and Gomolka, *Ber.*, 1909, 42, 4510.

[6] Smits, "*Theory of Allotropy*," translated by Thomas (Longmans, 1922), p. 240.

[7] Regnault, *Ann. Chim. Phys.*, 1853, [3], 38, 129.

[8] Wigand, *Ann. Physik*, 1907, [4], 22, 64.

[9] Hittorf, *loc. cit.*

The violet form can also be obtained from some preparations of red phosphorus by the following treatment. The finest particles are washed away in a stream of water until only dark steel-blue particles are left; these are boiled with 30 per cent. sodium hydroxide solution, washed again, boiled with 5 per cent. nitric acid, washed with hot and cold water, then with absolute alcohol and ether, and allowed to stand until dry in a vacuum desiccator with concentrated sulphuric acid.[2] The density of this preparation is about 2·2 (2·18 to 2·23).

The preparation of violet phosphorus may conveniently be carried out as follows:—The air is displaced, by means of carbon dioxide, from a hard glass tube, which is then one quarter filled with ordinary phosphorus, the remainder of the tube containing pieces of lead, preferably those which have served for a previous preparation. The carbon dioxide is then removed, the tube sealed on the pump, and placed inside an iron tube, the space between the walls being filled with magnesia. The whole is heated in a tube furnace for 8 to 10 hours at a moderate red heat. After opening, with the usual precautions, the crystalline phosphorus is removed from the surface and the crystals from the interior are collected after dissolving the lead in 1 : 1 nitric acid.

Crystals of violet phosphorus apparently identical with Hittorf's phosphorus have been obtained by maintaining the element at its melting-point in a sealed tube after starting the crystallisation by a slight supercooling. The tube was opened under carbon disulphide and the crystals separated from the white phosphorus in which they were embedded. They appeared as six-sided leaflets with a characteristic angle of 76–78° and short rounded obtuse angles at the ends, the normal or supplementary angle to which was 27–28°. Violet phosphorus from molten lead yielded two kinds of crystals, one of which was identical with that prepared as above. Both were pleochroic, and were described as dark orange in a direction parallel to the long side and lighter in a direction at right-angles to this. Their density was 2·35.[3]

Violet phosphorus, when rubbed to a very fine powder, assumes a red colour. It still exists, however, in the most stable form, *i.e.* the violet, because it still exerts the characteristic lower vapour pressure of this modification (p. 35).

Physical Properties.—*Density.*—The evidence on which this depends has been reviewed (p. 32). On the whole it seems improbable that the density is much, if at all, higher than 2·30.

Melting-point.—This determination has of course been carried out in sealed tubes. The values of different experimenters do not agree very well; they are:—630° C., Chapman;[1] 600–610° C., Stock and Gomolka;[2] 597° C. (when heated slowly) Stock and Stamm.[3] Fusion and solidification proceed as if the phosphorus were not a pure substance, but a mixture (see p. 39). The melting-points observed were also triple points when, as usual, the phosphorus was sealed in an evacuated tube. The melting-points are lower if the temperature of the bath is raised very slowly. In a bath at constant temperature the melting-point was found to be 589·5° C. by Smits and Bokhorst,[4] who used a graphical method (see p. 38) in interpreting their results.

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[1] Stock and Gomolka, *loc. cit.*

[2] Cohen and Olie, *loc. cit.* See also Boeseken, *loc. cit.*

[3] Marckwald and Helmholtz, *Zeitsch. anorg. Chem.*, 1922, 124, 81.

Vapour Pressure.—The determination of the values given below was beset with considerable difficulty,* especially that of securing inner equilibrium in the solid phase. The curve lies below that of liquid phosphorus, which is unstable with respect to the violet (and red) forms up to the melting-point, 589·5°, of violet phosphorus. The pressure at this triple point is 43·1 atm., while that calculated from the thermodynamical equations (*v. infra*) is 42·9 atm.

VAPOUR PRESSURES OF SOLID VIOLET PHOSPHORUS.[4]

t° C.	308·5	346	379·5	408·5	433·5	450·5	
p (atm.)	0·07	0·13	0·35	0·79	1·49	2·30	
t° C.	463·5	472·5	486·5	505	515	522·5	
p (atm.)	3·18	3·88	5·46	8·67	10·43	11·61	
t° C.	561	578	581	587·5	588	589	589·5
p (atm.)	24·2	34·35	36·49	41·77	42·10	42·6	43·1

It has already been shown (p. 33) that red phosphorus probably is not a unary substance, and that the difference between the vapour pressures of red and violet phosphorus below about 400° C. are probably due to the non-equilibrium conditions in the red form. Even in the case of the more uniform violet modification, however, time is required for the establishment of equilibria with vapour, and the values of the pressures even up to 500° C. are affected by an uncertainty on this account. Condensation of vapour proceeds in general more slowly than vaporisation, and especially is this the case where there is a great difference between the molecular complexities of the vapour and of the solid.

Heats of Vaporisation, Sublimation and Fusion.[5]—These latent heats have been obtained from the respective pressure-temperature relations of the liquid and solid violet phosphorus (p. 38). The Clausius equation

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[1] Chapman, *loc. cit.*

[2] Stock and Gomolka, *loc. cit.*

[3] Stock and Stamm, *Ber.*, 1913, 46, 3497.

[4] Smits and Bokhorst, *Zeitsch. physikal. Chem.*, 1916, 91, 248.

* *Note.*—A glass manometer of difficultly fusible glass was used. Jackson, *J. Chem. Soc.*, 1911, 99, 1066.

[5] Smits, "*Theory of Allotropy*," pp. 225 *et seq.*

$$\frac{dlnp}{dt}=\frac{Q}{RT^2}$$

in which it is assumed that the vapour (P_4) obeys the gas laws, is integrated and thrown into the form—

$$Tlnp=-\frac{Q}{R}+cT \quad . \quad . \quad . \quad . \quad (1)$$

If Q, the latent heat, does not vary with the temperature, a straight line will be obtained by plotting $Tlnp$ against T. This is so in the case of liquid violet phosphorus. The graph of liquid white phosphorus is slightly curved, and is a prolongation of that for liquid violet phosphorus. The integration constant c is obtained from the equation

$$c=\frac{T_2lnp_2-T_1lnp_1}{T_2-T_1}=\tan\alpha \quad . \quad . \quad . \quad (2)$$

where α is the angle between the graph and the axis of abscissæ. By introducing the c values into equation (1), the values of Q are obtained for the mean temperatures $\frac{T_2+T_1}{2}$.

For liquid violet phosphorus $c=9{\cdot}6$, $Q=9{,}900$ calories (from 551° to 591° C.), mean temp. 571° C.

For liquid white phosphorus $c=11{\cdot}1$, $Q=12{,}100$ calories (from 160° to 360° C.), mean temp. 260° C.

Thus the numerical value of Q diminishes by 2,200 calories between 260° and 571° C., and the temperature coefficient α in the equation

$$Q_T=Q_0+\alpha T$$

is found to be

$$\alpha=\frac{dQ}{dt}=-7{\cdot}1$$

This value of α is now introduced into the integrated form of the Clausius equation, and another equation is obtained which includes the variation of Q with T and which should apply to the whole vapour-pressure curve of liquid phosphorus on the assumption that it is continuous, *i.e.* that the liquid formed at lower pressures is really the same as that formed at higher pressures. The equations in question are

$$lnp=-\frac{Q_0}{RT}+\frac{\alpha}{R}lnt+c. \quad . \quad . \quad . \quad (3)$$

$$=-\frac{Q_0}{RT}-3{\cdot}6lnt+c \quad . \quad . \quad . \quad . \quad (4)$$

Q_0 is found to be 16,400 calories.

Putting equation (4) into the form

$$Tlnp+3{\cdot}6Tlnt=-\frac{Q_0}{R}+cT$$

Note.—$ln=\log_e$.

and plotting the left-hand side against T, a straight line should be obtained, and this is very nearly the case.

The *latent heat of vaporisation* of liquid phosphorus at its boiling-point is calculated from equation (3) and is found to be

$$Q_{LV} = 12{,}500 \text{ calories at } T_b = 553^\circ \text{ C. Abs.}$$

Hence we have

$$\frac{Q_{LV}}{T_b} = 22{\cdot}6$$

which is nearly the normal value.

The *heat of sublimation* of violet phosphorus can be calculated from the pressure-temperature relations in a similar manner. In the first place, c is calculated by equation (2) (p. 36) between $T_1 = 343{\cdot}5 + 273$ and $T_2 = 589{\cdot}5 + 273$ and is found to be 18·9. Since the $Tlnp/T$ graph is found to be rectilinear over this range of temperature it follows that Q_{SV} does not vary much, and it was possible to write the linear equation

$$Tlnp = 18{\cdot}9T - 13{,}050$$

If the value of Q/R is taken as 13,000 calories in round numbers the heat of sublimation of violet phosphorus works out at 25,800 calories. This is an abnormally high value as can be seen by comparing the ratio Q_{SV}/T_S with the normal ratio of about 30. T_S is the sublimation temperature, *i.e.* that temperature at which the vapour pressure of the solid is equal to 1 atmosphere. In the present case T_S was found by putting $p = 1$ in equation (1) and was 688° abs. or 415° C., the *sublimation temperature* of violet phosphorus.

Hence

$$\frac{Q_{SV}}{T_S} = \frac{25{,}800}{688} = 37{\cdot}5$$

the abnormal ratio referred to above. The excess of heat required in this sublimation is explained as being due to the change from a polymerised form having a lower energy content into the simpler P_4 molecule. This energy change has been found in a different way as the difference between the heats of combustion of polymerised and ordinary phosphorus (see p. 132), *i.e.* $4 \times 4{,}400 = 17{,}600$ calories per mol P_4. The difference $25{,}800 - 17{,}600 = 8{,}200$ calories is the physical latent heat of change of state solid $\longrightarrow$ vapour.

Finally the molar *heat of fusion* Q_{SL} is obtained in the usual way as the difference between the latent heat of sublimation Q_{SV} and that of evaporation Q_{LV} at the triple point, 862·5° abs.—

$$Q_{SL} = 25{,}800 - 10{,}200 = 15{,}600 \text{ calories}$$ [1]

Critical Constants.—These have been calculated from van der Waals' and other equations of state. Thus $t_c = 720{\cdot}6^\circ$ C., $p_c = 93{\cdot}3$ atm.[2] or $t_c = 675^\circ$ C., $p_c = 80$ atm.[3] Another estimate is $t_c = 695^\circ$ C.;[4] this value has been used to calculate the critical pressure by an extrapolation of the vapour-pressure curve from $t=634°$ C. The value of p_c so found is 88·2 atm.[1] or 82·2 atm.[2]

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[1] Smits, *loc. cit.*, p. 33.

[2] Marckwald and Helmholtz, *loc. cit.*

[3] van Laar, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, [2], 20, 138.

[4] Wahl, *Meddelan. den Fran. Finska Kemist*, 1913.

Theory of the Allotropic Forms.

The phase diagram (fig. 3) constructed with the aid of the table on p. 35 and the data on pp. 22, 23 represents the closest approach to equilibrium conditions which has been attained.[2] Pressures at lower temperatures are magnified in order to show all changes on one diagram. Lines are lettered, as usual, with the phases which can coexist; W_2 = white phosphorus formed at high pressures, W_1 = ordinary white phosphorus, L = liquid phosphorus, G = vapour or gaseous phosphorus, V = violet phosphorus.

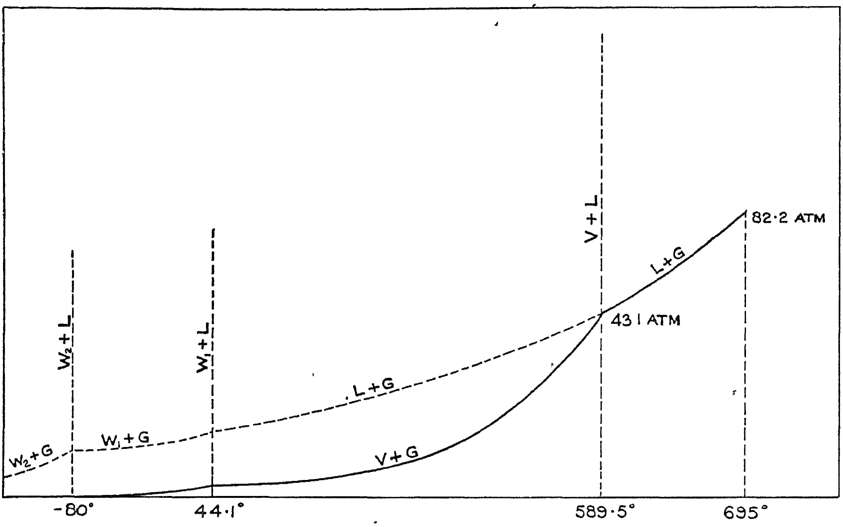

Fig. 3.—Pressure-temperature Diagram of Phosphorus.*

Curves which refer to unstable forms are represented by dotted lines, as also are the transformations of the condensed forms. The slopes of these curves can be calculated when the specific volumes of the two forms are known; thus the W_1+L line should slope slightly to the right, since the specific volume of liquid phosphorus is greater than that of solid white phosphorus near +44·1° C. The melting-point is therefore raised by an increase of pressure.

The solid white form really is only in a state of false equilibrium, being unstable with respect to the polymerised forms at all realisable temperatures. There are also the other forms—red, scarlet and black phosphorus—the behaviour of which under definite conditions of pressure and temperature cannot be stated with any certainty. Further, the melting-point even of the well-crystallised white phosphorus can be made to vary under certain conditions (see p. 15). In fact, all the condensed phases, liquid and solid, behave as mixtures rather than as single pure substances.

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[1] Smits, *loc. cit.*

[2] Smits and Bokhorst, *loc. cit.*

* *Note.*—The break at 44·1° should not appear in the V + G curve since this will fall asymptotically to zero pressure.

The existence of two or more molecular species is definitely postulated by Smits as follows :—[1]

(1) "Every phase, and therefore also every crystalline phase, of an allotropic substance is a state which, in certain circumstances, can behave as a poly-component phase."

(2) "The cause of this behaviour must be assumed to be the complexity, *i.e.* the existence of different molecular species, which are in inner equilibrium when the behaviour of the system is unary, or in other words when it behaves as a one-component system."

In the case of phosphorus there are probably several "molecular species," but the phenomena at temperatures which are not too high can be explained rationally by assuming only two—Pα, which is white, with a low melting-point and high vapour pressure, and Pβ, which is violet, with a high melting-point and low vapour pressure, and which probably is highly polymerised.

The density of the vapour is the same whether it is derived from white or red phosphorus, and at lower temperatures and not too low pressures corresponds to molecules P_4.

In the liquid the pseudo-components are supposed to be in a state of dynamic equilibrium which shifts with the temperature, but does not readjust itself instantaneously on sudden changes.

The solids, at any rate the polymerised forms, are regarded as solid solutions of Pα and Pβ in varying proportions. Temperature-concentration diagrams similar to those representing a two-component system have been constructed for these pseudo-components.

When the liquid is heated to between 400° and 500° C. it is highly supercooled with respect to violet phosphorus, which crystallises with explosive violence. When, however, the vapour is cooled rapidly so that the liquid passes rapidly through this range down to 30° C., the liquid white phosphorus, which is richer in Pα, and thus approximates more closely to the composition of the vapour, is deposited first, and subsequently solid white phosphorus, which also resembles the liquid and the vapour much more closely than does the polymerised form. This appearance of a metastable rather than a stable form was pointed out long ago by Frankenheim,[2] and stated formally as a generalisation, called by Ostwald[3] the Law of Successive Transformations, thus : "When a given chemical system is left in an unstable state it tends to change, not into the most stable form, but into the form the stability of which most nearly resembles its own, *i.e.* into that transient or permanently stable modification whose formation from the original state is accompanied by the smallest loss of free energy."

The condensation of phosphorus vapour, however, does not necessarily yield white phosphorus ; much depends upon the temperature to which the vapour has been heated and the rate of cooling.

It was noted by Hittorf[4] that the vapour evolved by red phosphorus at 440° C. was deposited in the yellow form. But Arctowski[5] found that when red phosphorus was heated in a vacuum at 100° C. it sublimed and condensed in the same form. This phenomenon was investigated in detail by Stock, Schröder and Stamm.[1] The phosphorus was introduced in varying amounts into a sealed quartz tube, heated to various temperatures and suddenly cooled by immersion in water. Cooling from the temperatures stated in the first column of the following table gave the products described in the second column :—

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[1] Smits, *loc. cit.*

[2] Frankenheim, *Annalen*, 1836, 39, 380.

[3] Ostwald, *Zeitsch. physikal. Chem.*, 1897, 22, 306.

[4] Hittorf, *loc. cit.*

[5] Arctowski, *Zeitsch. anorg. Chem.*, 1890, 12, 225.

Temperatures, ° C., from which Sudden Cooling was effected.	Appearance of Product.
400	Colourless drops.
450	Pale yellow drops.
550	Distinctly yellow drops.
600	Drops with a few purple flakes.
700	Some brownish-red solid.
900	Opaque brownish-red solid.
1000	Denser and more opaque.
1200	Phosphorus vapour at 5 mm. gave entirely red phosphorus.

An examination of the behaviour of red and violet phosphorus (and indeed all solid forms) in the light of this theory leads to the conclusion that they are mixtures, with the difference that while violet phosphorus is capable of behaving in a unary manner, red phosphorus is not. Violet phosphorus is a mixture, because when it is heated to 360° C. in a vacuum, and the vapour is thus rapidly removed, the vapour pressure falls.[2] The inner equilibrium has not in these circumstances time to adjust itself to the loss of the volatile $P\alpha$ molecules, the residue becomes poorer in this kind and therefore has a lower vapour pressure. The production of red phosphorus below 400° C. may be explained partly by an increase in the proportion of $P\alpha$ molecules in the solid solution of the pseudo-components, but principally by a delay in the establishment of the equilibrium, which leads to the production of solid solutions still richer in $P\alpha$, which are not in equilibrium but which constitute the ordinary red phosphorus. This therefore is not an allotropic modification, if such a modification is defined as a substance which can exist in inner equilibrium and which is able to behave in a unary manner.

BLACK PHOSPHORUS.

General.—This form must not be confused with the black substance which appears on the outside of sticks of white phosphorus which have been exposed to light, and which is neither a definite form nor a pure substance. The preparation of a dark substance by the sudden cooling of phosphorus could not be repeated, and this result probably was also due to impurities.

Black phosphorus was discovered by Bridgman,[3] who prepared it by subjecting white phosphorus at 200° C. to pressures of 12,000 to 13,000 kilograms per square centimetre.

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[1] Stock and Stamm, *Ber.*, 1913, 46, 3497. See also *ibid.*, 1910, 43, 4510.

[2] Lemoine, *Ann. Chim. Phys.*, 1871, [4], 24, 129; Smits and Bokhorst, *loc. cit.*, p. 288.

[3] Bridgman, *J. Amer. Chem. Soc.*, 1914, 36, 1244.

Physical Properties.—The density, 2·69, is much higher than that of violet phosphorus. The vapour pressures were found to be lower than those of the violet element at the same temperatures :—

t° C.	Black Phosphorus, p (mm.).
357·1	2·3
445·2	585

In spite of this relation between the vapour pressures the violet form could not be converted into the black at ordinary temperatures. Later investigations showed that the black form probably is only in a state of false equilibrium or suspended transformation at ordinary temperatures and pressures.[1]

The black phosphorus was with difficulty freed from the kerosene, through which pressure had been applied, by heating in evacuated tubes to 550° C. The vapour pressures of the product (which might also of course have been altered by this treatment) were now almost, if not quite, equal to, and above 560° C. greater than, those of the violet form. The conversion of the black into the violet was effected by heating in the presence of about 1 per cent. of iodine at 480° C. or without the iodine at about 575° C.

It has already been mentioned that black phosphorus has a greater electrical conductivity than other forms, and is therefore to be considered as the most " metallic " variety.[2] The conductivity, however, like that of graphite, increases with rise of temperature, and this form is therefore only pseudo-metallic.

X-ray Data.—The structure of black phosphorus has been calculated from the X-ray reflection spectrum, using the powder method of Debye and Scherrer. It is a rhombohedral space-lattice having a characteristic angle of 60° 47′, and a side of 5·96 Å. The unit cell contains 8 atoms, and therefore the volume of the unit molecular aggregate is [3]

$$\frac{8M \times 1{\cdot}65 \times 10^{-24}}{2{\cdot}699} = 151{\cdot}6 \times 10^{-24} \text{ c.c.}$$

where 2·699 is the density, Δ, of black phosphorus and $1{\cdot}65 \times 10^{-24}$ is the mean value of the constant $d\sqrt[3]{\frac{\Delta}{M}}$ in which d is the distance between the diffracting planes.

Black phosphorus and combined phosphorus give characteristic absorption spectra for X-rays, the limits of wavelength being different in the respective cases. Red phosphorus shows two limits, which are those characteristic of black and of combined phosphorus.[4] The absorption coefficient for X-rays is 5·68, as compared with 569 in the case of lead.[1]

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[1] Smits, Meyer and Beck, *Proc. K. Akad. Wetensch. Amsterdam*, 1905, 18, 992.

[2] Bridgman, *J. Amer. Chem. Soc.*, 1914, 36, 1244.

[3] Linck and Jung, *Zeitsch. anorg. Chem.*, 1925, 147, 288.

[4] Bergegren, *Compt. rend.*, 1920, 171, 624. See also de Broglie and Dauvilleer, *ibid.*, 1920, 171, 626.

In its chemical properties black phosphorus is on the whole similar to red phosphorus. It ignites in air at about 400° C., and is insoluble in carbon disulphide.

SCARLET PHOSPHORUS, AND THE TRANSITIONS TO VIOLET PHOSPHORUS.

It has already been shown that the transition through the various grades of red phosphorus to violet phosphorus proceeds continuously as higher temperatures and longer times of heating are progressively applied. Liquid phosphorus, when in the early stage of transformation, shows a fine scarlet colour and probably then contains the form known as **scarlet phosphorus** or **Schenck's phosphorus**, from its discoverer.

Preparation.—Scarlet phosphorus is prepared by exposing to light a solution of phosphorus in carbon disulphide or carbon tetrachloride, or by boiling a 10 per cent. solution of phosphorus in phosphorus tribromide.[2] In the latter case the product contains considerable quantities of the solvent, in which it is slightly soluble. The solvent may, however, be removed by reducing the tribromide with mercury at a temperature over 100° C. The remaining tribromide and also the mercuric bromide may then be extracted with ether.[3] The lighter coloured preparations are more reactive than the darker, on account no doubt of their finer state of division.

It may also be noted that liquid phosphorus prepared by melting in sealed tubes under high pressures may deposit scarlet crystals.

Scarlet phosphorus has a density of 2·0, *i.e.* slightly less than that of red phosphorus. It is isotropic, and in this respect resembles red phosphorus which has been prepared at comparatively low temperatures. Red phosphorus which has been prepared at higher temperatures shows distinct evidence of crystalline structure.

Scarlet phosphorus is thus a transitional form and can be converted into the red variety by heating for some time at 300° C. in an atmosphere of carbon dioxide.

The chemical properties of the various forms of phosphorus have already been described (Chap. II., pp. 27–29).

THE ATOMIC WEIGHT OF PHOSPHORUS.

Historical.—In his tables published in 1818 Berzelius[4] gave 31·36 as the atomic weight of phosphorus. Other values obtained before and after this time did not agree even so well as this with the value accepted to-day. The reactions principally employed in this early period were the displacement of gold and silver from their chloride and sulphate respectively by elementary phosphorus. These reactions, on the assumption that one atom of phosphorus precipitates $\frac{5}{3}$ of an atom of gold and 5 atoms of silver, led to the weighted mean just quoted. The reactions are, however, in reality rather complex (see p. 28). It happened that the right condition, *i.e.* an excess of silver sulphate, was chosen to give the ratio $P : 5Ag$. If, however, the metal is completely deposited the ratio is $P : 4Ag$ nearly.

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[1] Aurén, *Phil. Mag.*, 1917, [6], 33, 471. Further references include: Turner, *Phys. Review*, 1925, [2], 26, 143; Bose, *ibid.*, 1926, [2], 27, 521; McLennan and Clark, *Proc. Roy. Soc.*, 1922, 102, A, 405; Allison, *J. Washington Acad.*, 1926, 16, 7.

[2] Schenck, *Ber.*, 1902, 35, 351; *ibid.*, 1903, 36, 979 and 4202; idem, *Zeitsch. Elektrochem.*, 1905, 11, 117.

[3] Wolf, *Ber.*, 1915, 48, 1272.

[4] Berzelius, *Schweigger's J.*, 1818, 23, 119; "*Lehrbuch,*" 5th ed., vol. iii., 1845, 1188.

Schrötter [1] determined the ratio of the element to its pentoxide by burning a weighed quantity of amorphous phosphorus in dry oxygen and weighing the oxide. The method is fraught with many difficulties. Unconsumed phosphorus was carried forward, and the combustion had to be completed in the successive bulbs in which the product was collected and weighed. It is also probable that backward diffusion or other contact with water vapour introduced an error. The minimum atomic weight deduced from these experiments was 30·94, the maximum 31·06 and the mean 31·03. But on account of the known incompleteness of the combustion the value 31·00 was assigned.

This experimental result happened to agree with that of Dumas,[2] who by means of the ratio PCl_3 to AgCl found $P = 31{\cdot}0_4$, a result which, taking the probable accuracy as 1 in 300, is not affected by recalculating from Dumas' ratios with our fundamental atomic weights.

Determinations of the molecular weight of phosphine by the method of limiting densities led to atomic weights of 30·98 [3] and 30·91.[4] The compressibility of phosphine was not known, however, with sufficient accuracy to allow a reliable calculation of the limiting density.

In an attempt to settle the question by a comparison of all the best methods known at the time, v. der Plaats [5] decomposed silver nitrate with phosphorus, burned red phosphorus to the pentoxide and also determined the ratio of silver to its orthophosphate. The results, based on Ag = 107·90, are—

Ratio determined .	$P : 5Ag$	$Ag_3PO_4 : 3Ag$	$2P : P_2O_5$
Atomic weight . .	30·93	30·99	30·98

The concordance is not sufficiently good to justify a recalculation to our fundamental value Ag = 107·88.

Standard Methods and Results.

In the more recent determinations which have led to the accepted value of the atomic weight the method of decomposition of the halides has been followed with the aid of all the present knowledge as to the proper conditions for the conversion of halogen hydrides into silver halides. An interesting method has also been worked out by which silver phosphate is converted into the bromide. The results obtained by this method, which will be described first, give additional weight to those obtained from the phosphorus halides.

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[1] Schrotter, *Ann. Chim. Phys.*, 1853, [3], 38, 131; idem, *J. prakt. Chem.*, 1851, 53, 435.

[2] Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 129.

[3] Berthelot, D., *Compt. rend.*, 1898, 126, 1415.

[4] Ter-Gazarian, *J. Chim. phys.*, 1909, 7, 337.

[5] v. der Plaats, *Compt. rend.*, 1885, 100 52.

Atomic Weight from the Ratio Silver Bromide to Silver Phosphate.

Silver orthophosphate, prepared by several methods, one of which is indicated below, was converted into silver bromide, the equations involved being :—

$3AgNO_3 + Na_2HPO_4 = Ag_3PO_4 + 2NaNO_3 + HNO_3$. (1)*

$Ag_3PO_4 + 3HBr = 3AgBr + H_3PO_4$ . . (2)[1, 2, 3]

The silver nitrate was prepared by dissolving precipitated silver in nitric acid, which had been twice redistilled and condensed in a platinum condenser. The silver was precipitated from the commercial nitrate by means of ammonium formate. After washing, it was fused with sugar charcoal, scrubbed, cleaned with ammonia and nitric acid, dissolved in the redistilled nitric acid, the solution evaporated to saturation, precipitated with more nitric acid, centrifuged and the nitrate recrystallised. The hydrobromic acid was prepared by passing hydrogen through the purest bromine (see p. 45) and then combining the mixed gases over heated platinised asbestos. The condensed acid was twice boiled with more bromine and once with bromine liberated by means of potassium permanganate, then distilled through a quartz condenser. The Na_2HPO_4 was treated with hydrogen sulphide, boiled, filtered free of a green precipitate (due to iron), then recrystallised fifteen times. It contained about 0·01 milligram of arsenic in 10 grams, an amount entirely insufficient to affect the results. By nephelometry no chloride or other substances were found which could be precipitated by silver nitrate in nitric acid solution. $NaNH_4HPO_4$ was prepared and purified in a similar manner.

The solutions which were allowed to interact were about 0·03 N in order to avoid inclusions in the precipitates. The latter were well washed, and allowed to stand in water for at least 24 hours. Silver orthophosphate was stable in the presence of the moderate amounts of acid produced by some of the reactions which were tried. If silver nitrate is poured into excess of disodium hydrogen phosphate the precipitate settles rapidly, but precipitation is incomplete. If disodium ammonium phosphate is poured into silver nitrate the precipitate settles rapidly and the solution remains nearly neutral, according to the equation

$$Na_2NH_4PO_4 + 3AgNO^3 = Ag_3PO_4 + 2NaNO_3 + NH_4NO_3$$

By a combination of methods, for an account of which the original paper should be consulted, pure Ag_3PO_4 was obtained and dried by heating in a platinum boat in a current of dry air free from carbon dioxide. After weighing, it was dissolved in nitric acid and the solution was poured into an excess of hydrobromic acid, with the precautions usually employed in the quantitative precipitation of silver bromide.

The ratio $3AgBr : Ag_3PO_4$ varied between 1·34558 and 1·34570 as extremes, the mean value being 1·34562. It was considered that the mean value was, if anything, slightly low owing to a possible occlusion of Ag_2HPO_4. It was noted that the samples of silver phosphate prepared under more acid conditions gave a ratio of 1·34558, while those under less acid conditions gave a ratio of 1·34564. If Ag is taken as 107·88 and the percentage of Ag in AgBr as 57·4453, the two mean values of the bromide-phosphate ratio give 31·043 and 31·037 respectively as the atomic weight of phosphorus.

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* *Note.*—And other equations, *e.g.* that given below.

[1] Baxter, *J. Amer. Chem. Soc.*, 1908, 30, 286.

[2] Baxter and Jones, *ibid.*, 1910, 32, 298.

[3] *Carnegie Institution of Washington,* Publication 135.

In view of the fact that the methods to be described each have their own sources of error it seems that the phosphate results should be taken into account in assigning the atomic weight.

Ratios $PBr_3 : 3AgBr$ *and* $PBr_3 : 3Ag$.

The preceding method is open to the criticism that silver orthophosphate contains only 7·4 per cent. of phosphorus. Phosphorus tribromide is somewhat better in this respect, containing 11·5 per cent. of phosphorus; but on the other hand the preparation and quantitative decomposition of this compound in a manner suitable for atomic weight determinations present great difficulties, the nature of which is apparent from the following narrative.[1]

Outline of Process.—Pure dry bromine was allowed to act on pure dry phosphorus in a vacuum; the PBr_3 was distilled into receivers which were sealed and weighed, then decomposed by breaking under an ammoniacal solution of hydrogen peroxide. The solution was acidified with nitric acid and the bromine precipitated and weighed as silver bromide.

The Reagents.—The water, nitric acid and ammonia were purified by redistillation and the usual methods, and the silver by the methods in common use for its preparation as a standard element in atomic weight determinations. The hydrogen peroxide was a c.p. sample free from sulphuric and halogen acids. The nitrogen used in the preparation of the PBr_3 was prepared by passing air and ammonia over heated copper gauze (see this Vol., Part I., p. 25). The phosphorus was twice distilled with steam in an all-glass apparatus. The bromine was distilled from concentrated potassium bromide (which removes all but a trace of chlorine), then converted into potassium bromide by action on a solution of potassium oxalate. To remove iodine the solution of potassium bromide was boiled with some of the partly purified bromine, and finally with small portions of potassium permanganate. It was then evaporated to dryness and fused. From this fused potassium bromide bromine was prepared by dissolving in water, adding sulphuric acid and enough potassium permanganate to liberate three-quarters of the halogen. This was distilled a second time from the bromide, which was nearly pure. The separated bromine was dried by resublimed phosphorus pentoxide, from which it was distilled immediately before use.

Preparation of Phosphorus Tribromide.—An excess of bromine was necessary on account of the solubility of phosphorus in PBr_3. Distillation of this from red phosphorus yields a product which contains too little bromine. The phosphorus (14 grams) was freed from water by pressing between hardened filter-papers and placed in a distillation flask containing dry nitrogen. The flask was then placed in boiling water and the contents subjected to a current of dry nitrogen, with shaking, to eliminate all steam from the liquid phosphorus. The flask was then evacuated and closed. It was cooled with ice-water, and the calculated amount of pure dry bromine admitted gradually from a tap funnel. After addition of nearly the theoretical amount of bromine the PBr_5 in the upper part of the flask was decomposed with hot water and more bromine admitted until the tribromide assumed a reddish colour due to excess of bromine, when such excess amounted to a few centigrams. Dry nitrogen was then admitted so as to produce a slight excess pressure, and the tribromide then fractionally distilled in a vacuum, the fractions being collected in a number of receivers placed in series. In this distillation a residue of a few grams was left in each of the first two receivers, this containing any dissolved phosphorus which was present. The bulk of the distillate in the third receiver now contained a slight excess of bromine. This was removed by bubbling through the warm liquid vapour derived from the second receiver. This process was continued for some time after the distillate became colourless. The residue in the third receiver, about 100 grams, was redistilled into several small bulbs, which were then sealed at their capillary junctions. The first and last samples collected showed equally a slight yellow tint when warm. This is probably characteristic of the pure tribromide.

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[1] Baxter, Moore and Boylston, *J. Amer. Chem. Soc.*, 1912, 34, 259.

A bulb and contents, after weighing, was broken by shaking under a solution of ammoniacal hydrogen peroxide in a stout flask closed by a glass stopper. The decomposition of the PBr_3 was complete in 5 minutes, but the flask was allowed to stand for 24 hours with occasional shaking in order to effect complete absorption of the fumes of NH_4Br. The cooled solution was filtered through a small paper, which was burned at as low a temperature as possible. All the broken glass was thus collected and weighed. The filtrate was acidified with nitric acid, introduced by a thistle funnel at the bottom of the solution, in order to avoid any loss of bromine set free locally and temporarily. The bromine, present as hydrobromic acid, was then determined in two ways—

(*a*) By finding the amount of silver which combined with it completely.

(*b*) By weighing the silver bromide precipitated.

Both determinations were carried out with the same solution.

(*a*) A quantity of silver which was equivalent to the bromine present within a few tenths of a milligram was dissolved in nitric acid with the usual precautions, the solution treated with an excess of nitric acid and added to the solution prepared from the PBr_3 with constant agitation. After standing, portions of the clear solution were tested in a nephelometer for excess of bromide or of silver. The bromide was always found to be in slight excess. The solution was then adjusted with N/100 $AgNO_3$, shaken, allowed to stand, and the adjustment repeated until the amounts of silver and of bromine were again equivalent. After standing for a week, a nephelometer test showed that there was again an excess of bromide, apparently due to the diffusion of occluded bromide out of the precipitate. The deficiency of silver was again made up, the final end-point being reached in about a fortnight.

(*b*) The precipitated AgBr was washed by decantation with water and collected on a Gooch-Munroe-Neubauer crucible, which was then heated gradually to 200° C. and kept at that temperature for 18 hours or more. After cooling, the bromide was weighed by substitution for a similar counterpoise. The precipitate was then transferred to a porcelain crucible and fused. The loss in weight on fusion seldom amounted to more than 0·001 per cent. of the weight of the precipitate. The clear yellow colour of the fused bromide was an additional guarantee of purity, since a very small percentage of impurity is sufficient to produce a perceptible darkening. The amounts of AgBr which were dissolved in the filtrate and wash water were also determined.

The concordance of the two methods (*a*) and (*b*) could be checked by means of the ratio Ag : AgBr, which as a mean of seventeen results was 0·574462. This is almost identical with the value 0·574453 which had already been considered to be the most probable.[1] Three series of determinations were carried out, each including five to eight separate experiments, and there were thirty-six in all. The means of each of the sets carried out according to methods (*a*) and (*b*) are given in the following tables. The atomic weight of phosphorus is calculated from these results using Ag = 107·880 and Br = 79·916.

WEIGHTS OF PHOSPHORUS TRIBROMIDE CORRESPONDING TO THREE PARTS BY WEIGHT OF SILVER AND OF SILVER BROMIDE, AND VALUES OF THE ATOMIC WEIGHT OF PHOSPHORUS.

Method (*a*).		Method (*b*).	
Ratio PBr_3 : 3Ag.	Atomic Weight.	Ratio PBr_3 : 3AgBr.	Atomic Weight.
0·836660	31·031	0·480629	31·033
0·836640	31·022	0·480628	31·032
0·836644	31·025	0·480611	31·022
0·836648	31·026	0·480623	31·029

A given percentage error in the experimental work is multiplied nine times in the calculation of the atomic weight, *i.e.* an experimental error of 0·01 per cent. affects the calculated atomic weight of phosphorus by 0·027 unit. The highest individual value was 31·040, the lowest 31·013, which corresponds almost exactly to 0·01 per cent. accuracy in the experimental work. Of the thirty-six results, however, twenty-seven fell between 31·035 and 31·021, a fluctuation only half as great. The variations in the mean results are about 0·002 per cent., which corresponds to about 0·006 unit in the atomic weight. The means of the means agree to 0·003 unit. Giving a slightly greater weight to method (*a*) the investigators deduce from these results an atomic weight of 31·027.

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[1] Baxter, *J. Amer. Chem. Soc.*, 1906, 28, 1322.

Ratios $PCl_3 : 3AgCl$ and $PCl_3 : 3Ag$.

Since the percentage of phosphorus is considerably higher in the chloride than in the bromide it was considered that the atomic weight might be deduced with even greater accuracy from the former compound.[1] The methods used were similar, although not identical; the most important points of difference will be noted.

Chlorine prepared from manganese dioxide and pure HCl was liquefied and the dry gas evolved from the liquid was admitted to the dry phosphorus in a vacuum. In this case phosphorus pentachloride was formed in considerable quantity and was removed only by several distillations. It could not be inferred with such confidence that the trichloride was free from pentachloride as that the tribromide was free from bromine. The trichloride was decomposed and oxidised in the manner already described. In the subsequent estimation of the silver chloride less difficulty was experienced in freeing this from occluded chloride, but more difficulty in determining accurately the amount of silver chloride remaining in solution. It was found possible, however, to diminish the solubility by adding an excess of silver nitrate solution and partly washing the precipitated chloride with this solution.

The silver chloride was dried at 190° C. and weighed as usual in series III. In series I and II the exact amount of silver nitrate required for complete reaction was found by adjustment, using the nephelometer as already described. The means of the experiments in each series are given in the following table :—

WEIGHTS OF PHOSPHORUS TRICHLORIDE CORRESPONDING TO THREE PARTS BY WEIGHT OF SILVER AND OF SILVER CHLORIDE.

Method (*a*).		Method (*b*).	
Ratio $PCl_3 : 3Ag$.	Atomic Weight.	Ratio $PCl_3 : 3AgCl$.	Atómic Weight.
0·424509	31·017	0·319509	31·022
0·424506	31·016		

The average atomic weight is given as 31·018. The investigators remark : " If the trichloride actually contained a trace of pentachloride it would account for the fact that the average result of this research is very slightly lower than that of the tribromide work."

General Conclusions.—The three main determinations of the atomic weight of phosphorus with their results are—

From . . .	Ag_3PO_4	PBr_3	PCl_3
Atomic weight . .	31·04	31·027	31·018

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[1] Baxter and Moore, *J. Amer. Chem. Soc.*, 1912, 34, 1644.

In the fixing of standard atomic weights the results obtained from PBr_3 have been preferred for reasons that will be evident from the data already adduced. Although these results appear to be the least affected by systematic errors, nevertheless they involve such errors, and it seems hardly justifiable as yet to trust the results as far as units in the fifth significant figure. It may, however, be asserted with the greatest confidence that the atomic weight is known to be—

$$31{\cdot}03 \pm 0{\cdot}01$$

Thus there is no doubt that all chemical determinations concur in assigning to phosphorus an atomic weight slightly greater than 31·00. Nevertheless phosphorus, when analysed by the method of mass spectra, has hitherto proved to be a pure element; no isotopes are present to account for the departure from the rule of whole numbers. There are two possible explanations—

(1) " The whole number rule is not, and never was supposed to be, mathematically exact, for this would imply an identical packing effect in the case of all atoms, an exceedingly improbable supposition." [1]

(2) It is possible that an isotope accompanying $P = 31{\cdot}00$ in small amount has not yet been detected, as in the case of sulphur ($S = 32{\cdot}06$), the spectrograph of which shows two faint lines at 33 and 34, originally ascribed to hydrides, but afterwards shown to be due to isotopes of higher atomic weight.[2] Opinions founded on later work, however, have been less favourable to this hypothesis, and slight deviations from the whole number rule (on the oxygen scale) are now recognised in the case of " pure " elements, as appears from the quotation below.[3]

The purely chemical evidence as to the atomic weight of phosphorus is supplemented by that derived from mass spectra.[3]

" Ever since the discovery of the whole number rule it has been assumed that in the structure of atoms only two entities are ultimately concerned, the proton and the electron. If the additive law of mass was as true when an atomic nucleus is built of protons plus electrons as when a neutral atom is built of nucleus plus electrons, or a molecule of atoms plus atoms, the divergences from the whole number rule would be too small to be significant, and, since a neutral hydrogen atom is one proton plus one electron, the masses of all atoms would be whole numbers on the scale $H = 1$. The measurements made with the first mass-spectrograph were sufficiently accurate to show that this was not true. The theoretical reason adduced for this failure of the additive law is that, inside the nucleus, the protons and electrons are packed so closely together that their electromagnetic fields interfere and a certain fraction of the combined mass is destroyed, whereas outside the nucleus the distances between the charges are too great for this to happen. The most convenient and informative expression for the divergences of an atom from the whole number rule is the actual divergence divided by its mass number. This is the mean gain or loss per proton when the nuclear packing is changed from that of oxygen to that of the atom in question. It will be called the 'packing fraction' of the atom and expressed in parts per 10,000. Put in another way, if we suppose the whole numbers and the masses of the atoms to be plotted on a uniform logarithmic scale such that every decimetre equals a change of 1 per cent., then the packing fractions are the distances expressed in millimetres between the masses and the whole numbers.

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[1] Aston, "*Isotopes*," chap. viii., par. 96 ff., Arnold, 1923; *Phil. Mag.*, 1920, [6], 40, 628; 1925, [6], 49, 1191.

[2] Aston, *Nature*, 1926, 117, 893.

[3] Aston, *Proc. Roy. Soc.*, 1927, A, 115, 487.

"*Phosphorus.*—The element was introduced in the form of phosphine, which gives the lines P, PH, PH_2, PH_3. If plenty of carbon monoxide is present its line will be practically unaffected by the presence of small quantities of Si^{28}, inevitably present and of mass so far unknown. So that the series CO : P : PH_3 can be employed to give values for phosphorus. . . . From the known values of H, C and O and the sum of the two intervals the 'packing fraction' of P can be calculated. The mean of six consistent values corresponds to a packing fraction $-5·6$ and therefore a mass 30·9825. No mass-spectrum has given the slightest reason for supposing that phosphorus is complex, so that it seems probable that the chemical atomic weight of 31·02 is too high."

The method of limiting densities when applied to phosphine also gives a lower result for the atomic weight of phosphorus. Phosphine was prepared from phosphonium iodide by means of potassium hydroxide, and was fractionated. The densities were investigated at pressures of 1 down to 0·25 atmosphere. Assuming a linear relation between pv and pressure, $(pv)_0/(pv)_1$ is calculated to be 1·0091. If the normal litre of oxygen weighs 1·4290 gram and the coefficient of deviation from Boyle's law per atmosphere is $-0·00096$, then $PH_3 = 34·000$ and $P = 30·977$.[1]

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[1] Ritchie, *Proc. Roy. Soc.*, 1930, A, 128, 551; "*First Report of the Committee on Atomic Weights,*" *J. Chem. Soc.*, 1931, 1617.

CHAPTER IV.

PHOSPHORUS IN COMBINATION.

PHYSICAL PROPERTIES.

THE volume which is occupied by the atom of phosphorus when it is combined with one or two other elements to form liquid compounds has been deduced from the molar volumes of such compounds on the assumption that the other elements possess constant and characteristic atomic volumes in these compounds. Thus, from the molar volumes of PCl_3 and PBr_3 at their boiling-points Kopp [1] assigned to phosphorus the atomic volume 25·2. The exact determinations by Thorpe [2] of the densities and coefficients of expansion of PCl_3, PBr_3, $POCl_3$, $PSCl_3$, $POBrCl_2$ and $PCl_2(OC_2H_5)$ gave values for the atomic volume of phosphorus which ranged between 24·0 and 26·1, the mean being about 25·3. The value derived from the density of liquid PH_3 (*q.v.*), using Kopp's value for hydrogen, is 29·1. These variations do not depend on experimental errors, nor, in the comparison of such compounds as PCl_3 and PBr_3, can they be ascribed to differences in constitution. It has been suggested that the differences between the molar volumes of the liquid compounds at their boiling-points (or other temperatures at which the vapour pressures are equal) and the sums of the atomic volumes of the liquid elements at the same vapour pressures are also some function of the affinities which come into play during the combinations.[3] The volumes measured at the respective boiling-points are :—Cl, 22·76 ; Br, 26·8 ;[2] P, 20·5 ; therefore $P+3Cl=88·8$ and $P+3Br=100·9$. According to Thorpe also $PCl_3=93·34$ [2] and $PBr_3=108·8$.[2] The combination with chlorine under conditions of equal vapour pressure is accompanied by an expansion of 4·5 units, and that with bromine by 7·9 units, in excess of the values which would obtain if Kopp's additive law held good. The comparison has been extended to the oxyhalides [2] and the pentahalides [4] with the result that the changes of volume on combination were found to be different in each case.

In attempting to determine the structure of such compounds as $POCl_3$ the molar volume of the compound at its boiling-point may be diminished by that of PCl_3,[2] leaving 7·8, which is Kopp's value for oxygen linked to two elements, and leads to a formula $Cl_2=P-O-Cl$. If, however, the molar volume of $POCl_3$ is diminished by the atomic volumes of P and 3Cl, the remainder, 12·2, is the atomic volume of doubly-linked oxygen, which leads to a formula $Cl_3 \equiv P = O$.[1] The present views on valency, as developed, *e.g.*, in this Volume, Part I., put the whole matter in rather a different light.

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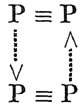
[1] Kopp, *Annalen*, 1856, 100, 14.

[2] Thorpe, *Trans. Chem. Soc.*, 1880, 37, 378.

[3] Prideaux, *Trans. Chem. Soc.*, 1906, 91, 1711; 1909, 95, 445; 1910, 97, 2032.

[4] Prideaux, *Trans. Chem. Soc.*, 1906, 91, 1711.

It is improbable that phosphorus is trivalent in $POCl_3$, and further, in such compounds it is exercising its maximum valency. Since the atomic volume calculated on the assumption of a double bond between the phosphorus and the oxygen agrees most closely with the atomic volume of elementary phosphorus, it is probable that in the liquid element as well as in $POCl_3$ phosphorus is exercising this maximum valency, which includes " mixed bonds," thus



See also the discussion on the structure of P_4O_6 (p. 128).

The Volume of Phosphorus in Liquid Compounds under Conditions of Maximum Contraction.—The volumes which liquid compounds would occupy if they remained in this state at temperatures not far removed from the absolute zero represent the closest packing possible at ordinary external pressure and under the influence of the internal or intrinsic pressure alone of non-oriented molecules, *i.e.* those which are not arranged in a space-lattice. These volumes can be obtained by shorter or longer extrapolations from the actual observed liquid volumes.

The formula of Cailletet and Mathias[2] gives the mean isobaric densities of a liquid and its saturated vapour as a rectilinear function of the temperature. Thus

$$\frac{D_L + D_V}{2} = \frac{D_0}{2} + aT$$

in which the meaning of the symbols is obvious, and $D_0/2$ is half the limiting density at the absolute zero obtained by the extrapolation.

The specific volumes v_0 ($=1/D_0$) are found in the case of many liquids to have a mean value equal to 0·26 of v_c (the critical volume),[3] while according to van der Waals' equation[4] they should be equal to 0·33 of v_c ($v_c = 3b$). In either case the volumes v_0 at maximum contraction are corresponding volumes and should therefore be additively related to those of the constituent elements. It has been shown[5] that the most closely additive relations are obtained if the limiting volumes are calculated by the equation

$$D_L - D_V = D_0\left(1 - \frac{T}{T_c}\right)^{0 \cdot 3}$$

From the differences in molar volumes ${}_{M}V_0$ (or M/D_0) of homologous series, etc., the atomic volumes ${}_{A}V_0$ of each element are calculated in the usual way. The value assigned to phosphorus is 12·7. The atomic volumes are added together to give $\Sigma_A V_0$, and the sums are compared with the molar volumes found, $_{M}V_0$.

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[1] Ramsay and Masson, *Trans. Chem. Soc.*, 1881, 39, 52.

[2] Cailletet and Mathias, *Compt. rend.*, 1886, 102, 1202; *ibid.*, 1887, 104, 1563.

[3] Berthelot, D., *Arch. Neerlandaises*, 1900, [2], 5, 446.

[4] See this Series, Vol. I., and "*A Text-book of Physical Chemistry*," Vol. I., J. Newton Friend (Griffin), 1932.

[5] Sugden, *Trans. Chem. Soc.*, 1927, 1780.

MOLAR VOLUMES OF PHOSPHORUS COMPOUNDS AT ABSOLUTE ZERO.

Compound.	Formula.	$_{M}V_0$.	$\Sigma_A V_0$.	Observer.
Phosphorus trichloride	PCl_3	69·6	70·6	Thorpe.[1]
,, tribromide	PBr_3	78·6	79·0	Sugden, Reed and Wilkins.[2]
,, oxychloride	$POCl_3$	73·4	75·6	,, ,, ,,
Triethyl phosphate .	$PO(OEt)_3$	140·5	139·8	,, ,, ,,
Triphenyl phosphate .	$PO(OPh)_3$	230·2	226·8	,, ,, ,,
,, phosphine .	PPh_3	206·4	206·8	Walden and Swinne.[3]

Further information on the structure of phosphorus compounds is given by the **parachor**, which is a function of surface tension and molar volume, the molar volumes in effect being compared under conditions of equal surface tension.[4] For a given liquid the expression

$$\frac{\sigma^{\frac{1}{4}}}{D_L - D_V}$$

is independent of the temperature.[5] The molar parachor

$$\frac{M\sigma^{\frac{1}{4}}}{D_L - D_V}$$

is found to be additively composed of terms due to each of the atoms (which may be called the atomic parachors) plus terms due to double or triple linkages, and to various types of cyclic structures. The mean parachor of phosphorus as calculated from some binary compounds, such as PCl_3, etc., is 37·3 (36·1 to 38·9). In another system it is 40·5.[6]

	PCl_3.	PBr_3.	$P(C_6H_5)_3$.
P_M	199·0 [7] 201·1 [8]	242·9 [2]	607·7 [3]
ΣP_A (without phosphorus)	162·9	204·0	570·0

The parachors of phosphorus and the other atoms were summed and compared also with the molar values of $POCl_3$, etc. (p. 54). A different series of atomic parachors has also been proposed.[6]

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[1] Thorpe, *Trans. Chem. Soc.*, 1880, 37, 141, 386.
[2] Sugden, Reed and Wilkins, *Trans. Chem. Soc.*, 1925, 127, 1525.
[3] Walden and Swinne, *Zeitsch. physikal. Chem.*, 1912, 79, 700.
[4] Macleod, *Trans. Far. Soc.*, 1923, 19, 38; Sugden, *Trans. Chem. Soc.*, 1924, 125, 1177.
[5] D_L = density of liquid, D_V = isobaric density of vapour, σ = surface tension.
[6] Mumford and Phillips, *Trans. Chem. Soc.*, 1928, 155; 1929, 2112.
[7] Morgan and Daghlien, *J. Amer. Chem. Soc.*, 1913, 33, 657.
[8] Ramsay and Shields, *Trans. Chem. Soc.*, 1893, 63, 1089.

	$POCl_3$.	$PO(OC_2H_5)_3$.	$PO(OC_6H_5)_3$.
P_M	217·6 [1]	399·1 [2]	686·5 [2]
ΣP_A	220·6	403·0	687·7
$P_M - \Sigma P_A$ . . .	−3·0	−3·9	−1·2

The differences have the sign and magnitude which is associated with a "mixed" bond, and this confirms the structure assigned on p. 52. The ethyl ester of phenylmethylphosphinic acid had a parachor of 420·5; that calculated on the assumption of an ordinary double bond was 442·1, while on the assumption of a "mixed" or semipolar bond it was 417·3. The structure was therefore given as

$$(CH_3)(C_6H_5)(C_2H_5O){\equiv}P \cdots\cdots > O$$ [3]

The **atomic refraction** shows considerable variability with constitutive influences, whether it is determined by Gladstone's formula

$$\mathrm{A}r_{\mathrm{G}} = \frac{n-1}{D}A$$

or by Lorentz and Lorenz's formula

$$\mathrm{A}r_{\mathrm{L}} = \left(\frac{n^2-1}{n^2+2}\right)\frac{A}{D}$$

(*Note.*—A = atomic weight, r_{G} = refractivity according to Gladstone's formula, r_{L} = refractivity according to Lorentz and Lorenz's formula.) The atomic refraction $\mathrm{A}r_{\mathrm{G}}$ of the element is 18·68 (solid), 18·89 (liquid),[4] or 18·69 (mean of solid and liquid),[5] while the value $\mathrm{A}r_{\mathrm{L}}$ was 9·10 (mean of solid and liquid).[5]

The following values have been calculated from the molar refractivities of the principal liquid (or gaseous) compounds:—[6]

	PH_3 (liquid).	PH_3 (gaseous).	$P(C_2H_5)_3$.	PCl_3.	PCl_5.	PBr_3.	P_4O_6.	$POCl_3$.
$\mathrm{A}r_{\mathrm{G}}$	13·75	13·75	17·24	14·89	16·65	20·01	9·71	8·92
$\mathrm{A}r_{\mathrm{L}}$	9·10	8·63	9·47	8·32	8 81	9·72	5·33	4·92

Atomic refractivities of phosphorus in its compounds are calculated as the difference between the molar refractivities and the sums of the refractivities of the other atoms. They vary according to the structure assigned, namely, whether oxygen is to be considered as singly- or doubly-linked. Molar refractivities appear to be affected by constitutive influences to about the same extent as molar volumes at the boiling-points, V_M, since the ratios of V_M to Mr_L for all the compounds considered range between 4·77 and 5·01, mean 4·9.[1]

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[1] Ramsay and Shields, *Trans. Chem. Soc.*, 1893, 63, 1089.

[2] Sugden, Reed and Wilkins, *Trans. Chem. Soc.*, 1925, 127, 1525.

[3] Gibson and Johnson, *Trans. Chem. Soc.*, 1928, 92.

[4] Gladstone, *Chem. News*, 1887, 55, 300.

[5] Damien, "*Réch. sur le pouvoir réfringent des liquides*," Paris, 1881.

[6] Zecchini, *Zeitsch. physikal. Chem.*, 1893, 12, 505; *Gazzetta*, 1893, 23, i., 97. See also Kanonikoff, *J. prakt. Chem.*, 1885, [2], 31, 359; Haagen, *Annalen*, 1867, 131, 117.

When the refractivities of gaseous compounds are calculated to standard conditions, the values of $n-1$ or $(n-1)10^6$ are often found to be nearly additively composed of those of their components, that is $(n-1)10^6$ is nearly equal to $\Sigma(n_A-1)10^6$. The following table enables this comparison to be made between observed and calculated refractivities.[2] The property is only approximately additive, the deviations from this relation being great in some cases.[3, 4]

REFRACTIVITIES OF PHOSPHORUS COMPOUNDS AND THOSE OF THEIR ELEMENTS.

Compound.	Refractive Index (n).		(n) Calculated for Gas from Lorentz and Lorenz's Formula.	Refractivity $(n-1)10^6$.	Refractivities of Components, P=599.	Sum.	Difference per cent. Columns (5) and (7).
	Gas.	Liquid.					
PH_3	1·000786	..	..	786	$599+(3\times69\frac{1}{2})$	807·5	−2·7
PCl_3	1·001730	..	..	1730	$599+(3\times384)$	1751	−1·2
PBr_3	..	1·6866	1·002450	2450	$599+(3\times562{\cdot}5)$	2286·5	+7·1
P_4S	..	2·0661	1·003025	3025	$(4\times599)+551$	2947	+2·6
P_2O_3	..	1·5405	1·001725	1725	$(2\times599)+(3\times135)$	1603	+7·7
$POCl_3$	..	1·4602	1·001715	1715	$599+135+(3\times384)$	1886	−9·1
$PSCl_3$	..	1·57547	1·002281	2281	$599+(3\times384)+551$	2302	−0·9

Stereochemistry.—Compounds of the type POX_3 may, as already pointed out, have one or other of two constitutions (see p. 52) or may exist in tautomeric equilibrium, but if the halogens X are replaced by hydrocarbon or other organic radicals R, the compound will be fixed in one or other of the two isomeric forms. This isomerism has been well established in the case of the compounds having the empirical formula $OP(C_6H_5)_3$.[5] One of these, phenoxydiphenylphosphine, is an oily liquid, prepared by the condensation of phenol with diphenylchlorophosphine :—

$$C_6H_5OH+(C_6H_5)_2PCl=(C_6H_5)_2P.OC_6H_5+HCl$$

The other, triphenylphosphine oxide, is a solid melting at 153·5° C., and is prepared by the action of water on triphenylbromophosphine bromide :—

$$H_2O+(C_6H_5)_3PBr_2=(C_6H_5)_3PO+2HBr$$

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[1] Arbuzov and Ivanov, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 2015; A, 1925, ii., 165.

[2] Cuthbertson, C. and M., *Phil. Trans.*, 1905, 204, A, 323.

[3] Cuthbertson and Metcalfe, *Phil. Trans.*, 1908, 207, A, 135; *Proc. Roy. Soc.*, 1908, 80, A, 411.

[4] Cuthbertson, C. and M., *Proc. Roy. Soc.*, 1910, 83, A, 151.

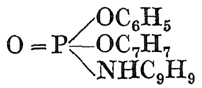
[5] Michaelis and la Coste, *Ber.*, 1885, 18, 2118.

That the three ordinary valencies of phosphorus in compounds of the type POX_3 or POR_3 do not act in one plane, but are distributed in space symmetrically with respect to one another, was demonstrated by Caven,[1] who replaced chlorine atoms in the trichloride one at a time but in different succession by various groups such as RNH— or RO—, forming, for example, the anilino-, *p*-toluidino- and then the *p*-toluidino-anilino chloride.

No signs of isomerism were detected in the mono-, di- or tri-substitution products. It was therefore stated that "the centres of gravity of the three chlorine atoms lie at the angles of an equilateral triangle, and if an imaginary line is drawn through the centre of this triangle and at right angles to its plane, the centres of gravity both of the phosphorus atom and of the oxygen atom are situated on this line."

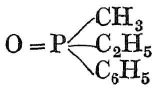
On account of the theories of valency alluded to before (p. 52),[2] compounds of the types $[PR_4]X$ and $[OPR_3]$ are of the same stereochemical type, and contain an atom of phosphorus co-ordinated to four atoms or groups which are symmetrically disposed in space. When the groups denoted by R are different, the resulting compounds $PR_1R_2R_3R_4X$ and $POR_1R_2R_3$ should be capable of existing in optically active forms.

The first preparation of the type $PR_1R_2R_3R_4X$ could not be resolved,[3] nor could an anilino-*p*-toluidinophosphoric acid [1] be resolved into optically active isomers by fractional crystallisation with active bases. The first compound which was proved to contain an asymmetric phosphorus atom was phenyl-*p*-tolylphosphoric acid, the *dl*-hydrindamine of which—



was found to be a mixture of two compounds having different melting-points. The *d*- and *l*-hydrindamines when separately prepared each yielded on fractional crystallisation a less soluble fraction of lower lævo-rotatory power and a more soluble fraction of higher lævo-rotatory power, thus showing a resolution of the acid.[4]

The compound methylethylphenylphosphine oxide



also contains an asymmetric phosphorus atom.[5] It was prepared by combining ethyldiphenylphosphine with methyl iodide, setting the base free with silver oxide and boiling with water :—

$$(C_6H_5)_2(C_2H_5)(CH_3)POH = C_6H_6 + (C_6H_5)(C_2H_5)(CH_3)PO$$

This compound, which could be distilled without decomposition, was combined with the calculated amount of *d*-bromocamphorsulphonic acid and the product crystallised from ethyl acetate. The recrystallised product had a molecular rotation, M_D, of +321°, while that of bromocamphoric acid and its salts with inactive substances was +48°. On passing ammonia into a solution of the camphorsulphonate in benzene, the ammonium salt was quantitatively precipitated, and the solution on evaporation gave colourless crystals of the methylethylphenylphosphine oxide, which had a molecular rotation, M_D, of +39° in water and +57° in benzene.

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[1] Caven, *Trans. Chem. Soc.*, 1902, 81, 1362.

[2] See also Part I. of this Volume.

[3] Michaelis, *Annalen*, 1901, 315, 38.

[4] Kipping and Luff, *Trans. Chem. Soc.*, 1909, 95, 1993.

[5] Meisenheimer and Lichtenstadt, *Ber.*, 1911, 44, 356. See also Radcliffe and Brindley, *J. Soc. Chem. Ind.*, 1923, 42, 64.

Further evidence as to structure in space is derived from an examination of the electric moments due to the dipoles of some compounds.

The Dipole Moment of Phosphine.—Molecules which are not polar in the sense of being strong acids, bases or salts, may yet show an inner polarity when investigated by certain physical methods. The use of the dielectric constant and the refractivity in calculating the polarisation of molecules is described in certain monographs and text-books, *e.g.* "*The Dipole Moment and Chemical Structure*," Debye-Deans (Blackie), 1931; "*Recent Advances in Physical Chemistry*," Glasstone (Churchill), 1931.

The total molar polarisation, *i.e.* that due to 1 gramme-molecule of the compound, is given by the Mosotti-Clausius equation :—

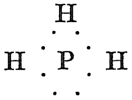
$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{D} = P = \frac{4\pi N}{3} \cdot \gamma + \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT}$$

in which ϵ is the dielectric constant, M and D have their usual significance, N is the Avogadro number, and γ is the molecular polarisability due to induced dipoles. We are not concerned at present with the first term on the right, which is the distortion polarisation, P_D, *i.e.* that which is due to the dipoles which are set up in molecules by the applied field of force. The second term is the polarisation due to the permanent dipoles existing in the molecules before the field is applied. A permanent dipole is present whenever combination with partial separation of electric charges has taken place in such a way that the centre of gravity of all the positive charges does not correspond with that of the negative charges. If the distance between the charges e is d, then $de = \mu$ is the dipole moment of each molecule. Boltzmann's constant $k = R/N$, in which R is the universal gas constant and N is the Avogadro number, *i.e.* the number of molecules in a gramme-molecule. Since all these constants have known values and the temperature is known, the dipole moment μ can be calculated, and on certain assumptions it gives the configuration of the molecule. The following values have been found in the case of the hydrogen compounds of this group :—

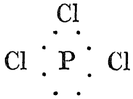
	NH_3.	PH_3.	AsH_3.
$\mu \times 10^{18}$	1·55	0·55	0·15

The existence of these permanent dipole moments indicates that the hydrogen atoms are not in the same plane as the tervalent element, but that this occupies the apex of a tetrahedron, of which the three hydrogen atoms form the corners. The diminution of the moment with rise of atomic weight is attributed to a decrease in the height of the tetrahedra, and also to the distortion of the octets of electrons on the N, P and As atoms by the positive charges on the H atoms.

The Representation of Phosphorus Compounds by Electronic Theories of Valency.—The compounds in which phosphorus is trivalent are saturated in the sense that all the covalent bonds on the element are made up, with the completion of the outer octet of electrons, the phosphorus atom thus assuming the argon type with three completed shells of 2, 8, 8 electrons of which only the outermost are shown by the formulæ—[1]

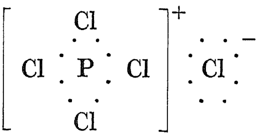


$$\begin{array}{c} \mathrm{H} \\ \cdot\,\cdot \\ \mathrm{H}\ \vdots\mathrm{P}\vdots\ \mathrm{H} \\ \cdot\,\cdot \end{array}$$



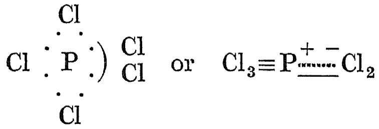
$$\begin{array}{c} \mathrm{Cl} \\ \cdot\,\cdot \\ \mathrm{Cl}\ \vdots\mathrm{P}\vdots\ \mathrm{Cl} \\ \cdot\,\cdot \end{array}$$

If we admit the hypothesis[2] that the three quantum orbits of the second series may contain a maximum of 6, 6 instead of 4, 4 electrons, it follows that PCl_5 also, and other quinquevalent compounds, may be written with ordinary valencies or duplet bonds only, giving shells of 10 ⊖. If, however, 8 is the maximum possible (failing the completion of 12), then PCl_5 must be constituted either as NH_4Cl, or it must contribute two electrons to a pair of chlorine atoms, thus developing a "mixed bond." In the first case



$$\left[\begin{array}{c} \mathrm{Cl} \\ \cdot\,\cdot \\ \mathrm{Cl}\ \vdots\mathrm{P}\vdots\ \mathrm{Cl} \\ \cdot\,\cdot \\ \mathrm{Cl} \end{array}\right]^{+} \begin{array}{c} \cdot\,\cdot \\ \vdots\mathrm{Cl}\vdots \\ \cdot\,\cdot \end{array}^{-}$$

would be potentially ionisable, a property which has been to some extent confirmed experimentally (see p. 96).[3] One of the chlorines in PCl_4^+ is held by a "mixed bond." In the second case



$$\begin{array}{c} \mathrm{Cl} \\ \cdot\,\cdot \\ \mathrm{Cl}\ \vdots\mathrm{P}\vdots\Big)\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix} \\ \cdot\,\cdot \\ \mathrm{Cl} \end{array} \quad \text{or} \quad Cl_3\equiv P\overset{+\ -}{\underline{\cdots\cdots}}Cl_2$$

also contains a "mixed bond," uniting two chlorine atoms which are not connected with one another, and being united in a different manner from the other three should be more easily split off and replaced as a whole by O, *e.g.* to give $POCl_3$. The latter compounds, as well as H_3PO_4 and all others in which phosphorus is said to be quinquevalent, can be represented by formulæ of similar type.[4] They, as well as all compounds in which non-metals from Group IV onwards show valencies higher than the typical hydrogen valency towards other non-metals, must be represented as having one or more "mixed bonds," and as being co-ordination compounds, according to one definition of such compounds.[5]

The oxy-acids of phosphorus can be represented by constitutional formulæ in which there are 3 ordinary valencies and a "mixed bond" (phosphoric) or 3 ordinary valencies with a tautomeric change to 3 ordinary valencies and a "mixed bond" (phosphorous and hypophosphorous). Thus if $POCl_3$ is represented as $Cl_3{\equiv}P\overset{+\ -}{\cdots\cdots}O$ or $Cl_3{\equiv}P\cdots\cdots{>}O$, then phosphoric acid is represented as $(HO)_3{\equiv}P\cdots\cdots{>}O$.

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[1] See this Volume, Part I., Chapter II.

[2] Sidgwick, *Trans. Chem. Soc.*, 1923, 725.

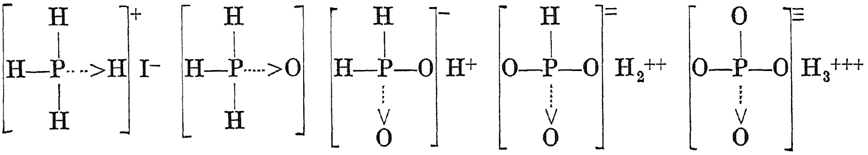
[3] Holroyd, *J. Soc. Chem. Ind.*, 1923, 42, 348.

[4] Prideaux, *J. Soc. Chem. Ind.*, 1923, 42, 672; Lowry, *Phil. Mag.*, 1923, [6], 45, 1105.

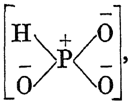
[5] Prideaux, *J. Soc. Chem. Ind.*, 1925, 44, 25.

The phosphorus probably is the central atom, possessing the co-ordination number 4, in all compounds which were considered formerly to contain quinquevalent phosphorus. The complete series between the quadrivalent hydride and oxide will appear as—

PH_4I OPH_3 H_3PO_2 H_3PO_3 H_3PO_4



The corresponding formulæ, *e.g.* for the phosphite ion, as written by Lowry, are—



, etc.

The phosphites, and possibly the hypophosphites, are also capable of existing as tervalent forms which can be fixed as the esters, such as $P(OEt)_3$, and according to the evidence of X-rays these forms predominate in the solid or liquid compounds, whereas in solution they change into the unsymmetrical tautomeric forms. The evidence is discussed under that section which is devoted to the acids in question.

CHAPTER V.

THE PHOSPHIDES.

BINARY compounds of the metals and the less electronegative non-metals with phosphorus are made by methods which recall those employed in the preparation of nitrides. The most important of these methods may be classified as follows :—

(1) Direct union of the element with phosphorus under various conditions. The metal may be heated with red phosphorus in an indifferent gas, or the vapour of phosphorus may be passed over the heated metal. By this means phosphides of the alkali metals, of the alkaline earth metals, of many ferrous and non-ferrous base metals, as well as of the "noble" metals such as gold and platinum, may be prepared.

(2) Reduction of phosphates with carbon at a high temperature. This method is chiefly applicable to the phosphates of the alkaline earth metals.

(3) The action of phosphine or phosphorus in liquid ammonia upon a solution of an alkali metal in liquid ammonia.

(4) The action of phosphine on aqueous solutions of metallic salts or passage over the dry salts.

(5) Heating the metals in the vapour of phosphorus trifluoride or trichloride.

Although the metallic phosphides are described under the respective metals in the appropriate Volumes of this Series, a selection will also be brought under review here, since they illustrate the reactivity of phosphorus and of phosphine towards elements of the different groups.

Alkali Phosphides.—Soon after the discovery of the alkali metals the direct combinations of these with phosphorus vapour were recorded.[1,2] The combination can also be effected under petroleum, the unchanged phosphorus being removed by carbon disulphide.[3]

When alkali metals are brought into contact with red phosphorus in liquid ammonia, ammonio-phosphides such as $NaP_3.3NH_3$ and $KP_5.3NH_3$ are formed, and can be deprived of their ammonia at 180° C., leaving the phosphides as brown solids. In liquid ammonia sodium and potassium are also capable of displacing one hydrogen from phosphine, giving crystalline monophosphides (phosphamides), $NaPH_2$ and KPH_2, which decompose on heating giving eventually K_3P and Na_3P.[4,5]

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[1] Davy, *Phil. Trans.*, 1808, 98, 333.

[2] Gay-Lussac and Thénard, *Rech. phys. Chim.*, 1811, 1, 208.

[3] Vigier, *Bull. Soc. chim.*, 1861, [1], 3, 7.

[4] Hugot, *Compt. rend.*, 1895, 121, 206; 1898, 126, 1719.

[5] Joannis, *Compt. rend.*, 1894, 119, 557.

Rubidium and cæsium phosphides have been made by similar methods and by distilling phosphorus in a vacuum with the alkali metal. The formulæ are given as Rb_2P_5 and Cs_2P_5; K_2P_5 is also known.[1]

Alkaline Earth Phosphides.—An impure calcium phosphide, made by exposing lime at a red heat to the vapour of phosphorus, was used in the preparation of phosphine.[2] Calcium phosphide probably is also formed during the manufacture of phosphorus by the electric furnace method (*q.v.*). It has been prepared by heating calcium phosphate and lamp black in the electric arc furnace, and appeared as a crystalline reddish-black substance.[3] Calcium phosphide prepared in this manner is only acted upon slowly by water at the ordinary temperature, but readily by aqueous solutions of strong acids. Concentrated nitric and sulphuric acids, and oxygen and chlorine, do not attack it at ordinary temperatures, but on heating it is oxidised, *e.g.* by chlorine above 100° C. and by oxygen above 300° C.

Strontium and barium phosphides have been prepared by similar methods.[4]

Magnesium phosphide was first obtained from the metal and organic substances containing phosphorus,[5] but is best prepared by heating the metal in phosphorus vapour or with red phosphorus in an atmosphere of hydrogen.[6, 7]

Phosphides of the alkali and alkaline earth metals are decomposed by water or dilute acids, giving the hydroxides or salts of the metals respectively, together with phosphine and other "hydro-phosphors." They are only slightly affected by oxidising agents such as concentrated nitric acid. They burn when heated slightly below a red heat in oxygen. They are also attacked by the halogens when heated.

Copper, Silver and Gold Phosphides.—The copper phosphides are crystalline compounds of metallic appearance and properties which are usually prepared by direct union of the elements.[8] Phosphorus begins to combine with copper at about 400° C., and at 700° C. the copper was found to take up 20 per cent.,[9] some of which was expelled at higher temperatures. Slightly above the melting-point of the phosphide 14 per cent. was retained, which corresponds to tri-cuprous phosphide, Cu_3P.[9] The velocity of the combination increases between 600° and 700° C.[10] At ordinary pressures 15 per cent. of phosphorus is the limit of the amount which will remain dissolved in the fused mixture, and some of this is present as red phosphorus.[11]

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[1] Bossuet and Hackspill, *Compt. rend.*, 1913, 157, 721; 1912, 154, 209.

[2] Dumas, Thénard, *loc. cit.*, under "Phosphine"; Rose, *Annalen*, 1828, 12, 543.

[3] Renault, *Compt. rend.*, 1899, 128, 883; Moissan, *ibid.*, 128, 787.

[4] Jaboin, *Compt. rend.*, 1899, 129, 765.

[5] Bunsen, *Annalen*, 1866, 138, 292; Schönn, *Zeitsch. anal. Chem.*, 1869, 8, 53.

[6] Blunt, *Trans. Chem. Soc.*, 1865, 18, 106; Parkinson, *ibid.*, 1867, 20, 309.

[7] Gautier, *Compt. rend.*, 1899, 128, 1167.

[8] Pelletier, *Ann. Chim. Phys.*, 1789, [1], 1, 93; Granger, "*Contribution à l'étude des phosphures métalliques*," Paris, 1898; Lupke, *Zeitsch. phys. Chem. Unterricht*, 1890, 3, 282.

[9] Heyn and Bauer, *Zeitsch. anorg. Chem.*, 1907, 52, 129.

[10] Edwards and Murphy, *J. Inst. Metals*, 1922, 22, 183.

[11] Huntingdon and Desch, *Trans. Far. Soc.*, 1908, 4, 51; Tucker, *J. Soc. Chem. Ind.*, 1906, 25, 622.

Cu_3P is a crystalline steel-grey or silvery-white substance which is harder than wrought iron. The melting-point is about 1018° C. and is lowered by additions of copper, as that of pure copper is by small additions of phosphorus; the Cu-Cu_3P freezing-point curves meet at a eutectic which corresponds to 8·2 per cent. of phosphorus with a freezing-point of 707° C.[1]

The toughness and resistance to corrosion of the phosphor-bronzes are due to the presence of solid solutions of the phosphides in copper.

Cu_3P was also prepared by the action of phosphine on ammoniacal cuprous oxide and on the metal at about 200° C.[2] and on cuprous chloride.[3] Cu_5P_2 was made by the action of PF_3 or PCl_3 on copper at a red heat,[4] also by the action of phosphine on cupric hydroxide or carbonate,[2] and red phosphorus on cupric nitrate.[5] When heated to a red heat it gave Cu_3P and Cu. Cu_3P_2 is said to be formed by the action of phosphine on cupric chloride. When yellow phosphorus was boiled with cupric sulphate and the precipitate washed and treated with acid dichromate the residue had this composition.[6] The higher phosphides, of which CuP and CuP_2 have been reported, are powders of uncertain composition, easily oxidised by nitric acid or by heating in oxygen.[4, 7, 8, 9]

Other phosphides which have been prepared by direct combination, or by reaction in solution, are—Cu_5P_2,[4] Cu_2P,[4] Cu_3P_2,[6, 10] CuP,[4, 10, 11, 12] CuP_2.[4]

Silver phosphides, AgP, Ag_2P_3 and AgP_2, were said to be produced by heating the elements together, or by passing phosphorus vapour over heated silver.[4, 13, 11] Molten silver absorbs phosphorus freely, but rejects most if not nearly all on solidification.[14, 15] Silver phosphides have also been prepared by other reactions, and it is noteworthy that the action of phosphine on silver nitrate gives a compound, $Ag_3P.3AgNO_3$,[16, 17] analogous to that which is first formed in the well-known test for arsine.[16]

Gold, like silver, when in the molten state dissolves phosphorus and rejects it on solidification.[18] A phosphide AuP has been prepared by passing a mixture of dry phosphine and ether vapour into an ether solution of gold chloride.[19] The phosphorus is only loosely combined and is given off when the compound is warmed. Such phosphides behave like free phosphorus; they burn in the air, are oxidised by nitric acid, etc., and hydrolysed by water and alkalies.

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[1] Heyn and Bauer, *loc. cit.*; Hiorns, *J. Soc. Chem. Ind.*, 1906, 25, 622.

[2] Rubenovitch, *Compt. rend.*, 1898, 127, 271.

[3] Kulisch, *Annalen*, 1885, 231, 242.

[4] Granger, *Compt. rend.*, 1897, 124, 896.

[5] Senderens, *Compt. rend.*, 1887, 104, 177.

[6] Böttger, *Met. Rev.*, 1878, 2, 456.

[7] Abel, *Trans. Chem. Soc.*, 1865, 18, 249.

[8] Katz, *Arch. Pharm.*, 1904, 242, 129.

[9] Christomanos, *Zeitsch. anorg. Chem.*, 1904, 41, 309.

[10] Rose, *Annalen*, 1832, 24, 321.

[11] Emmerling, *Ber.*, 1879, 12, 152.

[12] Huntingdon and Desch, *Trans. Far. Soc.*, 1908, 4, 51; Tucker, *J. Soc. Chem. Ind.*, 1906, 25, 622.

[13] Schrötter, *Sitzungsber. K. Akad. Wiss. Wien*, 1849, 3, 301.

[14] Pelletier, *Ann. Chim. Phys.*, 1792, [1], 13, 109.

[15] Percy, "*Silver and Gold*," London, 1880, 1, 137.

[16] Poleck and Thummel, *Ber.*, 1883, 16, 2435.

[17] Vitali, *l'Orosi*, 1892, 15, 397; *ibid.*, 1893, 16, 10.

[18] Hautefeuille and Perrey, *Compt. rend.*, 1884, 98, 1378.

[19] Cavazzi, *Gazzetta*, 1884, 15, 40.

Zinc Group.—Zinc phosphides have been made chiefly by reactions (1) and (2) (p. 60). Molten zinc unites readily with phosphorus.[1] A compound Zn_3P_2 was prepared by the action of phosphorus vapour on zinc dust;[2] the zinc oxide present was reduced and also gave phosphide.[3] The phosphide was a grey, well-crystallised substance which did not mix with molten zinc. It was sublimable in hydrogen over 1000° C. and when heated in the air oxidised to zinc phosphate.[4] It was not attacked by water, but acids gave phosphine and zinc salts.[5] The hydrophosphide, obtained by the action of phosphine on zinc ethide in ether cooled with ice and salt, is much less stable. It is a white powder which is at once decomposed by cold water giving phosphine and zinc hydroxide.[6]

Cadmium phosphides have been obtained by direct union,[7] as well as by the action of phosphine on ammoniacal cadmium sulphate.[8]

Mercury forms several phosphides, *i.e.* Hg_3P, Hg_3P_2, Hg_3P_4, which have been described as resulting from the action of phosphine in aqueous solution on mercurous or mercuric salts.[9, 10] These products were easily oxidised by air, halogens and aqua regia.

Boron is hardly affected by phosphorus even at high temperatures,[11] but there are indications of a reaction when BPO_4 is heated with sodium.[12] A phosphoiodide BPI_2 or BPI is made by heating BI_3 with phosphorus, or by bringing the same substances together in CS_2 solution. When the phosphoiodide was heated to 500° C. in hydrogen, BP was left as a maroon-coloured powder, which was not affected by water or mineral acids up to 400° C., but was hydrolysed by boiling alkalies or by superheated steam, giving borates or boric acid respectively and phosphine.[11] It was violently oxidised by nitric acid and burned in oxygen. When heated at 200° C. in a current of ammonia the phosphorus was displaced by nitrogen and the very stable boron nitride, BN, was formed.

Aluminium Phosphide was made by a reaction between red phosphorus and aluminium powder.[13, 14] It formed yellow crystals. These materials when heated in an electric furnace yielded Al_3P and AlP, which were crystalline substances of a metallic appearance.[15, 16] Al_3P_7 was obtained when phosphorus and aluminium were heated to a white heat in a current of hydrogen.

Titanium Group.—The phosphides of the elements of Group IV A have in most cases been prepared, although their compositions have not been established with certainty. A method which seems to succeed in cases where others fail is the double decomposition of phosphine with the chlorides (Wohler's reaction), *i.e.* with those of silicon, titanium and zirconium. This method was not successful, however, with $ThCl_4$.[1]

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[1] Pelletier, *loc. cit.*; Lewis, *Chem. News*, 1902, 87, 211.
[2] Schrötter, *Sitzungsber. K. Akad. Wiss. Wien*, 1849, 3, 301.
[3] Renault, *Compt. rend.*, 1873, 76, 283.
[4] Jolibois, *Compt. rend.*, 1908, 147, 801.
[5] Lupke, *loc. cit.*
[6] Sabatier, *Compt. rend.*, 1896, 123, 256.
[7] Emmerling, *Ber.*, 1879, 12, 152.
[8] Kulisch, *Annalen*, 1885, 231, 347; Brukl, *Zeitsch. anorg. Chem.*, 1922, 125, 252.
[9] Brukl, *Zeitsch. anorg. Chem.*, 1922, 125, 252.
[10] Christomanos, *Zeitsch. anorg. Chem.*, 1905, 45, 140.
[11] Moissan, *Ann. Chim. Phys.*, 1895, [7], 6, 296; Besson, *Compt. rend.*, 1890, 110, 80, 516; *ibid.*, 1891, 113, 78.
[12] Vogel, *Repert. Pharm.*, 1870, 18, 611.
[13] Fonzes-Diacon, *Compt. rend.*, 1900, 130, 1315.
[14] Matignon, *Compt. rend.*, 1900, 130, 1393.
[15] Rossel and Franck, *Ber.*, 1894, 27, 53.
[16] Franck, *Chem. Zeit.*, 1898, 22, 288.

The phosphides of titanium and zirconium to which were assigned the formulæ TiP and ZrP_2 are described as yellow or grey crystalline substances, which conduct electricity. They burned when heated in air, but were not affected by aqueous acids or aqueous oxidising agents. Thorium phosphide has been made by reducing $ThCl_4$ with phosphorus vapour.

Tin Phosphides.—Several well-defined phosphides of tin have been made by the dry methods. The early work [2] was of a qualitative nature. Phosphides of tin may be made by heating metaphosphoric acid or a phosphate and silica with carbon and tin or stannic oxide.[3]

When phosphorus and tin are melted together in a sealed tube, two liquid layers are formed, and the maximum amount of phosphorus taken up by the tin is 8 per cent.,[4] while by heating tin and phosphorus in a sealed tube at 620° C. for 10 hours grey crystals were obtained which contained 40 per cent. of phosphorus and which after purification by hydrochloric acid, alkali and nitric acid had the composition SnP_3.[5] The density was 4·1 at 0° C. Alloys of tin with about 13 per cent. of phosphorus contained Sn_4P_3,[5, 6] which had a density of 5·18 and was attacked by aqueous acids.

Commercial phosphor-tin may contain up to 10 per cent. of phosphorus as phosphides, the crystals of which are revealed by etching with dilute nitric acid. Phosphor-tin is much used for making phosphor-bronzes.[7]

The action of phosphine on tin salts also gives phosphide.[8]

Lead Phosphides.—Phosphorus is only slightly soluble in molten lead (about 1·5 per cent.).[9] Most of that which is dissolved is thrown out as violet phosphorus (*q.v.*) when the lead solidifies, but some crystals of a phosphide are also formed.[10] Precipitates are obtained by passing phosphine over lead acetate [11] or into alkaline or ammoniacal alcoholic lead acetate solutions, consisting of unstable phosphides,[12, 13] such as Pb_3P_2, which is decomposed by acids with evolution of phosphine.

Arsenic Phosphides, brown substances of indefinite character, were obtained early in the nineteenth century by various methods such as (1) by heating the elements together,[1] (2) allowing phosphorus to stand in solutions of arsenious acid,[2] (3) by the action of phosphine on arsenic halides.[3] The properties of these substances resemble in general those which would be possessed by mixtures—they burn in air giving the mixed oxides, decompose on heating with vaporisation of phosphorus, are oxidised by nitric acid, etc.

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[1] Gewecke, *Annalen*, 1908, 361, 79.
[2] Pelletier, Schrötter, Emmerling, *loc. cit.*, and others.
[3] Natanson and Vortmann, *Bull. Soc. chim.*, 1877, 10, 1459; Mellmann, *German Patent*, 1887, 45175; Seyboth, *ibid.*, 1899, 106966.
[4] Vivian, *J. Inst. Metals*, 1920, 23, 325.
[5] Jolibois, *Compt. rend.*, 1909, 148, 636.
[6] Stead, *J. Soc. Chem. Ind.*, 1897, 16, 206.
[7] Nursey, *Chem. Zeit.*, 1885, 9, 641.
[8] v. Grotthus, *Ann. Chim. Phys.*, 1807, [1], 64, 19.
[9] Pelletier, *loc. cit.* See also Hautefeuille and Perrey, *Compt. rend.*, 1884, 98, 1378.
[10] Stock and Gomolka, *Ber.*, 1909, 42, 4510.
[11] Rose, *Annalen*, 1832, 24, 326.
[12] Landgrebe, *Schweigger's J.*, 1830, 60, 184.
[13] Blondlot, *Compt. rend.*, 1874, 78, 1130.

Antimony in the liquid state dissolves phosphorus giving a brittle mass of metallic appearance. A red amorphous powder has also been made by the action of phosphorus on antimony tribromide dissolved in carbon disulphide.[4]

Bismuth also gives a brittle substance when melted with phosphorus. When phosphine is passed into a solution of bismuth trichloride or trinitrate a black powder containing phosphorus is precipitated.[5]

Chromium Phosphides have been prepared from the elements or by the action of phosphorus vapour on potassium dichromate, or from carbon and chromium phosphate.[6] These compounds have the appearance of grey powders, which are hardly attacked by dilute acids but are decomposed by alkalies.

Molybdenum and **Tungsten Phosphides** have been prepared by heating the trioxides of these elements with phosphoric acid to about 1400° C. in a carbon crucible.[7] They appeared as steel-grey crystals having densities of 5 to 6, far below the densities of the metals. Molybdenum phosphide could be oxidised by heating in the air or with chlorine. The tungsten compound was less reactive and could be burnt only in oxygen or with potassium chlorate. It was not attacked by acids. Wohler assigned the formulæ MoP and W_4P_2 to these substances.

A phosphide WP has been prepared by heating the diphosphide with copper phosphide in a graphite crucible. This had a similar appearance to Wohler's phosphide, W_4P_2, but a density of 8·5.[8] It was more easily oxidised, being attacked by chlorine and hot nitric oxide, and by nitro-hydrofluoric acid. A higher phosphide, WP_2, was also prepared by the action of phosphine on WCl_6 at a red heat. This compound burned in the air, and was in most respects more reactive than WP.[8] Nitrogen was found to displace the phosphorus at a high temperature, giving the very stable nitride.

The phosphides of manganese and of the metals of the iron group are numerous and important.

Manganese Phosphides.—Compounds containing manganese and phosphorus were prepared at the end of the eighteenth and beginning of the nineteenth century using the methods described by Pelletier, Percy, Rose, Schrötter and Wohler (*loc. cit.*). The freezing-point-composition diagram of the two elements[9] shows a eutectic at 964° C. (first additions of phosphorus), a maximum freezing-point at 1390° C.

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[1] Landgrebe, *Schweigger's J.*, 1830, 60, 184.

[2] Blondlot, *Compt. rend.*, 1874, 78, 1130.

[3] Besson, *Compt. rend.*, 1890, 110, 1260; Janowsky, *Ber.*, 1875, 8, 1636.

[4] Ramsay and McIvor, *Ber.*, 1873, 6, 1362.

[5] Cavazzi and Tivoli, *Gazzetta*, 1891, 21, 306; Cavazzi, *Gazzetta*, 1884, 14, 219.

[6] Rose, Granger, *Ann. Chim. Phys.*, 1898, [7], 14, 38.

[7] Wohler, *Annalen*, 1851, 79, 244; *ibid.*, 1859, 109, 374.

[8] Defacqz, *Compt. rend.*, 1900, 130, 915; *ibid.*, 1901, 132, 32.

[9] Schemtschuschny and Efremoff, *Zeitsch. anorg. Chem.*, 1908, 57, 247.

corresponding to Mn_3P_2,[1] another eutectic at 1095° C., and another maximum at 1990° C. corresponding to MnP.[2, 3] Alloys containing between 10 and 20 per cent. of phosphorus are magnetic. The monophosphide MnP was a black powder which was fairly easily oxidised by heating in the air.[3]

Iron Phosphides.—Cast-iron which has been made from phosphatic ores contains phosphides which seriously affect the properties of the metal. Various compounds rich in phosphorus have been prepared by heating iron in phosphorus vapour, or iron with phosphoric acid, bone-ash, sand and carbon (Pelletier, Wöhler, *loc. cit.*, Berzelius; also Hatchett[4]). The freezing-point diagram of the system iron-phosphorus shows several maxima and minima. The melting-point of iron was lowered from 1510° C. to about 1400° C. by the addition of 1·7 per cent. of phosphorus, but this was not an end-point of crystallisation.[5, 6] The first eutectic was found at 1003° C. with 10·2 per cent. of phosphorus, the solid phases being Fe and Fe_3P. The maximum freezing-point corresponding to Fe_3P was about 1100° C.[6, 10] There was a halt-point of crystallisation, or another eutectic, between this compound and Fe_2P, which melted at 1350° C.[7] Solid solutions of these compounds, which may be recognised microscopically,[8] increase the hardness of pure iron from 3·5 to 5·0 or 5·5, but above about 1 per cent. of phosphorus render it brittle. Other phosphides which have been reported are FeP,[9] Fe_3P_4[9] and Fe_2P_3.[10] The lower phosphides FeP and Fe_2P retain their phosphorus up to a red heat. The former has also been prepared at a red heat by the action of phosphine, thus :—

$$2FeS + 2PH_3 = 2FeP + 2H_2S + H_2$$ [11, 12]

$$FeCl_3 + PH_3 = FeP + 3HCl$$ [13]

Most of the phosphides are insoluble or only slowly soluble in single acids, but are attacked by aqua regia and chlorine. Fe_3P dissolves in hydrochloric acid, thus :—

$$2Fe_3P + 12HCl + 8H_2O = 6FeCl_2 + 2H_3PO_4 + 11H_2$$

When iron containing phosphides is dissolved in acids one of the products is phosphine, which is formed in greater proportion (*i.e.* more of the phosphorus is present as phosphine) as the amount of phosphorus diminishes, *i.e.* between 0·1 and 0·03 per cent.[14]

Cobalt Phosphides.—The phosphides of this metal are produced by similar methods. Co_2P [1, 2] has a maximum freezing-point of 1386° C., and the eutectic between this and the freezing-point of the pure metal is at 1022° C. and corresponds to 16·6 per cent. of phosphorus.[2]

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[1] Wedekind and Veit, *Ber.*, 1907, 40, 1259; Granger, *Compt. rend.*, 1907, 144, 190.

[2] Schemtschuschny and Efremoff, *Zeitsch. anorg. Chem.*, 1908, 57, 247.

[3] Hilpert and Dieckmann, *Ber.*, 1911, 44, 2831; *ibid.*, 1914, 47, 780.

[4] Hatchett, *Phil. Trans.*, 1804, 94, 315.

[5] Stead, *J. Soc. Chem. Ind.*, 1914, 33, 173; *ibid.*, 1903, 22, 340.

[6] Sakalatwalla, *J. Iron and Steel Institute*, 1908, 77, ii, 92.

[7] Konstantinoff, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1220.

[8] Arnold, *J. Iron and Steel Institute*, 1894, 45, i, 107.

[9] Freese, *Zeit. Chem.*, 1868, [2], 4, 110; Dennis and Cushman, *J. Amer. Chem. Soc.*, 1894, 16, 477; *Annalen*, 1867, 132, 225.

[10] Le Chatelier and Wologdine, *Compt. rend.*, 1909, 149, 709.

[11] Freese, *loc. cit.*; Schrötter, *Sitzungsber. K. Akad. Wiss. Wien*, 1849, 3, 301.

[12] Hvoslef, *Annalen*, 1856, 100, 99.

[13] Dennis and Cushman, *loc. cit.*

[14] Stead, *J. Soc. Chem. Ind.*, 1897, 16, 206.

The combination of phosphorus with **nickel** was studied by Pelletier, Davy and Maronneau (*loc. cit.*), also by Lampadius [3] and Berthier.[4] The methods included heating reduced nickel in the vapour of PCl_3, heating copper phosphide and nickel in an electric arc furnace, the precipitation of a solution of the sulphate by nascent PH_3 derived from phosphorus and alkali.[5] The thermal diagram of the nickel-nickel phosphide system showed a first eutectic on the nickel side at about 886° C. and 11 per cent. phosphorus.[6] The first compound Ni_3P freezes at about 965° C., the second, Ni_5P_2, at about 1185° C.[6] The compound Ni_2P crystallised from the melt in grey needles at about 1112° C.; it is insoluble in single acids, but is attacked by chlorine or fused alkali. This compound was also made by heating copper phosphide and nickel in an electric arc furnace [7] and by several of the methods mentioned above.[8] Ni_3P_2 and Ni_2P_3 have also been reported.

Some of the metals of the platinum group, including **platinum** itself, form phosphides. These alloys were investigated in a qualitative manner by Pelletier,[9] Granger [10] and others. The compound Pt_5P_3, formed by heating finely divided platinum with phosphorus at a white heat,[11] was a white substance of metallic appearance, which lost phosphorus when heated, giving Pt_2P, and platinum when treated with aqua regia, leaving PtP. These compounds were insoluble in single acids and either slightly soluble or insoluble in aqua regia.[11] The black precipitate produced by the action of PH_3 on $PtCl_4$ may be a hydrophosphide $Pt(H_2P_2)$.[12]

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[1] Maronneau, *Compt. rend.*, 1900, 130, 656.

[2] Schepeleff and Schemtschuschny, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 862.

[3] Lampadius, *Schweigger's J.*, 1814, 10, 114.

[4] Berthier, *Ann. Chim. Phys.*, 1824, [2], 25, 94.

[5] Schenck, *Trans. Chem. Soc.*, 1873, 26, 826; 1874, 27, 214.

[6] Konstantinoff, *Zeitsch. anorg. Chem.*, 1908, 60, 410.

[7] Maronneau, *Compt. rend.*, 1900, 130, 657.

[8] Schenck, *loc. cit.* See also Struve, *J. prakt. Chem.*, 1860, [1], 79, 321; Kulisch, *Annalen*, 1885, 231, 357.

[9] *Loc. cit.*

[10] *Loc. cit.*

[11] Clarke and Joslin, *Chem. News*, 1883, 48, 285.

[12] Kulisch, *Annalen*, 1885, 231, 355; Cavazzi, *Gazzetta*, 1883, 13, 324.

CHAPTER VI.

PHOSPHORUS AND HYDROGEN.

Phosphine.

Comparison with Ammonia and Hydrogen Sulphide.—The electronegative character of an element is shown by—

(*a*) Electrolytic dissociation of hydrogen ion in its hydrogen compounds.

(*b*) Displacement of hydrogen from hydrogen compounds by alkali and other metals.

(*c*) Stability of hydrides towards heat.

With respect to condition (*a*), phosphorus has none of the negative character possessed by its neighbour sulphur in the sixth group. With respect to (*b*), the phosphides and the nitrides may well be compared, and the modes of formation and stability of these compounds show that phosphorus is less electronegative than its congener nitrogen. With respect to (*c*), the dissociation of phosphine is more rapid and more complete than that of ammonia. There is apparently no reversible equilibrium between phosphorus and hydrogen as there is between nitrogen and hydrogen. Both hydrogen sulphide and ammonia are formed to a limited extent by direct combination at moderate temperatures and pressures, whereas phosphine is not formed in this way. [*Note.*—The production of phosphine has been observed when white phosphorus is heated in a sealed tube with hydrogen.[1] (See also p. 27.)]

Historical.—While investigating the action of alkalies on phosphorus Gengembre [2] in 1783 prepared a spontaneously inflammable gas. This reaction was expected to produce a " liver of phosphorus " or alkali polyphosphide similar to " liver of sulphur " or alkali polysulphide, which is prepared from sulphur under analogous conditions. Several other chemists about this time prepared phosphine by similar methods, or by heating phosphorous acid.[3] The composition of the gas, as an analogue of ammonia, was demonstrated by Davy,[4] and the difference in composition between the gaseous hydride and the liquid hydride (*q.v.*) to which the spontaneous inflammability is due was established by Dumas.[5] It was demonstrated by Graham [6] that the spontaneous inflammability could be removed by means of carbon dioxide, hydrogen chloride, nitric oxide, arsenious oxide, concentrated sulphuric, phosphoric and arsenic acids.

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[1] Ipatieff and Nikolaieff, *Ber.*, 1926, 59, B, 595.

[2] Gengembre, *Mém. Acad.*, 1785, 10, 651. See also Kirwan, *Phil. Trans.*, 1786, 76, 118; Raymond, *Phil. Mag.*, 1800, 8, 154; *Crell's Annalen*, 1783, 1, 450.

[3] Pelletier, *Ann. Chim. Phys.*, 1792, [1], 13, 101.

[4] Davy, *Phil. Trans.*, 1812, 102, 405.

[5] Dumas, *Ann. Chim. Phys.*, 1826, [2], 31, 113.

[6] Graham, *Phil. Mag.*, 1834, [3], 5, 401; *Trans. Roy. Soc. Edin.*, 1835, 13, 88.

Occurrence.—The pale glow which hovers over marshes, and which, under the name of " will o' the wisps," " Jack o' lanterns," etc., has been the subject of many legends, has been attributed to traces of phosphine with other gases produced by the decomposition of organic matter. This is rendered probable by the observation that phosphine is produced by the putrefaction of proteins.[1]

Preparation.—(*a*) The original method is still in general use. The alkali employed may be hydroxide of sodium, potassium, calcium[2] or barium. The reaction is usually represented by the equation

$$4P + 3KOH + 3H_2O = PH_3 + 3KH_2PO_2$$

This reaction really amounts to a hydrolysis of phosphorus, which can be effected also by water at high temperatures. The equations reduced to their simplest forms and dissected are :—

$$\begin{gathered} 3P + 3H_2O = 3OPH + 3H \\ P + 3H = PH_3 \\ 3OPH + 3H_2O = 3H_3PO_2 \end{gathered}$$

The phosphine so obtained usually inflames spontaneously on coming into contact with the air ; each bubble as it escapes forms a beautiful vortex ring of smoke. It was early shown that the spontaneous inflammability is due to the presence of small quantities of a hydride, liquid at ordinary temperatures,[3, 4] which has the empirical composition $(PH_2)_x$[3] and the molecular composition P_2H_4. The phosphorus must therefore react also according to the equation

$$6P + 4KOH + 4H_2O = 4KH_2PO_2 + P_2H_4$$

The presence of hydrogen in proportions up to 50[5] or 60[3] per cent. has been accounted for by the oxidation-hydrolysis of the hypophosphite :—[6]

$$KH_2PO_2 + 2H_2O = KH_2PO_4 + 2H_2$$

Details of Preparation.—A tubulated retort is filled with alkali and the phosphorus is added in small pieces. The tubulure is then closed by a delivery tube, which is connected with a Kipp's apparatus or other source of hydrogen (the air may also be displaced by adding a little ether). The neck of the retort is connected with a tube which dips under water. The air is displaced by hydrogen and the retort then gently warmed so as to melt the phosphorus and give a steady evolution of gas. When sufficient has been collected the residual gas is expelled by a current of hydrogen and the phosphorus allowed to solidify before the retort is opened.

If phosphine which is not spontaneously inflammable is required, the gas is washed by passing it through a Woulfe bottle containing concentrated hydrochloric acid or alcoholic potash.

The gas prepared in this manner contains hydrogen (up to 90 per cent.), but can be prepared pure by allowing water, dilute alkali or aqueous ether to drop on to phosphonium iodide.[1] The product may be mixed with carbon dioxide, dried by phosphorus pentoxide and condensed in liquid air. The condensate is distilled, rejecting the first and last fractions, the middle being pure dry phosphine.[2]

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[1] Gautier and Étard, *Compt. rend.*, 1882, 94, 1357.

[2] Raymond, *loc. cit.*

[3] Dumas, *loc. cit.*

[4] Thénard, *Ann. Chim. Phys.*, 1845, [3], 14, 5.

[5] Hofmann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1871, 84; *Ber.*, 1871, 4, 200.

[6] Dulong, *Ann. Chim. Phys.*, 1816, [2], 2, 141.

(*b*) Heating hypophosphorous or phosphorous acid or their salts (*q.v.*)[3] gives phosphine :—

$$2H_3PO_2 = PH_3 + H_3PO_4$$

(*c*) The action of water or dilute acids on alkali or alkaline earth phosphides[4] affords a method of preparation. The reactions shown by the following equations will be succeeded by others which produce hypophosphites, etc. :—

$$Na_3P + 3H_2O = PH_3 + 3NaOH \text{ [5]}$$
$$Na_3H_3P_2 + 3H_2O = 3NaOH + 2PH_3 \text{ [6]}$$

Similarly calcium phosphide is readily attacked by water or dilute acids giving phosphine.[3, 7, 8] A fairly pure sample of the gas may be made from calcium phosphide which has been produced in the electric furnace.[9] The reaction is more complex than that represented by the equation

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$$

Magnesium phosphide,[10] aluminium phosphide[11] and phosphides of several other metals also yield phosphine when treated with acids.

(*d*) A pure phosphine may be made by the action of alkalies or even water upon phosphonium iodide[12] or bromide.[13] Crystalline phosphonium iodide, prepared as described on p. 78, is mixed with broken glass in a flask fitted with a tap-funnel and delivery tube. A solution of one part of caustic potash in two parts of water is added slowly through the tap-funnel. The gas is not spontaneously inflammable if the last portions are rejected.

$$PH_4I + KOH = KI + PH_3 + H_2O$$

The gas should be washed with concentrated hydrochloric acid (to remove any P_2H_4), alkali (to remove HCl and HI), and then dried with phosphorus pentoxide.

(*e*) Among many reactions by which phosphine can be prepared may be mentioned that which takes place between hydrochloric acid and diamidophosphorous acid, $(NH_2)_2.POH$.[14]

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[1] Messinger and Engels, *Ber.*, 1888, 21, 326.

[2] Gazarian, *J. Chim. phys.*, 1909, 7, 337; *Compt. rend.*, 1909, 148, 1397.

[3] Dulong, Dumas, Hofmann, *loc. cit.*; Rose, *Annalen*, 1839, 46, 633.

[4] Thénard, *loc. cit.*

[5] Winter, *J. Amer. Chem. Soc.*, 1904, 26, 1484.

[6] Hugot, *Compt. rend.*, 1898, 126, 1719.

[7] Pearson, *Phil. Trans.*, 1792, 82, 289.

[8] Matignon, *Compt. rend.*, 1900, 130, 1390.

[9] Moissan, *Compt. rend.*, 1899, 128, 787.

[10] Lupke, *Zeitsch. phys. Chem. Unterricht*, 1890, 3, 280.

[11] Matignon, *loc. cit.*; Fonzes-Diacon, *Compt. rend.*, 1900, 130, 1314.

[12] Hofmann, *Ber.*, 1871, 4, 200.

[13] Sérullas, *Ann. Chim. Phys.*, 1831, [2], 48, 91. See also Messinger and Engels, *Ber.*, 1888, 21, 326.

[14] Thorpe and Tutton, *Trans. Chem. Soc.*, 1891, 59, 1019.

General Properties.—Phosphine is a colourless gas which may be condensed at low temperatures to a colourless liquid and frozen to a white solid (see p. 73). The boiling-point of the liquid is considerably below that of ammonia. The gas has a strong odour recalling that of decayed fish, and resembling rather the odour of the lower alkylamines than that of ammonia. It does not support ordinary combustion, and is poisonous [1, 2]—dilutions as large as 1 in 10,000 of air [3] cause death in a few hours. The effects, such as embrittling of the teeth and bones, are somewhat similar to those of phosphorus.[4] The solubility in water (about 26 volumes in 100 at 17° C.) is far lower than that of ammonia. The gas also is only sparingly soluble in alcohol and ether. It is easily decomposed by heat, depositing phosphorus in the red form and giving 3/2 of its volume of hydrogen in accordance with the equation

$$4PH_3 = 4P + 6H_2$$

The molecular weight was indicated by rough determinations of the density by the early workers ; these results were, however, in all cases too low on account of admixture with hydrogen (*v. supra*).

Physical Properties.—*Density.*—The density corresponds to simple molecules, PH_3, but deviations from the laws of a perfect gas are observed. The weight of a normal litre is 1·5293 to 1·5295 gram,[5] a value which shows that under these conditions it agrees closely with Avogadro's theory. At pressures of 10 atmospheres or more, however, and at temperatures from 24·6° to 54·4° C. the compressibility is much greater than is allowed by Boyle's law. The following values refer to 24·6° C. :—[6]

p (atm.) .	1·0	10	15	20	25	30
pv . .	1·0	0·97	0·98	0·80	0·75	0·70

Viscosity.—The relative value, based on that of air (viz. $2{\cdot}191 \times 10^{-4}$ C.G.S. units at 15° C.), was found to be $1{\cdot}129 \times 10^{-4}$ at 15° C. and $1{\cdot}450 \times 10^{-4}$ C.G.S. units at 100° C.[7] The relative collision area, $\pi r^2 \times 10^{15}$ (in which r is the radius of the molecules in cm.), calculated from Chapman's formula, is 0·911, while for NH_3 and AsH_3 the values are 0·640 and 0·985 respectively.

Absorption in the Infra-red.—The methods of determining this property are briefly described as follows.[8] The radiation from a Nernst filament was passed through a rock-salt lens, then through either of two similar tubes, one of which was evacuated and the other filled with the gas at a known pressure. A rocking arrangement allowed either tube to be thrown quickly into the path of the rays. The beam was focussed on the collimator slit of an infra-red spectro-

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[1] Blyth, "*Poisons, Their Effects and Detection,*" (Griffin), London.
[2] Clark and Henderson, *Chem. News*, 1879, 39, 102.
[3] Jokote, *Arch. Hygiene*, 1904, 49, 275.
[4] Brenner, *Zeit. Med. St Petersburg*, 1865, 6, 4.
[5] Gazarian, *J. Chim. phys.*, 1909, 7, 337; *Compt. rend.*, 1909, 148, 1397.
[6] Briner, *J. Chim. phys.*, 1906, 4, 476.
[7] Rankine and C. J. Smith, *Phil. Mag.*, 1921, [6], 42, 601.
[8] Robertson and Fox, *Proc. Roy. Soc.*, 1928, A, 120, 128.

meter furnished with a prism of rock salt, quartz or fluorite. On emerging from the second slit of the spectrometer the radiation was received by a bismuth-silver thermopile, the current from which was registered by a Paschen galvanometer.

Phosphine, arsine and stibine showed a number of deep bands, also fine structure and smaller bands. The intensity of the bands decreased as a rule in passing towards the visible end of the infra-red spectrum. Bands numbered I to VI formed a nearly harmonic sequence, in which the wavelengths of corresponding bands increased with increase in the atomic weight of the Fifth Group element. In the following table the wavelengths λ in microns ($\mu = 0{\cdot}001$ mm.) and the wave-numbers (per cm.) are given for corresponding bands. The percentage absorption a refers to the gas in the tube under a pressure of one atmosphere. The ratios of the wave-numbers of the corresponding bands for each pair of gases are nearly constant.

ABSORPTION SPECTRA IN THE INFRA-RED.

Gas.	Wavelengths of Bands.	λ.	ν.	a.
NH_3	6·132, 2·998, 1·967, 1·513, 1·212	6·132	1630·8	92
PH_3	8·889, 4·297, 2·929, 2·193, 1·783	8·889	1125·0	80
AsH_3	9·946, 4·713, 3·235, 2·403, 1·951	9·946	1005·4	79
		Ratio of ν PH_3/NH_3	0·689	Mean 0·685
		Ratio of ν AsH_3/PH_3	0·893	Mean 0·907

Solubility.—Phosphine dissolves in 5 to 10 times its volume of water at ordinary temperatures. The solubility, expressed as "Bunsen's absorption coefficient," * is 0·26 volume at N.T.P. in 1 volume of water at 17° C.[1]

When the liquefied gas was brought into contact with water and solidified by releasing the pressure, the resulting crystalline solid was found to be a hydrate, perhaps $PH_3.H_2O$.[2]

Phosphine is only slightly soluble in alcohol or ether. It is readily absorbed by wood charcoal, to the extent of about 500 volumes by 1 volume of the charcoal. Coconut charcoal absorbs 69 volumes of the gas at 0° C.[3]

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* *Note.*—See Volume I. of this Series, and this Volume, Part I., "Solubility of Nitrogen." Also "*A Text-book of Physical Chemistry,*" Vol. I., J. Newton Friend (Griffin), 1932.

[1] Stock, Böttger and Lenger, *Ber.*, 1909, 42, 2855.

[2] Cailletet and Bordet, *Compt. rend.*, 1882, 95, 58.

[3] Hunter, *Phil. Mag.*, 1865, [4], 29, 116.

The gas may be condensed under pressure at a temperature which is attainable by the use of solid carbon dioxide.[1] It can be liquefied at the ordinary temperature under a pressure of 30 atmospheres.[2]

The principal thermal constants are as follows :—

Boiling-point, −85° C.,[3] −87·4° C.[4]
Melting-point, −132·5° C.[3]
Critical temperature, 54° C.,[2] 52·8° C.,[5] 51·3° C.[6, 7]
Critical pressure, 70·5,[2] 64,[5] 64·5 atm.[6, 7]
Critical volume, 4·6 c.c./gram.[2]

Liquid Phosphine.—The *vapour pressures* and *isobaric densities* of liquid (D_L) and vapour (D_V) for liquid phosphine are as follows :—

t° C. .	−105·9	−101·2	−97·7	−93·1	−86·6	−86·2[8]	..	..
p (mm.)	237	319	393	498	719	760[8]	..	..
D_L .	0·760	0·756	0·753	0·746	0·745	..[8]	..	..
D_V .	$0{\cdot}0_379$	$0{\cdot}0_2101$	$0{\cdot}0_2122$	$0{\cdot}0_2151$	..	..[8]	..	..
t° C. .	+49·4	44·4	39·4	29·4	24·6	18·4	8·4	2·4[2]
p (atm.)	62·4	56·1	50·8	41·3	37·1	32·6	27·2	23·4[2]
D_L .	0·417	0·469	0·502	0·536	0·545	0·559	0·595	0·618[2]

From the first set of results the density of the liquid at its boiling-point is 0·744, and increases with falling temperature according to the equation[8]

$$D_T = 0{\cdot}744[1 + 0{\cdot}0008(T_b - T)]$$

The *vapour pressure* has also been expressed by the formula[4]

$$\log p = -845{\cdot}57/T + 1{\cdot}75 \log T - 0{\cdot}0_261931T + 4{\cdot}61480$$

The *surface tension* of liquid phosphine indicates a certain degree of association, since the coefficient of decrease of molar surface energy with increase of temperature is about 1·7 instead of 2·0 :—

t° C. . .	−105·9	−101·2	− 97·6	− 93·1
σ . .	22·783	22·095	21·533	20·798[8]
$\sigma(V_M)^{2/3}$.	287·2	279·6	273·4	265·4

The *refractivity* of the liquid is 1·323 for white light at 11·0° C. and 1·317 for the D line at 17·5° C.[9]

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[1] Faraday, *Phil. Trans.*, 1845, 135, 155.

[2] Skinner, *Proc. Roy. Soc.*, 1887, 42, 283.

[3] Olszewsky, *Monatsh.*, 1886, 7, 372; *Anz. Akad. Krak.*, 1908, 375, 483; *Phil. Mag.*, 1895, [5], 39, 188.

[4] Henning and Stock, *Zeit. Phys.*, 1921, 4, 226.

[5] Leduc and Sacerdote, *Compt. rend.*, 1897, 125, 397.

[6] Guye, *Bull. Soc. chim.*, 1909, [4], 5, 339.

[7] Briner, *J. Chim. phys.*, 1906, 4, 476.

[8] McIntosh and Steele, *Proc. Roy. Soc.*, 1904, 73, 450. See also Archibald, Steele and McIntosh, *Zeitsch. physikal. Chem.*, 1906, 55, 140.

[9] Bleekrode, *Proc. Roy. Soc.*, 1884, 37, 339.

The *dielectric constant* is 2·55 at −60° C. and 2·71 at −25° C.[1]

Chemical Properties.—*Decomposition.*—Phosphine is an unstable gas which can be decomposed by heat alone, and is easily oxidised by oxygen and by oxidising agents such as the halogens.

The velocity of decomposition at constant volume and at temperatures between 300° and 500° C. was studied by van't Hoff and his co-workers.[2] Concentrations of the undecomposed phosphine at any time can be calculated from the pressure, which, of course, rises during the reaction. The way in which the velocity constant can be calculated from the pressure is as follows.

The equation is arrived at in the following way:—A fraction x of 1 original mol of PH_3 at a pressure p_0 is decomposed after a time t giving $3x/2$ mols of hydrogen and $(1+x/2)$ mols of the mixed gas, which will therefore have a pressure $p=(1+x/2)p_0$.

If the equation of a unimolecular reaction is referred to the concentration c_0 of PH_3 at the beginning and c after time t, then

$$K=\frac{1}{t}\log_e\frac{c_0}{c}=\frac{1}{t}\log_e\frac{1}{1-x}$$

or

$$\frac{1}{t_2-t_1}\log_e\frac{c_1}{c_2}=\frac{1}{t_2-t_1}\log_e\frac{1-x_1}{1-x_2}$$

Now

$$1-x=\frac{3p_0-2p}{p_0}$$

Therefore

$$K=\frac{1}{t}\log_e\frac{p_0}{3p_0-2p}$$

or

$$\frac{1}{t_2-t_1}\log_e\frac{3p_0-2p_1}{3p_0-2p_2}$$

Also, at the end of the reaction $p_\infty=\frac{3}{2}p_0$.

The final form of the equation

$$K=\frac{1}{t_2-t_1}\log_e\frac{p_\infty-p_1}{p_\infty-p_2}$$

is equivalent to

$$K=\frac{1}{t_2-t_1}\log_e\frac{c_1}{c_2}$$

The reaction appears to be unimolecular in any one vessel, but the constant K is not the same in different vessels. Hence it was supposed that the decomposition took place on the walls of the vessel. The constant rises with rise of temperature, and above 660° C. there is no constant:—[3]

t° C. .	572	645	650	656	660	683
10^3K .	0·54	3·6	4·4	5·6	12	11 to 22

The effect of surface on the reaction has been further studied by adding powdered fused silica, which caused a great increase in the velocity of decomposition.[1] The heat of activation of the PH_3 molecules calculated from the rate of increase in the velocity constant with temperature was 40,000 to 50,000 calories.[1]

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[1] Palmer and Schlundt, *J. Physical Chem.*, 1911, 15, 381.

[2] Kooij, *Zeitsch. physikal. Chem.*, 1893, 12, 156.

[3] Trautz and Bhandakar, *Zeitsch. anorg. Chem.*, 1919, 106, 95.

The effect of the electric discharge was investigated by the early workers; red phosphorus is deposited [2, 3] and other hydrophosphors are formed.[4, 5]

The effect of light has been studied, but the results are not consistent. Some decomposition may take place with the production of a reddish deposit, and the spontaneously inflammable fraction may be destroyed.[6] The amounts and intensities of the short-wave radiations as well as other conditions were not known or controlled by the earlier investigators.[7, 8]

Oxidation.—Although pure phosphine does not itself in the ordinary way inflame spontaneously with air, yet it does so when the pressure is reduced. This observation was made almost simultaneously by Davy [9] and de la Billardière.[10] In the words of Davy—" I found the phosphoretted hydrogen produced a flash of light when admitted into the best vacuum that could be made by an excellent pump of Nairn's construction."

The oxidation under reduced pressure was found to take place at a fairly uniform speed at 50° C. and pressures of 760 down to about 400 mm.[11] If mixtures of air and PH_3 were used corresponding to about 2 volumes of PH_3 to 1 volume of oxygen, the diminution of pressure per hour was uniformly 0·5 to 3·0 per cent. of the initial value. There was in only one case a slight increase in the velocity immediately before explosion occurred. Moisture retarded the reaction. Moist mixtures of phosphine and oxygen were not explosive with air at low pressures, but dry mixtures of phosphine and oxygen exploded when the oxygen pressure was reduced to 0·1 atmosphere or any lower value.[12, 13]

Slow oxidation at low pressures proceeds according to the equation

$$PH_3 + O_2 = H_2 + HPO_2$$

At higher pressures both metaphosphorous and phosphorous acids are formed, thus :—

$$4PH_3 + 5O_2 = 2HPO_2 + 2H_3PO_3 + 2H_2$$ [13]

If the gas was very thoroughly dried, as over phosphorus pentoxide, soda-lime or crystallised glycerine, it took fire spontaneously in air. The explosion which takes place after some hours of slow oxidation of phosphine with moist air has been attributed to the accumulation of hygroscopic compounds such as H_3PO_2 and H_3PO_3, which dry the remaining gases.[1]

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[1] Hinshelwood and Topley, *Trans. Chem. Soc.*, 1924, 125, 393. See also Dushman, *J. Amer. Chem. Soc.*, 1921, 43, 397; Drummond, *ibid.*, 1927, 49, 1901.

[2] Dalton, *Ann. Phil.*, 1818, 11, 7.

[3] Hofmann, *Ber.*, 1871, 4, 200.

[4] Graham, *Phil. Mag.*, 1834, [3], 5, 401.

[5] Thénard, *Compt. rend.*, 1873, 76, 1508.

[6] Amato, *Gazzetta*, 1884, 14, 58.

[7] Trautz and Bhandakar, *loc. cit.*

[8] Roy, *Proc. Roy. Soc.*, 1926, 110, A, 543.

[9] Davy, *Phil. Trans.*, 1812, 102, 405; Rose, *Annalen*, 1839, 46, 633.

[10] de la Billardière, *Ann. Chim. Phys.*, 1817, [2], 6, 304. See also Dumas, *Ann. Chim. Phys.*, 1826, [2], 31, 113.

[11] "*Studies in Chemical Dynamics,*" van't Hoff-Cohen, translated by Ewan (Williams and Norgate, 1896).

[12] van de Stadt, *Zeitsch. physikal. Chem.*, 1893, 12, 322.

[13] Kooij, *loc. cit.*

The explosion of phosphine with oxygen takes place at higher pressures when the phosphine is in considerable excess. Thus 0·5 c.c. of oxygen was mixed with 0·5 and up to 6·0 c.c. of phosphine and the expansion was determined at which the mixture would explode (at 50° C.). A total expansion of 1 volume to 5 volumes was required for the first mixture, but only 6·5 to 9·6 volumes for the second.[2]

The vigorous combustion of phosphine produces orthophosphoric acid. A combustion with the production of 85 per cent. of this acid gave +311 calories[3] at constant pressure. Values calculated for the heat of formation of gaseous phosphine are −11·6 Cals.,[4,5] −9·1 Cals.,[6] and −5·8 Cals.[7] The free energy of formation from solid phosphorus and hydrogen at 25° C. is −3·3 Cals.[8]

Halogens attack phosphine vigorously giving halides of hydrogen and usually of phosphorus as well. These reactions were early investigated by Thomson, Balard and Hofmann.[9,10,11] The action of sulphur was also investigated by Davy[12] and Dalton.[13,14,15]

Phosphine is absorbed by acid cuprous chloride giving an addition product $CuCl.PH_3$.[16] It precipitates phosphides from some metallic salts (see under "Phosphides").

Phosphine reacts with the lower halides of phosphorus giving halogen hydracids and free phosphorus or a compound containing more phosphorus.[17,18,19] With the higher halides it gives the lower halides and halogen hydracids, thus :—

$$3PCl_5 + PH_3 = 4PCl_3 + 3HCl$$ [18]

In relation to halides of boron, phosphine resembles ammonia, giving addition compounds of similar but not identical type such as $2BF_3.PH_3$ and $BCl_3.PH_3$, which are, however, more easily dissociated than the corresponding ammines.

Phosphonium Compounds.

Phosphine, like ammonia, has a much lower affinity for water than it has for the halogen hydracids, no doubt on account of the fact that water gives a very low concentration of hydrogen ion and the halogen hydracids in water high concentrations of hydrogen ion (Werner), the hydrates in both cases being less stable than the hydrohalides. The formation of hydroxides and hydrohalides consists partly in the addition of hydrogen ion to the anhydro-base. This process takes place to a much greater extent with ammonia than with phosphine. Indeed phosphine does not appear to form a hydroxide at all with water, but simply dissolves as an indifferent gas.* The case is different with the halogen hydracids; these do form phosphonium salts of varying stability, the iodide being the most stable.[1]

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[1] Rose, *Annalen*, 1832, 24, 158.
[2] van't Hoff-Cohen, "*Studies in Chemical Dynamics*."
[3] Lemoult, *Compt. rend.*, 1909, 149, 554; *ibid.*, 1907, 145, 374.
[4] Ogier, *Compt. rend.*, 1878, 87, 210.
[5] Berthelot and Petit, *Compt. rend.*, 1889, 108, 546.
[6] Forcrand, *Compt. rend.*, 1901, 133, 513.
[7] Lemoult, *Compt. rend.*, 1907, 145, 374.
[8] Drummond, *J. Amer. Chem. Soc.*, 1927, 49, 1901.
[9] Thomson, *Ann. Phil.*, 1820, 15, 227.
[10] Balard, *Ann. Chim. Phys.*, 1834, [2], 57, 225.
[11] Hofmann, *Annalen*, 1857, 103, 355; *Ber.*, 1870, 3, 660; 1871, 4, 200.
[12] Davy, *Phil. Trans.*, 1812, 102, 405; Vauquelin, *Ann. Chim. Phys.*, 1824, [2], 25, 401.
[13] Dalton, *Phil. Trans.*, 1818, 108, 316.
[14] Jones, *Trans. Chem. Soc.*, 1876, 29, 641.
[15] Cavazzi, *Gazzetta*, 1886, 16, 169.
[16] Riban, *Compt. rend.*, 1879, 88, 581.
[17] Besson, *Compt. rend.*, 1889, 109, 644; 1890, 110, 516, 1258; 1890, 111, 972.
[18] Mahn, *Zeitsch. Chem.*, 1869, [2], 5, 729.
[19] Gladstone, *Phil. Mag.*, 1849, [3], 35, 345.

Phosphonium Chloride, PH_4Cl, is formed when the component gases are mixed under a pressure of about 20 atmospheres. Under atmospheric pressures it can only exist at temperatures below about −25° C.[2] It can be melted under pressure at +28·5° C.[3] (Other determinations gave 25° C.[4] and 26° C.[5])

The change of volume on melting is very great, being about +0·73 c.c./gram at +40° C. The critical volume is 3·5 c.c./gram.[5] The critical temperature is given as 50° to 51° C.,[6] 48° C.,[5] 48·8° to 50·1° C.,[7] 49·1° C.,[8] and the critical pressure as 80 to 90 atm.,[9] 96 atm.,[5] 74·2 to 75·0 atm.[10] and 72·7 atm.[11] The heat of formation of 1 mol of gaseous PH_4Cl is +16·4 Cals.; that of the solid is +43·4 Cals., and therefore the heat of sublimation is +27·0 Cals.[12] The dissociation pressures have also been investigated.[13]

Phosphonium Bromide, PH_4Br, was made by Sérullas in 1831 from the component gases by direct union.[14] Its dissociation pressure reaches only 1 atmosphere slightly below +38° C.[13] It can also be made by passing phosphine into the most concentrated aqueous hydrobromic acid,[15] or hydrogen bromide dissolved in phosphoryl chloride,[16] or from phosphine and bromine.[14] It forms colourless cubic crystals which sublime at about +30° C.[17] The heat of formation of the solid from the gases PH_3 and HBr is +23 Cals., while that evolved when the initial materials are bromine (liquid), hydrogen and phosphorus (solid) is +44·1 Cals.[15]

Phosphonium Iodide, PH_4I, is the most stable of these compounds, being formed by direct union of the gases at ordinary temperatures and atmospheric pressure with the production of a crystalline

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* *Note.*—A crystalline hydrate is said to be formed under high pressures—see under "Solubility of Phosphine."

[1] Tammann, *Zeitsch. Elektrochem.*, 1902, 8, 158. See also Skinner, *Proc. Roy. Soc.*, 1887, 42, 283.

[2] Ogier, *Compt. rend.*, 1879, 89, 705.

[3] Scheffer, *Zeitsch. physikal. Chem.*, 1909, 71, 214.

[4] van't Hoff, *Rec. Trav. chim.*, 1885, 4, 305.

[5] Skinner, *Proc. Roy. Soc.*, 1887, 42, 283.

[6] van't Hoff, *loc. cit.*, and *Ber.*, 1885, 18, 2088.

[7] Tammann, "*Krystal. u. Schmelzen,*" Leipzig, 1903.

[8] Briner, *Compt. rend.*, 1906, 142, 1214, 1416.

[9] van't Hoff, *loc. cit.*

[10] Tammann, *loc. cit.*

[11] Briner, *loc. cit.*, and *J. Chim. phys.*, 1906, 4, 267, 476.

[12] Briner, *loc. cit.*

[13] Johnson, *J. Amer. Chem. Soc.*, 1912, 34, 877.

[14] Sérullas, *Ann. Chim. Phys.*, 1831, [2], 47, 87.

[15] Ogier, *Compt. rend.*, 1879, 89, 705.

[16] Besson, *Compt. rend.*, 1896, 122, 140, 1200.

[17] Bineau, *Ann. Chim. Phys.*, 1838, [2], 68, 430.

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compound.[1] It may also be made by a considerable number of reactions between phosphorus, iodine and water. These substances may be heated together in a retort:—

$$2P + I_2 + 4H_2O = PH_4I + H_3PO_4 + HI$$ [2]

Or the water may be allowed to drop on to phosphorus triiodide or on to a mixture of phosphorus and iodine.[3, 4] The preparation of a small quantity is most conveniently effected as follows :—

10 grams of phosphorus are placed in a retort with a wide tubulure through which is passed a tap-funnel and a delivery tube connected with a source of dry carbon dioxide. An equal weight of carbon disulphide is added, and then 17 grams of iodine. The carbon disulphide is then distilled off in a current of carbon dioxide by placing the retort in a basin of warm water. The mouth of the retort is then connected with a wide tube which fits into the mouth of a wide-mouthed bottle, which is also connected with a draught exit to draw off the uncombined hydrogen iodide. 8·5 grams of water are then placed in the tap-funnel and allowed to drop slowly on to the phosphorus and iodine. The phosphonium iodide which sublimes into the wide tube is afterwards pushed into the bottle—

$$5I + 9P + 16H_2O = 5PH_4I + 4H_3PO_4$$

Physical Properties.—The crystals appear to belong to the cubic system and were so described by the earlier investigators. They are really, however, tetragonal,[5] the ratio of the longer axis to the shorter axis being 1 : 0·729.[6] X-ray photographs showed that the dimensions of the unit cell were 6·34, 6·34, 4·62 Å,[6] and that the space-lattice was very similar to that of the form of ammonium chloride which is stable at low temperatures. The density of the solid is 2·860.[5] The dissociation pressures are tabulated on p. 80 and reach one atmosphere at about +62° C. The heat of formation of the solid from gaseous [7] phosphine and hydrogen iodide is +24·17 Cals., and the heat of decomposition by water giving gaseous phosphine and a solution of HI is +4·77 Cals.

Chemical Reactions.—Phosphonium iodide is hydrolysed by water, and is still more rapidly decomposed by alkalies, giving phosphine and an iodide. The phosphine is displaced by ammonia giving ammonium iodide,[8] and even by ethyl alcohol giving ethyl iodide, with phosphine in both cases.[9] It is hardly affected by aqueous acids, except those which are also oxidising agents.

As might be expected, phosphonium iodide acts as a reducing agent in most cases, although it is not oxidised by oxygen or air at ordinary temperatures. Chlorine water gives phosphorus and P_2H,[10] and chlorine

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[1] de la Billardière, *loc. cit.*

[2] Sérullas, *loc. cit.*; Rose, *Pogg. Annalen*, 1832, 24, 154; 1839, 46, 636.

[3] Hofmann, *Trans. Chem. Soc.*, 1871, 24, 380.

[4] v. Bayer, *Annalen*, 1870, 155, 266; Holt and Myers, *Zeitsch. anorg. Chem.*, 1913, 82, 281.

[5] Wagner, *Zeitsch. Kryst. Min.*, 1911, 50, 47.

[6] Dickinson, *J. Amer. Chem. Soc.*, 1922, 44, 1489.

[7] Ogier, *Ann. Chim. Phys.*, 1880, [5], 20, 5.

[8] Messinger and Engels, *Ber.*, 1888, 21, 326.

[9] Sérullas, *loc. cit.*

[10] Cain, *Chem. News*, 1894, 70, 80.

DISSOCIATION PRESSURES OF PHOSPHONIUM HALIDES.*

Phosphonium Chloride.

Solid, amorphous.[1]

t° C. . .	−80	−60	−45
p (mm.) .	7·8	50·4	196·0

Solid, crystalline.[1]

t° C. . .	−80	−60	−40	−20
p (mm.) .	9·6	62·0	284	1260

Solid, crystalline.[1]

t° C. . .	0·0	18·2	28·2
p (atm.) .	8·9	22·6	48·7

Liquid.

t° C. .	25·0	30·0 †	40·0	45·0	49·1 ‡	50·1 ‡
p (atm.) .	45 [1]	49 [2]	61·0 [2]	67·5 [2]	72·7 [2]	75·0 [1,3]

Phosphonium Bromide.

Solid.[4]

t° C. . .	−80	−24	0·0
p (mm.) .	1	8	56 §

Liquid.[4, 5]

t° C. . .	7·5	19·0	31·6	38·8
p (mm.) .	101	222	507	794
t° C. . .	7·6	19·8	34·3	..
p (mm.) .	118·6 [5]	266·8 [5]	602 [5]	..

* Only a selection of the values is given.

[1] Tammann, "*Kryst. u. Schmelzen,*" Leipzig, 1903.

† Triple point. ‡ Critical temperature.

[2] Briner, *J. Chim. phys.*, 1906, 4, 476, and *loc. cit.*

[3] See also Scheffer, *loc. cit.*; Johnson, *loc. cit.*, p. 77. [4] Johnson, *loc. cit.*

§ The pressures were obtained with a glass spiral manometer.

[5] Isambert, *Compt. rend.*, 1883, 96, 643.

Phosphonium Iodide.

Solid.[1,2]

t° C. .	15·0	19·2	30·0	50·0	62·6	66·0
p (mm.) .	36·0 [1]	50·0	107·8	368·1	760·0	917·5 [1,*]
t° C. .	0	11·4	24·4	45·8	56·4	..
p (mm.) .	8 [2]	24	74	286	536 [2]	..

gas gives similar products at first, while an excess gives PCl_5 even at low temperatures.[3] Chloric, bromic and iodic acids and their salts, silver nitrate and nitric acid oxidise it with inflammation.[4] Carbon disulphide at temperatures above 140° C.[5] is said to give $P(CH_3)_3HI$.

Liquid Hydrogen Phosphide.

The analysis of this compound shows that it is hydrogen hemiphosphide, $(PH_2)_x$, and the molecular weight corresponds to tetrahydrogen diphosphide, P_2H_4.

This liquid, which is the cause of the spontaneous inflammability of phosphine prepared by methods (*a*), (*b*), (*c*) (pp. 69, 70), was isolated by passing through a freezing mixture the gas resulting from the action of water upon calcium phosphide.[6, 7] The condensate was a mobile liquid having a density of about 1·01 and vaporising between 30° and 40° C. The boiling-point at 735 mm. was found to be 57° to 58° C., and on careful distillation there is no residue.[8] The vapour density (probably of the products of decomposition) is 74·73 to 77·0 and the empirical formula is PH_2; hence, on the analogy of hydrazine the constitutional formula has been written as $H_2=P-P=H_2$.

The compound is unstable and decomposes when heated; when kept it changes slowly in the dark and quickly in the light into the gaseous and solid hydrides. Since 100 parts by weight give 38 parts of the solid and 62 parts of the gaseous hydride this decomposition may be represented by the equation

$$5PH_2 = 3PH_3 + P_2H$$ [8]

Preparation.—This is best carried out in a Woulfe bottle having a capacity of about 3 litres and furnished with three necks, through one of which hydrogen is admitted. Through another pieces of calcium phosphide are introduced into water, and the third is fitted with the exit tube which is cooled by a reflux condenser and connected with a spiral tube terminating in a wash-bottle, the whole of which is immersed in a freezing-mixture. Uncondensed gas is ignited in a draught. The bottle is warmed to about 60° C. in a water-bath and the calcium phosphide added as required. 100 grams of Ca_3P_2 give 3 to 4 c.c. of liquid phosphide.[1]

---

[1] Smith and Calvert, *J. Amer. Chem. Soc.*, 1914, 36, 1377. [2] Johnson, *loc. cit.*, p. 77.

* The pressures were obtained by the isoteniscope.

[3] Stock, *Ber.*, 1920, 53, 837. [4] Sérullas, *loc. cit.*

[5] Drechsel, *J. prakt. Chem.*, 1874, [2], 10, 180.

[6] Thénard, *Compt. rend.*, 1844, 18, 652; 1844, 19, 313.

[7] Hofmann, *Ber.*, 1874, 7, 531.

[8] Gattermann and Hausknecht, *Ber.*, 1890, 23, 1174. See also Croullebois, *Compt. rend.*, 1874, 78, 496, 805.

Solid Hydrogen Phosphide.

A yellow solid is formed during the decomposition of potassium phosphide by water,[2] and this solid is formed in many other reactions which yield the other hydrides, possibly as a secondary product resulting from the decomposition of the hemiphosphide by water (see p. 80). It is also formed by the exposure of phosphine to light,[3] and is one of the products of the action of chlorine upon phosphine.

Preparation.[4]—The mixed hydrogen phosphides generated by the action of water on calcium phosphide, in a 3-litre flask through which is passed a current of carbon dioxide, are passed through a condenser to remove most of the water vapour and then through a series of wide glass tubes packed with granular calcium chloride (which must leave no residue when dissolved in hydrochloric acid). The tubes are protected from the light by rolls of paper. After the whole apparatus has been filled with carbon dioxide, the calcium phosphide is introduced into the flask in amount sufficient to give a layer about 1 cm. deep. A steady stream of phosphine is evolved at 60° C., the spontaneously inflammable part of which is immediately decomposed by the calcium chloride with deposition of the solid hydrogen diphosphide. The escaping gas is led directly into the flue and burnt. The solid spreads through the tubes and appears in the final wash-bottle, which contains hydrochloric acid. The apparatus is then again filled with CO_2 and the last calcium chloride tube detached and used as the first of the next repeat operation. The contents of the calcium chloride tubes are dissolved in cold dilute hydrochloric acid. The hydrogen phosphide, which usually floats, is filtered off, washed with ice-cold water, then with alcohol and with ether which has been redistilled over sodium. This dissolves a little of the compound to give a yellowish colloidal solution. The solid is filtered off, centrifuged, dried for 12 hours in a vacuum desiccator over P_2O_5, and kept in a closed vessel of brown glass in a desiccator.[5]

Properties.—The diphosphide is a yellow powder, which is tasteless, odourless and insoluble in most solvents. It decomposes in the light giving phosphine, and is easily decomposed by heating in an atmosphere of hydrogen. It ignites in air at temperatures between 100° and 200° C.

The empirical formula is $(P_2H)_x$.[6] The molar weight, deduced from the lowering of the freezing-point of white phosphorus, corresponds to the formula $P_{12}H_6$.[7] The density is 1·83 at 19° C.[4] The heat of formation from white phosphorus and hydrogen is given as +35·4 Cals.[8]

---

[1] Gattermann and Hausknecht, *loc. cit.*

[2] Rose, *Annalen*, 1828, 12, 549.

[3] Leverrier, *Ann. Chim. Phys.*, 1835, [2], 60, 174; *ibid.*, 1837, [2], 65, 266.

[4] Stock, Böttcher and Lenger, *Ber.*, 1909, 42, 2847.

[5] Schenck, *Ber.*, 1903, 36, 990, 4204; Stock, Böttcher and Lenger, *ibid.*, 1909, 42, 2839.

[6] Thénard, *loc. cit.*, and *Compt. rend.*, 1847, 25, 892; Schenck, *Ber.*, 1903, 36, 991, 4204; Amat, *Ann. Chim. Phys.*, 1891, [6], 24, 358.

[7] Schenck and Buck, *Ber.*, 1904, 37, 915.

[8] Ogier, *Ann. Chim. Phys.*, 1880, [5], 20, 16.

Chemical Reactions.—$P_{12}H_6$ is dissociated when heated above 70° C. in an indifferent gas—into its elements at 175° C. in CO_2,[1] or into phosphorus and phosphine at 215° C. The ignition temperature in air is 120° to 150° C.[1] The only liquids which dissolve it without decomposition are phosphorus and P_2H_4. It dissolves in ammonia at $-40°$ C. with evolution of phosphine. After evaporation of the ammonia a black solid is left which appears to be an ammine of a higher hydrogen phosphide. Like the other phosphides it is easily oxidised by halogens, chlorates and nitric acid.[2]

The hydrogen of this phosphide appears to have a slight acidic character, since the phosphide dissolves in alcoholic alkalies giving deep red solutions which contain polyphosphides, similar to those which are formed by the action of alcoholic alkali on finely divided scarlet phosphorus. These compounds are easily hydrolysed by dilution, or by the addition of acids, with the precipitation of a yellow or reddish mixture of solid hydrogen phosphide and scarlet phosphorus (which possibly contains a suboxide or $P_4H.OH$[3,4]).

Higher Phosphides of Hydrogen.

When the diphosphide is gradually heated to 175° C. *in vacuo*, or when its ammoniate is heated, a reddish powder is formed to which the composition P_9H_2 has been assigned :[5]

$$5P_{12}H_6 = 6P_9H_2 + 6PH_3$$

This compound is fairly stable in dry air, but in moist air is converted into phosphine and phosphoric acid. It dissolves in liquid ammonia. A phosphide P_5H_2 has also been reported.[6]

Some **hydroxyphosphides** are formed also by oxidation and hydrolysis of a mixture of phosphorus and phosphorus trichloride,[1,7] or by the hydrolysis of tetraphosphorus diiodide, P_4I_2, when this is boiled with water.[8] The solid to which the composition $P_4H.OH$ has been assigned dissolves in alcoholic potash giving hydrogen and the potassium salt, $P_4H.OK$.

The Alkylphosphines.

On account of the instability of the phosphines and phosphonium salts, the hydrogen valency of phosphorus is more clearly displayed in their alkyl substitution products which also, as is usual, possess a more pronounced basigenic character * than the hydrogen compounds themselves. The methods of preparation of these compounds, and their properties, closely resemble those of the alkylamines.

The tertiary alkylphosphines were discovered by Thénard in 1845,[9] and the primary and secondary by Hofmann in 1871.[10] All may be prepared by general methods—by the action of phosphonium iodide on alkyl iodides or on alcohols, and by the action of zinc alkyls on phosphorus trichloride. The primary and secondary alkylphosphines are obtained as crystalline double salts with zinc iodide when the alkyl iodides are heated to 150° C. with phosphonium iodide in the presence of zinc oxide. The primary base is first liberated as a gas (PH_2CH_3) or as a volatile liquid ($PH_2C_2H_5$) on the addition of water, and is distilled off and condensed. The secondary bases $P(CH_3)_2H$ and $P(C_2H_5)_2H$ can be set free by the addition of potassium hydroxide to their hydriodides. The tertiary bases are prepared (as hydriodides) by heating phosphonium iodide with alcohols (CH_3OH, C_2H_5OH) at 150° to 180° C., and also by the action of zinc alkyls on phosphorus trichloride.

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[1] Leverrier, *Ann. Chim. Phys.*, 1837, [2], 65, 266.
[2] Thénard, Leverrier, *loc. cit.*
[3] Schenck, *loc. cit.*
[4] Stock, *Ber.*, 1903, 36, 1120; *ibid.*, 1908, 41, 1603.
[5] Stock, Böttcher and Lenger, *loc. cit.*
[6] Hackspill, *Compt. rend.*, 1913, 156, 1466.
[7] Gautier, *Ann. Chim. Phys.*, 1873, [5], 76, 49.
[8] Francke, *J. prakt. Chem.*, 1887, [2], 35, 341.
* *I.e.* when combined with HI, CH_3I, etc.
[9] Thénard, *Berzelius' Jahresbericht*, 1845, 26, 598.
[10] Hofmann, *Ber.*, 1871, 4, 205, 430, 605; 1872, 5, 104; 1873, 6, 302.

The boiling-points of alkylphosphines rise with increasing molecular weight, as is usual in homologous series :—

Primary.		Secondary.		Tertiary.	
	Boiling-point, ° C.		Boiling-point, ° C.		Boiling-point, ° C.
Methylphosphine— $P(CH_3)H_2$	-14	Dimethyl— $P(CH_3)_2H$	$+25$	Trimethyl— $P(CH_3)_3$	$+40$
Ethyl— $P(C_2H_5)H_2$	$+25$	Diethyl— $P(C_2H_5)_2H$	85	Triethyl— $P(C_2H_5)_3$	127
*Iso*propyl— $P(C_3H_7)H_2$	41	Di*iso*propyl— $P(C_3H_7)_2H$	118	..	..
*Iso*butyl— $P(C_4H_9)H_2$	62	Di*iso*amyl— $P(C_4H_9)_2H$	210	..	..

Alkyliodides of the quaternary phosphonium bases are made by heating (to over 150° C.) the theoretical proportions of the alcohols with phosphonium iodide, thus :—

$$4CH_3OH + PH_4I = P(CH_3)_4I + 4H_2O$$

They are well-crystallised salts, easily soluble in water, and highly dissociated even at dilutions of 32 litres to the mol.[1] The bases, liberated by the action of silver oxide on the iodides, are also highly dissociated, and therefore behave as strong alkalies. Thus, in the case of $P(CH_3)_4OH$:—

V	16	64	256 litres per mol
λ	214	221	223 " "

(Bredig.[1])

The mobility of the ion $P(CH_3)_4^+$ is 42·3, that of $P(C_2H_5)_4^+$ 32·7, the mobility diminishing with increasing addition of $-CH_2-$ to about 23 in the case of $P(C_5H_{11})(C_6H_5)_3^+$ (*iso*amyltriphenylphosphonium ion).

Alkylphosphines differ from the corresponding ammonia derivatives by the great ease with which they are oxidised even by atmospheric oxygen, either with spontaneous inflammation, as in the case of some of the less alkylated members, or with the formation of phosphine oxides, as in the case of trialkylphosphines. Thus oxygen at ordinary temperatures combines with $P(C_2H_5)_3$, giving $P(C_2H_5)_3O$, which may be distilled with steam.

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[1] Bredig, *Zeitsch. physikal. Chem.*, 1894, 13, 230, 301.

Triethylphosphine Oxide may be made in quantity by heating 1 part of phosphorus with 13 parts of ethyl iodide in a sealed tube at 175°–180° C. The product is distilled, first with ethyl alcohol to remove excess ethyl iodide, and then with concentrated potash, which removes the iodine and oxidises the compound. Thus :—

$$P(C_2H_5)_4I + KOH = P(C_2H_5)_3O + KI + C_2H_6$$ [1]

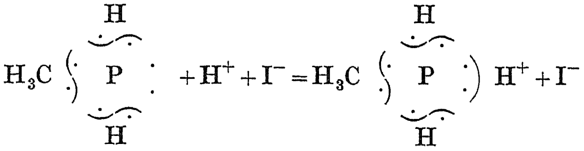
Triethylphosphine also combines with sulphur with evolution of heat to give the corresponding *triethylphosphine sulphide*, $P(C_2H_5)_3S$, a very stable compound, which can also be made by oxidation, or by hydrolysis, of the curious addition compound $P(C_2H_5)_3.CS_2$, a red crystalline solid which is itself made by direct union of $P(C_2H_5)_3$ and CS_2. The oxidation is effected by silver oxide, according to the equation

$$P(C_2H_5)_3CS_2 + 2Ag_2O = Ag_2S + 2Ag + CO_2 + P(C_2H_5)_3S$$

The hydrolysis occurs at 100° C. and yields the oxide as well as the sulphide :—

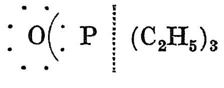
$$4P(C_2H_5)_3CS_2 + 2H_2O = 2P(C_2H_5)_3S + P(C_2H_5)_3O + P(C_2H_5)_3CH_3OH + 3CS_2$$

The structural formulæ of these compounds, whether written with the usual bonds or with valency electrons, are clearly quite analogous to those of the alkyl derivatives of ammonia (see this Volume, Part I.). Thus the presence of even one methyl group enables the phosphorus to accept a hydrogen ion from hydrogen iodide, giving a crystalline product which is not dissociated under ordinary conditions :—



$$H_3C \; \overset{H}{\underset{H}{P}} \; : + H^+ + I^- = H_3C \; \overset{H}{\underset{H}{P}} \; H^+ + I^-$$

In the alkylphosphine oxide (and sulphide) the lone pair of electrons on the phosphorus atom completes the octet of the oxygen (or sulphur), as in the case of amine oxides :—



$$:\ddot{\underset{..}{O}}:P \;\vdots\; (C_2H_5)_3$$

Oxidation of the primary and secondary alkylphosphines gives alkyl acids, and chlorination of these with PCl_5 gives the corresponding acid chlorides. These substances are of importance in elucidating the structure of the phosphorous acids, etc. (*q.v.*), in one tautomeric form of which the phosphorus is not trivalent, but has the same valency as exhibited in phosphoric acid or quaternary phosphonium bases. This form is fixed in the compounds obtained as follows :—

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[1] Crafts and Silva, *Trans. Chem. Soc.*, 1871, 24, 629.

When methylphosphine is passed into concentrated nitric acid it gives a crystalline dibasic acid (methylphosphinic acid), $P(CH_3)O(OH)_2$, and the action of PCl_5 on this yields $P(CH_3)OCl_2$.[1] Oxidation of $P(CH_3)_2H$ with nitric acid gives the monobasic dimethylphosphinic acid. Corresponding ethyl derivatives are also known.[1]

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[1] Hofmann, *loc. cit.*

CHAPTER VII.

PHOSPHORUS AND THE HALOGENS.

THE FLUORIDES OF PHOSPHORUS.

Phosphorus Trifluoride, PF_3.—Some early indications were obtained that phosphorus reacted with fluorides of zinc and lead,[1, 2] and that the fluoride resulting was a gas.[3] This gas was prepared in 1884 by heating lead fluoride with copper phosphide in a brass tube.[4] It is also produced by the action of fluorides of zinc, silver or lead on phosphorus trichloride or tribromide.[5] One of the most convenient methods of preparation is by the reaction between arsenic trifluoride, which is easily prepared and purified, and phosphorus trichloride, thus :—

$$PCl_3 + AsF_3 = PF_3 + AsCl_3$$

The apparatus consists of a distillation flask fitted with a tap-funnel. The side-tube of the flask is sealed to a condensing wash-bottle, which can be cooled in a mixture of solid carbon dioxide and alcohol, and the wash-bottle is joined to a condenser which is immersed in liquid air. After the whole apparatus has been thoroughly dried, the arsenic trifluoride is allowed to drop into the trichloride. The vapours of these two compounds are removed in the first condenser, and the phosphorus trifluoride is solidified in the second.[6]

Phosphorus trifluoride can also be made by the action of lead fluoride on phosphorus trichloride [7] and by the decomposition of the pentafluoride by means of electric sparks.

The composition has been established by the vapour density and by analysis (*e.g.* with silicon, see p. 87). The fluoride is a colourless gas which does not fume in the air, and is highly poisonous. It condenses to a colourless liquid at $-95°$ C. and freezes to a white solid at $-160°$ C. The heat of formation is 106·2 to 109·7 Cals.[8] per mol, therefore much greater than that of the trichloride, and the trifluoride also proves to be the more stable of the two compounds. It can be decomposed by electric sparks with deposition of phosphorus and formation of the pentafluoride, thus :—

---

[1] Davy, *Phil. Trans.*, 1808, 98, 43.

[2] Dumas, *Ann. Chim. Phys.*, 1826, [2], 31, 433.

[3] MacIvor, *Chem. News*, 1875, 32, 258.

[4] Moissan, "*Le Fluor et ses Composés*," Steinheil, Paris, 1900; also *Compt. rend.*, 1884, 99, 655, 970.

[5] Moissan, *Compt. rend.*, 1885, 100, 272, 1348; *ibid.*, 1886, 102, 763, 1245; *ibid.*, 1886, 103, 1257; *ibid.*, 1904, 138, 789.

[6] Moissan, *Ann. Chim. Phys.*, 1885, [6], 6, 433.

[7] Guntz, *Compt. rend.*, 1886, 103, 58.

[8] Berthelot, M., *Ann. Chim. Phys.*, 1885, 6], 6, 388.

$$5PF_3 = 3PF_5 + 2P$$ [1]

It can be reduced by heating with hydrogen :—

$$PF_3 + 3H_2 = PH_3 + 3HF$$

and also by heating with silicon or boron :—

$$4PF_3 + 3Si = 3SiF_4 + 4P$$

but is not reduced by heating with sulphur, phosphorus or arsenic. It is not affected by the metals copper, mercury, iron, cobalt and nickel at ordinary temperatures, but the same metals give phosphides at a red heat.[2] It is completely absorbed by sodium at the melting-point of this metal.[1]

Phosphorus trifluoride is easily oxidised. Although it does not burn in air it can be exploded with oxygen by electric sparks, one volume of the gas mixed with half a volume of oxygen giving one volume of phosphorus oxyfluoride :—

$$PF_3 + \tfrac{1}{2}O_2 = POF_3$$

It combines vigorously with all the halogens giving mixed pentahalides (*q.v.*). It is hydrolysed very slowly by cold water, rather more quickly by boiling water, and quickly by aqueous alkalies, giving in the last case alkali fluoride and phosphite. It was considered by Moissan [3] and by Berthelot [4] that the first product of hydrolysis was a fluophosphoric acid (*q.v.*), the potassium salt of which was fairly stable.

Phosphorus Pentafluoride, PF_5.—This compound was discovered by Thorpe, who prepared it by the reaction between AsF_3 and PCl_5 :—[5]

$$5AsF_3 + 3PCl_5 = 3PF_5 + 5AsCl_3$$

The same method and precautions may be adopted as already described for the trifluoride. The first condenser is, however, kept at about − 60° C. The pentafluoride can also be made by heating PCl_5 with PbF_2,[6] or by combining PF_3 with Br_2 and warming the product :—[3]

$$5PF_3Br_2 = 3PF_5 + 2PBr_5$$

The pentabromide being a solid is easily separated, and it only remains to free the gas from a small quantity of bromine by allowing it to stand over mercury. It can be made similarly from PF_3Cl_2.[7] It is produced, together with some PF_3, by the action of fluorine upon phosphorus.[8]

Phosphorus pentafluoride is a heavy colourless gas with an unpleasant smell; it strongly attacks the skin and respiratory tract. Unlike the trifluoride it fumes strongly in air and is rapidly absorbed by water. It neither burns nor supports combustion. It does not attack dry glass at room temperatures. The density is 4·5 (air = 1) according to Thorpe and Moissan, and the formula is established from this and the analysis. It condenses to a colourless liquid at −75° C. and freezes to a white solid at −83° C.

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[1] Moissan, *loc. cit.*, and "*Le Fluor et ses Composés.*"

[2] Granger, *Compt. rend.*, 1896, **123**, 176; 1895, **120**, 923.

[3] Moissan, "*Le Fluor et ses Composés.*"

[4] Berthelot, *Ann. Chim. Phys.*, 1885, [6], **6**, 358.

[5] Thorpe, *Annalen*, 1876, **182**, 201; *Proc. Roy. Soc.*, 1877, **25**, 122.

[6] Guntz, *loc. cit.*

[7] Poulenc, *Ann. Chim. Phys.*, 1891, [6], **24**, 548.

[8] Moissan, *loc. cit.*

This compound is by far the most stable pentahalide of phosphorus. It is not dissociated by moderate heat or weak sparks from an induction coil, but on strong sparking it gives PF_3 and F_2, the latter attacking the glass. The small extent of the dissociation is shown by the fact that the pentafluoride does not react with *iso*amyl alcohol at the boiling-point of the latter.[1] It is not attacked by oxygen, fluorine or iodine. With dry ammonia it forms an ammine, $PF_5.5NH_3$,[2] and with N_2O_4 an addition compound $PF_5.N_2O_4$.[3] It is completely hydrolysed by water (or alkalies) giving phosphoric and hydrofluoric acids (or their salts). It is not reduced by heating with phosphorus or sulphur.

Mixed Fluohalides.

Phosphorus Trifluorodichloride, PF_3Cl_2.—This compound is best prepared by mixing equal volumes of the trifluoride and chlorine confined over mercury, and allowing the mixture to stand for some days.[4] The volume diminishes to one half, and the composition and molecular weight of the product are thus determined by Gay-Lussac's law and by the density, viz. 5·4 (air = 1) :—

$$PF_3 + Cl_2 = PF_3Cl_2$$

It is a colourless gas with an unpleasant odour, and does not burn or support combustion. It condenses to a liquid at −8° C. When heated to over 200° C. it decomposes according to the equation

$$5PF_3Cl_2 = 3PF_5 + 2PCl_5$$

It is much more easily reduced than the pentafluoride. Hydrogen combines with the chlorine at 250° C. leaving PF_3. Many metals, *e.g.* aluminium, magnesium, tin, lead and iron, decompose it similarly, forming chlorides but not decomposing the trifluoride. Sodium absorbs it completely. Sulphur combines with the phosphorus and the chlorine, giving PSF_3 and S_2Cl_2. Hydrolysis with a limited amount of water splits off the chlorine first, thus :—

$$PF_3Cl_2 + H_2O = POF_3 + 2HCl$$

Phosphorus Trifluorodibromide, PF_3Br_2, was first produced by passing bromine into phosphorus trifluoride cooled by a freezing mixture. It is a pale brown fuming liquid which freezes to a yellow solid at −20° C. and decomposes at ordinary temperatures in a similar manner to the dichloride :—

$$5PF_3Br_2 = 3PF_5 + 2PBr_5$$

On complete hydrolysis it gives H_3PO_4, HF and HBr.[5]

The corresponding **diiodide,** PF_3I_2, is probably formed when the trifluoride is absorbed by iodine. It is a yellowish-red solid.

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[1] Lucas and Ewing, *J. Amer. Chem. Soc.*, 1927, 49, 1270.

[2] Thorpe, *loc. cit.*

[3] Tassel, *Compt. rend.*, 1890, 110, 1264.

[4] Moissan, "*Le Fluor et ses Composés*"; Poulenc, *Ann. Chim. Phys.*, 1891, [6], 24, 548.

[5] Moissan, "*Le Fluor et ses Composés.*"

Fluophosphoric Acid.—The tendency of fluorine to replace oxygen in oxy-acids, which is exemplified in such compounds as hydrofluoboric acid, is shown to some extent in the acids of phosphorus. The existence of alkali fluophosphates has already been alluded to (p. 87).

Salts of fluophosphoric acid are prepared by the action of alkali fluorides on phosphorus pentachloride. The reaction between NH_4F and PCl_5 proceeds with some violence at 80°–110° C. The product, NH_4PF_6, is dissolved in cold water, precipitated by nitron acetate, and again converted into the ammonium salt by the addition of ammonia and extraction of the organic base with chloroform. The alkali fluorides, KF and NaF, gave less violent reactions and smaller yields of fluophosphate. These salts resemble perchlorates chemically and halides in crystalline form.[1]

THE CHLORIDES OF PHOSPHORUS.

Phosphorus Dichloride, $(PCl_2)_n$.—By the action of a silent electric discharge upon a mixture of the gaseous trichloride and hydrogen a liquid was obtained which, after filtration to remove a yellow solid and distillation under reduced pressure, proved to have a composition corresponding to PCl_2. It decomposed quickly on heating into PCl_3 and a yellow solid, boiled with decomposition at about 180° C. and could be frozen to a solid which melted at $-28°$ C.[2]

Phosphorus Trichloride, PCl_3.—The action of chlorine on phosphorus was investigated by Gay-Lussac and Thénard,[3] and also by Davy.[4] It was shown that the phosphorus burns with a pale flame and that both a liquid and a solid compound are produced. The preparation of the pure liquid alone (namely, the trichloride) is best carried out in a retort (filled with dry carbon dioxide), the bottom being covered by a layer of sand. The dry and clean yellow phosphorus is introduced and melted in a current of dry carbon dioxide. The retort is kept in warm water and a current of dry chlorine is introduced through the inlet tube, which should be adjustable to the distance above the phosphorus which gives a brisk but not too violent reaction. The distillate may be purified by redistilling with a little yellow phosphorus.*

Phosphorus may also be combined to form the trichloride by passing its vapour over mercurous or mercuric chloride[3] or cupric chloride,[5] or by passing the vapour of sulphur monochloride over phosphorus,[6] or by heating red phosphorus with sulphuryl chloride.[7] It is possible to prepare it directly from calcium phosphate by heating this with silica and charcoal and passing over it the vapour of sulphur monochloride :—

$$4S_2Cl_2 + Ca(PO_3)_2 = 2PCl_3 + CaCl_2 + 3SO_2 + 5S$$ [8]

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[1] Lange and von Krueger, *Ber.*, 1932, 65, **B**, 1253.

[2] Besson and Fournier, *Compt. rend.*, 1910, 150, 102.

[3] Gay-Lussac and Thénard, "*Récherches physico-chimiques,*" Paris, 1811, 2, 176.

[4] Davy, *Phil. Trans.*, 1810, 100, 231; *ibid.*, 1811, 101, 1.

* The precautions which are required to secure absolutely pure halides of phosphorus are referred to in the section on "Atomic Weight" (pp. 45–48).

[5] Gladstone, *Phil. Mag.*, 1849, [3], 35, 345.

[6] de Claubry, *Ann. Chim. Phys.*, 1818, [2], 1, 213.

[7] Köchlin and Heumann, *Ber.*, 1883, 16, 479.

[8] Budnikoff and Shiloff, *J. Soc. Chem. Ind.*, 1923, 42, 378T.

Reactions of some theoretical interest which give the trichloride are :—

(*a*) Heating phosphorus in a sealed tube with HCl :—

$$2P + 3HCl = PCl_3 + PH_3 \ ^1$$

(*b*) Reduction of the pentachloride by hydrogen and some metals.

(*c*) Reduction of the oxychloride with charcoal at a red heat :—

$$POCl_3 + C = PCl_3 + CO \ ^2$$

Physical Properties.—Phosphorus trichloride is a colourless liquid which boils at 76° C. and freezes at about $-100°$ C. The vapour density and the analysis correspond to the molecule PCl_3. The liquid fumes in moist air with decomposition. It is immiscible with water, but is completely hydrolysed by it forming hydrochloric and phosphorous acids.

Gaseous PCl_3.—The vapour density has been determined as 4·7464 [3] and 4·75 [4] (air = 1). The thermal expansion is 0·00489 from 100° to 125° C. and 0·00417 from 125° to 180° C.[5] The specific heat is 0·1346 to 0·1347 between 111° and 246° C.[4] The refractive index for the D line is given as 1·001730.[6]

Liquid PCl_3.—The density has been determined by several investigators with the following results in grams per c.c. at 0° C. :—1·6119 (Buff),[7] 1·6162 (Pierre),[8] 1·61275 (Thorpe).[9] The densities can be calculated as the quotients of the density at 0° C. divided by the relative specific volume for other temperatures, *i.e.* as $D_t = D_0/v_t$, in which v_t, the coefficient of expansion, is given by the equations of Thorpe [9] (below) or that of Pierre.[8] The mean coefficient of expansion between 0° and 75° C. is 0·0013436,[9] and the specific volumes from 0° C. to the boiling-point are given by the equation [9]

$$v_t = v_0(1 + 0{\cdot}0011393t + 0{\cdot}0_5166807t^2 + 0{\cdot}0_84012t^3)$$

Hence the volume at the boiling-point 75·95° C. is 1·09827 times that at 0° C., and the molar volume at the boiling-point is 93·34.

Another series of results has been continued to a lower temperature, so as to include the density of the solid :—[10]

$t°$ C. .	-95	-95	-80	-50	-30	0·0	+20
D . .	1·9036 Solid	1·7876 Liquid	1·7601	1·7046	1·6671	1·6128	1·5778

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[1] Oppenheim, *Bull. Soc. chim.*, 1864, [2], 1, 163.
[2] Riban, *Bull. Soc. chim.*, 1883, [2], 39, 14.
[3] Regnault, *Compt. rend.*, 1853, 36, 676.
[4] Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 129.
[5] Troost and Hautefeuille, *Compt. rend.*, 1876, 83, 333.
[6] Mascart, *Compt. rend.*, 1874, 78, 801.
[7] Buff, *Ann. Suppl.*, 1866, 4, 152.
[8] Pierre, *Ann. Chim. Phys.*, 1847, [3], 20, 5.
[9] Thorpe, *Trans. Chem. Soc.*, 1880, 37, 141, 327.
[10] Koerber, *Ann. Physik*, 1912, 37, 1014.

An estimate of the limiting density at −273° C. is 2·11927, and this has been estimated to decrease with rise of temperature according to the equation[1]

$$D_t = 2{\cdot}11927 - 0{\cdot}00189994T + 0{\cdot}0_6 1183T^2$$

The compressibility of the liquid at 10·1° C. between 1 and 500 atmospheres was found to be $0{\cdot}0_4 72$.[2] At 20° C. the relative volume of the liquid was reduced from 1·0234 to 0·9862 by a pressure of 500 kilos. per sq. cm. and further to 0·7763 by 12,000 kilos.[3]

The vapour pressure measurements of Regnault[4] were expressed by the equation

$$\log p = 4{\cdot}7479108 - 3{\cdot}1684558 a^{\theta} \text{ (between } -20^\circ \text{ and } +50^\circ \text{ C.)}$$

in which $\log a = \bar{1}{\cdot}9968895$; or by[5]

$$\log p = 1{\cdot}2112[5{\cdot}6885 - 1000(\theta + 228)^{-1}]$$

The dielectric constant[6] at 22° C. is 4·7.

The boiling-point at normal pressure has been given as 74° to 78° C. by different investigators. It is very close to 76° C. The carefully determined values of Thorpe[7] are:—75·95° C. at 760 mm. and 76·25° C. at 768 mm. More recent values are 75·5° C. at 763 mm.[8] and 75° C. at 749 mm.[9]

The latent heat of vaporisation is given as 9·0 Cals. per mol at 0° C. and 6·9 to 7·1 at the boiling-point.[10, 11] The constant $Q_{\mathrm{LV}}/T_{\mathrm{b}} = 20$ is therefore normal.

The critical temperature has been given as 285·5° C.[12] and as 290·5° C.[13]

The melting-point is low, from −111·5°[14] to −90·0° C.[9]

The surface tension, as determined by Ramsay and Shields,[13] was 28·71 dynes/cm. at 16·4° C., and 24·91 dynes/cm. at 46·2° C. Molar surface energies corresponding to these are 562·3 and 499·8 ergs respectively, the decrease in molar surface energy per degree being 2·097, which is about the normal value. More recent determinations over a larger range are :—

t° C. .	−70	−20·5	0	+20·8	35·2	75·1[9]
D . .	1·744	1·653	1·613	1·574	1·547	1·475
σ . .	37·4	31·6	29·3	27·3	25·8	21·9

The value of the parachor has been given on p. 53.

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[1] Timmermanns, *Bull. Soc. chim. Belg.*, 1923, 32, 299.
[2] Amagat, *Ann. Chim. Phys.*, 1893, [6], 29, 68.
[3] Bridgman, *Proc. Amer. Acad.*, 1913, 49, 64.
[4] Regnault, *loc. cit.*, and *Phil. Mag.*, 1853, [4], 5, 473.
[5] Antoine, *Compt. rend.*, 1888, 107, 681, 778, 836.
[6] Walden, *Zeitsch. physikal. Chem.*, 1910, 70, 569.
[7] Thorpe, *loc. cit.*
[8] Walden, *Zeitsch. anorg. Chem.*, 1900, 25, 211.
[9] Jäger, *Zeitsch. anorg. Chem.*, 1917, 101, 172.
[10] Regnault, *loc. cit.*
[11] Andrews, *Phil. Mag.*, 1848, [3], 32, 321.
[12] Pawlesosky, *Ber.*, 1883, 16, 2633.
[13] Ramsay and Shields, *Trans. Chem. Soc.*, 1893, 63, 1089.
[14] Wroblewsky and Olszewsky, *Wied. Annalen*, 1883, 20, 243.

The refractive index of the liquid n has been determined at several wavelengths λ (in microns $=10^{-3}$ mm.).[1,2]

λ . .	0·263	0·298	0·394	0·589	0·768
n . .	1·664	1·59983	1·54274	1·51215	1·50340

These results may be compared with the following:—[3]

$$\begin{array}{lll} \lambda=0{\cdot}486 & 0{\cdot}589 & 0{\cdot}759\mu \\ n=1{\cdot}525 & 1{\cdot}516 & 1{\cdot}506 \end{array}$$

The molar depression of the freezing-point for the trichloride in benzene[4] is 0·636° and the molar elevation of the boiling-point in the same solvent is about 4·5°.

Chemical Properties.—Phosphorus trichloride mixes with organic liquids such as benzene[4] and nitrobenzene,[5] as also with the oxychloride, and with sulphur without reaction at ordinary temperatures.

In many respects the trichloride behaves as an unsaturated compound. Although it does not burn in the air it seems to absorb oxygen to some extent[6] and also ozone, giving the oxychloride.[7]

It is oxidised by sulphur trioxide,[8, 9] by concentrated sulphuric acid (to HPO_3),[9] by $SOCl_2$,[9] $SeOCl_2$[9] and $KClO_3$[10] as follows:—

$$PCl_3+SO_3=POCl_3+SO_2$$
$$PCl_3+2H_2SO_4=HPO_3+H.SO_3Cl+SO_2+2HCl$$
$$3PCl_3+SOCl_2=POCl_3+PCl_5+PSCl_3$$
$$3PCl_3+3SeOCl_2=3POCl_3+SeCl_4+Se_2Cl_2$$
$$3PCl_3+KClO_3=3POCl_3+KCl$$

The halogens convert it into penta-compounds. Thus fluorine gives PF_5[11] and chlorine PCl_5. The action of bromine varies with the conditions; substitution may occur, giving, *e.g.* PCl_2Br_3, as well as PCl_3Br_2 by addition.[12, 13, 14] Iodine may form a chloroiodide.[15] Bromine and iodine together act vigorously according to the equation:—

$$PCl_3+5Br+I=PBr_5+ICl_3$$ [16]

Phosphorus trichloride is chlorinated by selenium tetrachloride:—

$$6PCl_3+7SeCl_4=3(PCl_5)_2.SeCl_4+2Se_2Cl_2$$ [17]

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[1] Gladstone and Dale, *Phil. Trans.*, 1863, 153, 317.
[2] Martens, *Verh. Deutsch. phys. Gesells.*, 1902, 4, 148.
[3] Stiefelhagen, "*Dispers. fluss. trichloride,*" Berlin, 1905.
[4] Pickering, *Ber.*, 1891, 24, 1469.
[5] Kolossowsky, *J. Chim. phys.*, 1927, 24, 56.
[6] Odling, "*Manual of Chemistry,*" London, 1861.
[7] Remsen, *Amer. J. Sci.*, 1876, [3], 11, 365.
[8] Armstrong, *Proc. Roy. Soc.*, 1870, 18, 502.
[9] Michaelis, *Ber.*, 1872, 5, 411; *Annalen*, 1872, 164, 39.
[10] Dervin, *Compt. rend.*, 1883, 97, 576.
[11] Moissan, "*Le Fluor et ses Composés*"; Geuther, *Annalen*, 1887, 240, 208.
[12] Stern, *Trans. Chem. Soc.*, 1886, 49, 815.
[13] Prinvault, *Compt. rend.*, 1872, 74, 869.
[14] Wichelhaus, *Ber.*, 1868, 1, 80.
[15] Moot, *Ber.*, 1880, 13, 2029.
[16] Gladstone, *Trans. Chem. Soc.*, 1851, 3, 15.
[17] Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 5.

by antimony pentachloride :—

$$2SbCl_5 + PCl_3 = PCl_5.SbCl_5 + SbCl_3 \text{ }^{1}$$

and by sulphur monochloride :—

$$3PCl_3 + S_2Cl_2 = PCl_5 + 2PSCl_3 \text{ }^{2}$$

It chlorinates arsenic (in the presence of a little $AsCl_3$)[3] at 200° to 300° C., also antimony,[3, 4] phosphine[5] and arsine,[6] giving phosphorus in each case.

The reaction with cold water normally gives a solution of phosphorous and hydrochloric acids :—

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl \text{ }^{7}$$

Intermediate stages in the reaction have been noted, such as the production of phosphoryl monochloride, POCl, with small amounts of water.[8] The solution produced at first has stronger reducing power than the final solution, which was attributed to a first production of $P(OH)_3$ with subsequent change to the tautomeric $OPH(OH)_2$.[9] In concentrated or hot solution subsequent decomposition of the phosphorous acid may take place with the production of phosphoric acid and red phosphorus, which change has been represented by the equation

$$4H_3PO_3 + PCl_3 = 3H_3PO_4 + 3HCl + 2P \text{ }^{10}$$

The velocity constant of the decomposition, since this takes place at a surface of separation of two immiscible liquids, is that of a unimolecular reaction,[11] *i.e.* $\log \frac{a}{a-x} = kt \times aS$, in which a is the quantity of liquid and S is the reacting surface.

Phosphorus trichloride is used in numerous reactions with organic compounds containing hydroxyl to replace this radical by chlorine; by this means, for example, the chlorides of aliphatic alcohols, etc. may be obtained. The other product is phosphorous acid.

Heats of hydrolysis and solution in much water are given as 65·14 Cals.,[12] 62·3 Cals.,[13] 63·3 Cals.[14] Using these and other data the heat of formation of the liquid trichloride from solid phosphorus and gaseous chlorine is 73·3 Cals.,[15] 76·6 Cals.,[14] 75·8 Cals.[16]

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[1] Kohler, *Sitzungsber. K. Akad. Wiss. Wien*, 1880, 13, 875.

[2] Michaelis, *Ber.*, 1872, 5, 411; *Annalen*, 1872, 164, 39.

[3] Krafft and Neumann, *Ber.*, 1901, 34, 565.

[4] Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 5.

[5] Mahn, *Zeitsch. Chem.*, 1869, [2], 5, 729.

[6] Janowsky, *Sitzungsber. K. Akad. Wiss. Wien*, 1873, 6, 216.

[7] Davy, *Phil. Trans.*, 1810, 100, 231; *ibid.*, 1811, 101, 1.

[8] Besson, *Compt. rend.*, 1890, 111, 972; 1896, 122, 814; 1897, 125, 771, 1032; 1901, 132, 1556.

[9] Mitchell, *Trans. Chem. Soc.*, 1925, 127, 336.

[10] Kraut, *J. Chem. Soc.*, 1871, 24, ii, 660; *Ann. Chim. Pharm.*, 1871, 158, 332. See also Geuther, *Ber.*, 1872, 5, 925.

[11] Carrara and Zoppelari, *Gazzetta*, 1896, 26, i, 493.

[12] Thomsen, *Ber.*, 1873, 6, 710; 1883, 16, 37.

[13] Favre and Silbermann, *J. Pharm. Chim.*, 1853, [3], 24, 231, 311, 412.

[14] Berthelot and Luginin, *Ann. Chim. Phys.*, 1875, [5], 6, 307.

[15] Thomsen, "*Thermochemistry*," translated by Miss Burke, Longmans, 1908.

[16] Ogier, *Compt. rend.*, 1878, 87, 210.

By the action of ammonia on phosphorus trichloride in carbon tetrachloride ammoniates such as $PCl_3.6NH_3$ and $PCl_3.8NH_3$ have been obtained.[1] On heating, these ammines are decomposed with the formation of a phosphamide and ammonium chloride.

Phosphorus trichloride reacts with liquid hydrogen sulphide to produce phosphorus trisulphide at ordinary temperatures.[2]

Phosphorus Pentachloride, PCl_5, is produced by the action of excess of chlorine upon the trichloride until the mass is completely solid, and was thus prepared by Davy.[3] Its composition was established by Dulong's analysis, but the vapour density was found to be lower than the value which corresponds to simple molecules by Avogadro's law. The observed densities were 5·08 at 182° C. and 3·65 over 300° C.,[4] the latter density being about half the theoretical, namely, 7·22 (air = 1). This was one of the earliest known examples of abnormal vapour densities, and the abnormality was rightly attributed to a partial or nearly complete dissociation of the compound into PCl_3 and Cl_2. This dissociation is shown by an increasingly greenish-yellow colour in the vapour, originally colourless.[5] In accordance with the law of concentration action the dissociation was diminished by vaporising the compound in an atmosphere of PCl_3 in such a way as to increase the partial pressure of this vapour.[6] The measured density of the PCl_5 was thus brought nearer to the normal value (see also p. 95).

The pentachloride is best prepared in a stock bottle provided with entry and exit tubes for the chlorine and a tap-funnel for the trichloride and cooled externally. It is kept filled with chlorine, into which the trichloride is introduced, drop by drop.

Another convenient method is passing chlorine into a solution of the trichloride in carbon disulphide. The pentachloride is then precipitated.[7]

Physical Properties.—The density of the liquid under the pressure of its own vapour was determined by means of a glass dilatometer, into which was melted a suitable quantity of the compound and which was then evacuated and sealed. The volume of the liquid was read at various temperatures. The weight was obtained by difference, as well as from the weight of silver chloride which was obtained from the contents after hydrolysis.[8] Another method which was found suitable for this hygroscopic substance employed glass floats about 5 × 1 × 1 mm. which were heated in sealed tubes containing the liquid until they sank. They were calibrated by means of similar observations in a suitable mixture of bromoform and benzene.[9] By the first method the density of the liquid by a slight extrapolation was found to be 1·601 at its boiling-point. The specific volumes were given by the equation

$$v_{160+t} = v_{160}(1 + 0{\cdot}00107t)$$

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[1] Perpérot, *Compt. rend.*, 1925, 181, 662; *Bull. Soc. chim.*, 1925, [iv], 37, 1540.

[2] Ralston and Wilkinson, *J. Amer. Chem. Soc.*, 1928, 50, 258.

[3] Davy, *Phil. Trans.*, 1810, 100, 231; 1811, 101, 1.

[4] Cahours, *Compt. rend.*, 1845, 21, 625; *ibid.*, 1866, 63, 14.

[5] Deville, *Compt. rend.*, 1863, 56, 195, 322; 1866, 62, 1157; 1867, 64, 713.

[6] Wurtz, *Compt. rend.*, 1873, 76, 601.

[7] Muller, *Zeitsch. Chem.*, 1862, [1], 5, 295.

[8] Prideaux, *Trans. Chem. Soc.*, 1907, 91, 1711.

[9] Sugden, *Trans. Chem. Soc.*, 1927, p. 1184.

The specific volumes were 0·629 and 0·6433 and the corresponding densities 1·590 and 1·554 at 160° and 181° C. respectively. By the second method the density was given as

$$D_t = 1{\cdot}624 - 0{\cdot}00208(t - 150°)$$

From this the densities are 1·603 and 1·559 at 160° and 181° C. respectively.

The sublimation temperature has been estimated at 160° C.,[1] 160° to 165° C.,[2] 162·8° C.[3] A thermometer suspended in the vapour of the compound which was subliming freely and condensing on the bulb showed 160° C.[4] An extrapolation of the vapour pressure curve (see below) would give a somewhat higher temperature.

The melting-point (166·8° C.) [3] lay only slightly above the sublimation temperature. The liquid which had been formed in a closed tube under the pressure of its own vapour began to solidify at 162° C.[4]

The coefficient of expansion of the liquid is stated above.

The dissociation pressure (total) at various temperatures, based on measurements with the isoteniscope—[3]

t° C. . .	90	100	110	120	130	140	150	160
p (mm.) .	18	35	67	117	191	294	445	670
D (grams per c.c.) . .	$0{\cdot}0_3197$	$0{\cdot}0_3332$	$0{\cdot}0_3569$	$0{\cdot}0_2929$	..	$0{\cdot}0_22286$	$0{\cdot}0_23448$	$0{\cdot}0_24913$

may be used to calculate the heat of vaporisation with dissociation—[5]

t° C. .	90	100	110	120	140	150	160	
Q . .	14·2	15·6	16·6	16·9	15·6	14·9	14·9	Cals. per mol

The critical temperature determined in the usual manner by observation of the disappearance of the meniscus, was found to be 372° C. The ratio between the boiling-point and the critical temperature on the absolute scale was found to be normal.[6]

Dissociation.—The relative density (air = 1) diminishes rapidly with increase of temperature, as is shown by the tables above and below. At lower temperatures the density corresponds with single undissociated molecules PCl_5, and at 90° C. there is even a slight degree of association.

RELATIVE DENSITIES OF PCl_5 VAPOUR.[7]

t° C.	182	200	230	250	274	300	327	336
Rel. Density (air = 1)	5·078	4·851	4·302	3·991	3·840	3·674	3·656	3·656
Per cent. dissociation	41·7	48·5	67·4	80·0	87·5	96·2	97·3	97·3

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[1] Casselmann, *Annalen*, 1852, 83, 257.

[2] Naumann, *Ber.*, 1869, 2, 345.

[3] Smith and Calvert, *J. Amer. Chem. Soc.*, 1914, 36, 1363.

[4] Prideaux, *Trans. Chem. Soc.*, 1907, 91, 1711.

[5] Smith and Lombard, *J. Amer. Chem. Soc.*, 1915, 37, 2055.

[6] Prideaux, *Trans. Faraday Soc.*, 1910, 6, 155.

[7] Cahours, *Ann. Chim. Phys.*, 1848, [3], 23, 329; *Compt. rend.*, 1866, 63, 14.

DISSOCIATION PRESSURES OF PCl_5.[1]

t° C.	90	100	120	140	160
Gram-mols. PCl_5 per litre	$0{\cdot}0_3945$	0·00159	0·00446	0·01096	0·02368
Pressure in mm.	18	35	117	294	670

In this table the theoretical numbers of gram-mols. PCl_5 per litre if there were no association or dissociation have been calculated from the formula

$$n = \frac{273 \times p}{T \times 760 \times 22{\cdot}3}$$

Total pressures of the gaseous products in equilibrium with PCl_5 can be represented from the foregoing results by the equation

$$\log p = -\frac{6724{\cdot}22}{T} - 19{\cdot}1978 \log T + 68{\cdot}9701$$

The total molar heat of vaporisation is calculated from this equation as in the second table, p. 95.

By a comparison of the actual with the theoretical densities the degrees of dissociation, x, the partial pressures, p_1, p_2, p_3, of PCl_5, PCl_3 and Cl_2, respectively, and their concentrations can be determined.

The equilibrium constant $K_p = p_1/p_2p_3$ is expressed as a function of temperature by means of the equation

$$\log K_p = \frac{21798}{4{\cdot}571T} - 11{\cdot}50$$

By applying the Clapeyron equation the heat of dissociation, Q, of PCl_5 was found to be 21·8 Cals. per mol.[2]

The heat of formation of solid PCl_5 from its elements in their usual physical states is given as 104·99 Cals.[3] or 109·2 Cals.,[4] while the heat of decomposition by water is 123·4 or 118·9 Cals.[3, 4]

The liquid PCl_5 has a very low conductivity, both in the pure state [5] and when dissolved in some solvents, *e.g.* in benzene or PCl_3, but the solution in nitrobenzene was found to have a definite low conductivity.[6]

Chemical Properties.—The chlorine is displaced from phosphorus pentachloride by fluorine with great evolution of heat and the formation of PF_5.[7] Bromine has no action, but iodine is converted into ICl, which gives an addition compound $PCl_5.ICl$ with more of the PCl_5.[8]

On account of its ready dissociation the pentachloride is a most powerful chlorinating agent. Examples of this action on the non-metals are as follows :—

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[1] Smith and Lombard, *J. Amer. Chem. Soc.*, 1915, 37, 2055.
[2] Holland, *Zeitsch. Elektrochem.*, 1912, 18, 234.
[3] Thomsen, "*Thermochemistry*," translated by Miss Burke, Longmans, 1908.
[4] Berthelot and Luginin, *Compt. rend.*, 1872, 75, 100; *ibid.*, 1878, 86, 859.
[5] Voigt and Biltz, *Zeitsch. anorg. Chem.*, 1924, 133, 277.
[6] Holroyd, *Trans. Chem. Soc.*, 1925, 127, 2492.
[7] Moissan, "*Le Fluor et ses Composés*," Steinheil, Paris, 1900.
[8] Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 5.

Sulphur gives $PSCl_3$ [1] and also reacts according to

$$PCl_5 + 2S = S_2Cl_2 + PCl_3$$ [2]

Selenium is converted into the monochloride :—

$$PCl_5 + 2Se = Se_2Cl_2 + PCl_3$$ [3]

Liquid hydrogen sulphide gives $PSCl_3$.[4]

Arsenic is converted into the trichloride :—

$$6PCl_5 + 4As = 4AsCl_3 + 6PCl_3$$ [5]

Antimony reacted in a similar manner.[3] The metals, even the noble metals, are converted into chlorides, but at higher temperatures phosphides may be formed.

With acid anhydrides oxychlorides of the non-metal and of phosphorus are usually formed. Thus NO_2 gives NOCl, $POCl_3$ and Cl_2.[6] Sulphur dioxide even when dry reacted when heated with PCl_5, giving thionyl chloride :—

$$PCl_5 + SO_2 = SOCl_2 + POCl_3$$ [7]

Sulphur trioxide, when warmed with PCl_5, is slowly converted into pyrosulphuryl chloride :—

$$PCl_5 + 2SO_3 = S_2O_5Cl_2 + POCl_3$$ [8]

Selenium dioxide was found to give first a mixture of selenyl and phosphoryl chlorides ; the latter compound then chlorinated the selenium completely, the final result being the transference of the whole of the oxygen to the phosphorus and the chlorine to the selenium:—

$$SeO_2 + PCl_5 = SeOCl_2 + POCl_3$$
$$3SeOCl_2 + 2POCl_3 = P_2O_5 + 3SeCl_4$$ [9]

Phosphorus pentoxide gives phosphoryl chloride,[10] possibly through an intermediate addition compound.[11] In the case of phosphorus trioxide a reducing action was evident, phosphorus trichloride being formed along with the oxychloride.[12] The reaction with arsenic trioxide and probably with arsenic pentoxide was found to produce $AsCl_3$ and at the same time phosphoryl chloride in the case of the pentoxide.[13] The oxides of boron and silicon were both chlorinated to BCl_3 and $SiCl_4$, respectively, on heating with PCl_5, preferably in sealed tubes.[1]

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[1] Gladstone and Holmes, *Phil. Mag.*, 1849, [3], 35, 343; *Trans. Chem. Soc.*, 1851, 3, 5; Baudrimont, *loc. cit.*

[2] Goldschmidt, *Chem. Zentr.*, 1881, [3], 12, 489.

[3] Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 5.

[4] Ralston and Wilkinson, *J. Amer. Chem. Soc.*, 1928, 50, 258.

[5] Baudrimont, *loc. cit.*; Goldschmidt, *loc. cit.*

[6] Muller, *Annalen*, 1862, 122, 1.

[7] Kremers, *Annalen*, 1849, 70, 297; Persoz and Bloch, *Compt. rend.*, 1849, 28, 86, 289.

[8] Heumann and Köchlin, *Ber.*, 1883, 16, 479.

[9] Michaelis, *Annalen*, 1872, 164, 39.

[10] Bakunin, *Gazzetta*, 1900, 30, [ii], 340; Persoz and Bloch, *loc. cit.*

[11] Schiff, *Annalen*, 1857, 102, 111; *Zeitsch. anorg. Chem.*, 1894, 7, 91.

[12] Thorpe and Tutton, *Proc. Roy. Soc.*, 1891, 59, 1019.

[13] Hurtzig and Geuther, *Annalen*, 1859, 111, 159; Michaelis, *loc. cit.*

Metallic oxides as well as metals are usually converted into chlorides by the pentachloride, while metallic sulphides usually give the chlorides and phosphorus sulphides.

Although PCl_5 is a saturated compound it is capable of forming addition compounds. Among those which have been described are: $PCl_5.AsCl_3$, $PCl_5.AsCl_5$,[2] $PCl_5.SbCl_5$,[3] $2PCl_5.3HgCl_2$,[4] $PCl_5.FeCl_3$, $PCl_5.CrCl_3$.[5]

Several ammoniates have been described. A white crystalline substance, $PCl_5.8NH_3$, was precipitated when ammonia was passed into a solution of PCl_5 in CCl_4.[6]

A most important class of reactions in which PCl_5 plays a part is its hydrolysis by water or other compound containing the hydroxyl group with the substitution of chlorine for hydroxyl. Complete hydrolysis with an excess of water gives orthophosphoric and hydrochloric acids :—

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl$$

The heat of hydrolysis is 123·4 Cals.,[7] 118·9 Cals.[8] Steam may produce in the first place phosphoryl chloride, thus :—

$$PCl_5 + H_2O = POCl_3 + 2HCl$$

The formation of chlorosulphonic acid, $SO_2(OH)Cl$, as well as of pyrosulphuryl chloride, $S_2O_5Cl_2$, by the action of PCl_5 on sulphuric acid has given important information as to the constitution of this acid.

Phosphorus pentachloride is one of the most powerful reagents by which the hydroxyl of organic compounds can be replaced by chlorine. Alkyl chlorides, RCl, from alcohols, and acid chlorides, RCOCl, from acids, are often prepared by this method. The pentachloride is thereby converted first into the oxychloride, $POCl_3$, which may itself be used for the substitution of OH by Cl.

The structure of PCl_5 is considered under the heading "Phosphorus in Combination" (Chap. IV.).

The Chlorobromides.—Phosphorus trichloride is only partially miscible with bromine ; two layers are formed, which, on the addition of iodine, combine with evolution of heat and the formation of a reddish solid resembling PBr_5 :—

$$PCl_3 + 2\tfrac{1}{2}Br_2 + \tfrac{1}{2}I_2 = PBr_5 + ICl_3 \text{ [9]}$$

A mixture of PCl_3 and Br_2 in molecular proportions when moderately cooled (to 10° C. or thereabouts) deposited crystals having the composition PCl_3Br_2. These melted at 35° C. with decomposition and separation into two layers.[10] The compound resembles phosphorus pentabromide (*q.v.*) in appearance. When brought into contact with water it is said to give first HOBr, HBr and PCl_3, also $POBr_3$ and $POCl_3$.[1]

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[1] Gustavson, *Ber.*, 1870, 3, 990; Weber, *Annalen*, 1859, 107, 375; *J. prakt. Chem.*, 1859, [1], 77, 65.

[2] Cronander, *Ber.*, 1873, 6, 1406.

[3] Weber, *loc. cit.*

[4] Baudrimont, *loc. cit.*

[5] Cronander, *loc. cit.*

[6] Besson, *Compt. rend.*, 1890, 111, 972; 1892, 114, 1264.

[7] Thomsen, *Ber.*, 1883, 16, 37.

[8] Berthelot and Luginin, *Compt. rend.*, 1878, 86, 859.

[9] Gladstone, *Trans. Chem. Soc.*, 1851, 3, 15.

[10] Wichelhaus, *Annalen Suppl.*, 1868, 6, 277; Stern, *Trans. Chem. Soc.*, 1886, 49, 815; Michaelis, *Ber.*, 1872, 5, 9, 412.

At lower temperatures still more bromine can be combined, giving compounds such as PCl_2Br_3 by displacement of chlorine and PCl_2Br_5.[2]

Many other addition compounds have been reported by various workers. By mixing bromine with phosphorus trichloride, heating on the water-bath and then cooling to about −5° C. brown needle-shaped crystals have been obtained, the analysis of which leads to the formula PCl_3Br_8.[3] By allowing this compound to stand with PCl_3 in a sealed tube for some days red crystals separated which had the composition PCl_3Br_4.[4]

The Chloroiodides.—By allowing PCl_3 to stand with an excess of iodine, crystals were obtained having the composition PCl_3I.[5]

Iodine monochloride or trichloride was found to react with PCl_3 giving orange-red crystals of PCl_6I, which, by their formation, are probably constituted as $PCl_3.ICl_3$. The compound sublimed with partial decomposition and deliquesced in moist air with hydrolysis of the PCl_3.[6]

THE BROMIDES OF PHOSPHORUS.

Phosphorus Tribromide, PBr_3, was first prepared by Balard[7] who added bromine drop by drop to phosphorus. The reaction is violent, but may be moderated by the use of red phosphorus, by carrying out the reaction in CS_2 solution,[8] and by introducing the bromine as vapour.[9] On account of the formation of volatile phosphorus compounds it is advantageous to have an excess of bromine, which is easily removed by distillation, any phosphorus pentabromide also being decomposed during this operation.

It is generally prepared by dropping bromine from a tap-funnel on to red phosphorus in a flask.[10] The initial reaction occurs with flashes of flame, and external cooling is desirable. Afterwards the bromine is diluted by the PBr_3 and the combination proceeds less vigorously. If the phosphorus is in excess a little remains dissolved in the tribromide, which must be fractionally distilled after the addition of a slight excess of bromine. The reaction can also be carried out in the presence of benzene.

Phosphorus tribromide is a colourless liquid which is often slightly turbid in the cold but becomes clear on warming. It fumes in the air and is hydrolysed in a similar manner to the trichloride.

Physical Properties.—The density at 0° C. is given as 2·9249,[11] 2·92311[12] and 2·923.[13] The density at the boiling-point, 172·9° C., is 2·49541[12] (see also pp. 51, 100). The vapour density, 135·44 ($H=1$), corresponds to simple molecules PBr_3.[14]

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[1] Wichelhaus, *loc. cit.*; Geuther and Michaelis, *Jena Zeit.*, 1870, [1], 6, 242.

[2] Stern, *loc. cit.*

[3] Prinvault, *Compt. rend.*, 1872, 74, 868; Michaelis, *loc. cit.*

[4] Prinvault, *loc. cit.*

[5] Moot, *Ber.*, 1880, 13, 2030.

[6] Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 8.

[7] *Ann. Chim. Phys.*, 1826, [2], 32, 337; 1864, [4], 2, 5.

[8] Kekulé, *Annalen*, 1864, 130, 16.

[9] Lieben, *Annalen*, 1868, 146, 214; Pierre, *Ann. Chim. Phys.*, 1847, [3], 20, 5.

[10] Schenck, *Ber.*, 1902, 35, 354; Christomanos, *Zeitsch. anorg. Chem.*, 1904, 41, 276.

[11] Pierre, *Ann. Chim. Phys.*, 1847, [3], 20, 5.

[12] Thorpe, *Trans. Chem. Soc.*, 1880, 37, 141, 327.

[13] Jäger, *Zeitsch. anorg. Chem.*, 1917, 101, 173.

[14] Christomanos, *loc cit.*

The coefficient of expansion has been expressed by the equation

$$v_t = v_0(1 + 0{\cdot}0_3 84117t + 0{\cdot}0_6 542892t^2 + 0{\cdot}0_8 18893t^3)$$

between 0° C. and the boiling-point. Equations of this type have also been obtained by Pierre.[1] Relative volumes obtained from Thorpe's equation are :

t° C. . .	0	40	100	172·9
v . .	1·000	1·0348	1·0961	1·1714

Other values for the boiling-point are 170·2° C. at 750 mm.,[2] 172° C. at 752 mm.,[3] 176° to 177° C. at 772 mm.[4] The compound solidifies at −41·5° C.,[5] −50° C.,[6] and melts at −40° C.[6]

The following table gives relations between the surface tension and temperature :—[6]

SURFACE TENSIONS, DENSITIES AND MOLAR SURFACE ENERGIES OF PBr_3.

t° C. . .	−20	0	20·8	50·3	75·7	99·8	154	170
D . .	2·972	2·923	2·871	2·799	2·735	2·676	2·542	2·502
σ . .	45·8	44·7	43·2	41·3	38·9	36·0	28·4	26·3
$\sigma(V_M)^{2/3}$.	927·0	916·8	894·7	870·0	832·1	781·4	637·9	597·0

Another series of results was determined with the object of calculating parachors [4] (see p. 53).

PARACHORS OF PBr_3.

t° C. .	24	33	59·5	72·0
D . .	2·883	2·861	2·795	2·764
σ . .	45·8	44·1	38·1	37·1
$[P]$ . .	244·4	244·0	241·2	242·0

The critical temperature is calculated to be 441° C.[7]

The refractive index of the liquid for the D line (n_D) is 1·6945 at 19·5° C.[8]

The dielectric constant at 20° C. is 3·88.[9]

Chemical Properties.—The energy liberated during the combination of phosphorus and bromine to form PBr_3 is manifestly less than in the corresponding case of PCl_3. This is confirmed by measurements of the heat of combination—

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[1] *Loc. cit.*

[2] Jäger, *loc. cit.*

[3] Walden, *Zeitsch. anorg. Chem.*, 1900, 25, 211.

[4] Sugden, Reed and Wilkins, *Trans. Chem. Soc.*, 1925, 127, 1525.

[5] Jäger, *loc. cit.*; Christomanos, *loc. cit.*

[6] Jäger, *loc. cit.*

[7] Guldberg, *Christiania Ved. Selck.*, 1882, 20; *Zeitsch. physikal. Chem.*, 1890, 5, 378.

[8] Christomanos, *loc. cit.*

[9] Schlundt, *J. Physical Chem.*, 1902, 6, 157, 503.

$$P\ (\text{solid}) + 1\tfrac{1}{2}Br_2\ (\text{liq.}) = PBr_3\ (\text{liq.}) + 42{\cdot}6\ \text{Cals.}^1$$

The superior affinity of chlorine for phosphorus is shown by the fact that this halogen displaces the bromine from PBr_3 giving PCl_3.

An excess of bromine combines with PBr_3 giving the highly dissociated PBr_5 (*q.v.*).

Oxygen has no effect in the cold, but when passed into boiling PBr_3 a vigorous and sometimes explosive reaction may take place with the formation of bromine, $POBr_3$ and P_2O_5.[2]

The hydrolysis is complete and gives phosphorous and hydrobromic acids. The heat of hydrolysis was found to be 64·1 Cals.,[1] *i.e.* nearly the same as that of PCl_3.

Hydrogen sulphide was found to react with PBr_3 in a somewhat similar manner to water :—

$$2PBr_3 + 3H_2S = P_2S_3 + 6HBr\ ^3$$

Ammonia gave first an ammine and then an amide.[4]

Phosphorus tribromide attacks cork, rubber, wood, etc. It also reacts with hydroxylated compounds such as alcohols, and even with ether. It mixes freely with chloroform, benzene, etc., as well as with $AsCl_3$, $SnCl_4$, etc.

Phosphorus Pentabromide, PBr_5.—In the presence of excess of bromine phosphorus can form not only the pentabromide[5] but also, according to the thermal diagram, other perbromides.[6] It was discovered early[5] that the presence of some iodine greatly facilitates the combination, probably by the formation of ICl_3, thus :—

$$PCl_3 + \tfrac{1}{2}I_2 + 5Br = PBr_5 + ICl_3\ ^3$$

It is also produced by the decomposition of the dibromotrifluoride formed when trifluoride is passed into bromine at −10° C. :—

$$5PF_3Br_2 = 3PF_5 + 2PBr_5\ ^7$$

Properties.—Phosphorus pentabromide is a yellow crystalline solid which melts to a red liquid with decomposition. It fumes in the air. A red form has also been described, but this is probably PBr_7.[8]

The densities and specific volumes of the liquid under the pressure of its own vapour were determined in a sealed evacuated glass dilatometer.[9] One set of results was as follows :—

t° C. .	85	100	130	165
v . .	0·3530	0·3621	0·3755	0·3899

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[1] Berthelot and Luginin, *Ann. Chim. Phys.*, 1875, [5], 6, 307.
[2] Christomanos, *loc. cit.*; Demole, *Bull. Soc. chim.*, 1880, [2], 34, 201.
[3] Gladstone, *loc. cit.*
[4] Besson, *Compt. rend.*, 1890, 111, 972; 1896, 122, 814; 1897, 124, 763.
[5] Balard, *loc. cit.*
[6] Biltz and Jeep, *Zeitsch. anorg. Chem.*, 1927, 162, 32.
[7] Moissan, "*Le Fluor et ses Composés.*"
[8] Kastle and Beatty, *Amer. Chem. J.*, 1899, 21, 392; 1900, 23, 805.
[9] Prideaux, *Trans. Chem. Soc.*, 1909, 95, 545.

From these results and others the coefficient of expansion is calculated as

$$v_{t-85} = v_{85}\{1 + 0{\cdot}0019(t-85)\}$$

and

$$v_{t-100} = v_{100}\{1 + 0{\cdot}0012t\}, \quad \text{up to } 165^\circ \text{ C.}$$

The vapour is formed with dissociation. The pressures of the total vapour formed were determined by a static method.[1] From the results it was calculated that the boiling- (sublimation) point was 106° C.

The heat of formation

$$\text{P (solid)} + 2\tfrac{1}{2}\text{Br}_2 \text{ (liq.)} = \text{PBr}_5 \text{ (solid)} + 63{\cdot}5 \text{ Cals.}^2$$

was found to be greater than that of PBr_3, but less than that of PCl_5. The additional heat on combination with the last two atoms of bromine was found to be small.

$$\text{PBr}_3 \text{ (liq.)} + \text{Br}_2 \text{ (liq.)} = \text{PBr}_5 \text{ (solid)} + 20{\cdot}3 \text{ Cals.}^2$$

The hydrolysis with excess of water produces hydrobromic and phosphoric acids. The heptabromide, PBr_7, which was prepared by subliming PBr_5 with Br_2 in a sealed tube at 90° C.,[3] hydrolyses with the production of the same acids and bromine in addition. In the presence of a small amount of water the oxybromide $POBr_3$ may be produced. Hydrogen sulphide by an analogous reaction gave the sulphobromide :—

$$\text{PBr}_5 + \text{H}_2\text{S} = \text{PSBr}_3 + 2\text{HBr}^{\,4}$$

The pentabromide may also be used to replace hydroxyl groups in organic compounds by halogen. Thus :

$$\text{PBr}_5 + \text{CH}_3\text{COOH} = \text{POBr}_3 + \text{CH}_3\text{COBr} + \text{HBr}$$

An ammine, $PBr_5.9NH_3$, was formed by passing dry ammonia into a solution of PBr_5 in CCl_4.[5]

THE IODIDES OF PHOSPHORUS.

Phosphorus reacts energetically with iodine when heated in contact with it, or in dry organic solvents, giving orange to red crystalline products. Two of these, the diiodide and the triiodide, have been prepared by various reactions, and their properties well ascertained.

Phosphorus Diiodide, P_2I_4, was first prepared by fusing the constituents in equivalent proportions.[6] 50 grams of iodine and 4 grams of red phosphorus are melted in a flask and, after partial cooling, 2·5 grams of white phosphorus are added in small pieces.[7] Or, equal parts by weight of iodine and phosphorus are dissolved in carbon disulphide and the solution is cooled to 0° C., when the compound crystallises.[1] It has also been prepared by the action of iodine on phosphorous oxide :—

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[1] Prideaux, *loc. cit.*

[2] Ogier, *Compt. rend.*, 1881, 92, 85.

[3] Kastle and Beatty, *loc. cit.*

[4] Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 58.

[5] Besson, *loc. cit.*

[6] Gay-Lussac, *Ann. Chim. Phys.*, 1814, [1], 91, 5; Wurtz, *ibid.*, 1854, [3], 42, 129; *Compt. rend.*, 1854, 39, 335.

[7] Doughty, *J. Amer. Chem. Soc.*, 1905, 27, 1444.

$$5P_4O_6 + 8I_2 = 4P_2I_4 + 6P_2O_5 \ ^{2}$$

Properties.—Phosphorus diiodide forms orange-coloured crystals which belong to the triclinic system.[3] The analysis gave $(PI_2)_x$.[4] The vapour density, determined in the presence of nitrogen at a pressure slightly below 100 mm. and at 265° C., was between 18·0 and 20·2 (air = 1), which corresponds to a molecule P_2I_4.[5] At 15 mm. and 100° to 120° C. the compound dissociates into PI_3 and P.[6] The melting-point was given as about 110° C.[7] The heat of formation is given as

$$P + I_2 \text{ (solid)} = PI_2 + 9{\cdot}88 \text{ Cals.}^{8}$$

P_2I_4 can be ignited in a current of oxygen and burnt to phosphoric oxide and iodine. The hydrolysis appears somewhat complex and yields P, PH_3, HI and H_3PO_3.[9] The phosphine is a secondary product, since by gradual addition to water in the cold neither phosphine nor red phosphorus are formed :—

$$P_2I_4 + 5H_2O = 4HI + H_3PO_3 + H_3PO_2 \ ^{10}$$

P_2I_4 is soluble in CS_2 and slightly soluble in liquid H_2S. At about 100° C. it reacted with H_2S giving HI and a sulphoiodide $P_4S_3I_2$.[11]

Phosphorus Triiodide.—When solutions of iodine and phosphorus in CS_2, in the proportions of 3I to P, are mixed, a red colour appears and on cooling dark red needles separate.[12]

Other methods can be used. The action of hydrogen iodide on phosphorus trichloride either alone or in CCl_4 solution, or HI on $POCl_3$, also yields the triiodide.[6] Or, PI_3 can be separated from the products formed when PCl_5 is heated with PH_4I :—

$$3PCl_5 + 3PH_4I = PI_3 + PCl_3 + 12HCl + 4P \ ^{13}$$

Properties.—Phosphorus triiodide forms deep red tabular crystals belonging to the hexagonal system,[3] which melt at 55° to 61° C. The formula has been established by analysis [14] and by the vapour density, namely, 14·3 to 14·6 (air = 1) at 250° C. and reduced pressure. The heat of formation is slightly greater than that of the diiodide, thus :—

$$P + 1\tfrac{1}{2}I_2 \text{ (solid)} = PI_3 \text{ (solid)} + 10{\cdot}5 \text{ Cals.}^{15}$$

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[1] Corenwinder, *Ann. Chim. Phys.*, 1850, [3], 30, 342; *Annalen*, 1851, 78, 76.

[2] Thorpe and Tutton, *Trans. Chem. Soc.*, 1891, 59, 1022.

[3] Norderskjöld, *Bihang. Akad. Förh. Stockholm*, 1874, 2, 2.

[4] Corenwinder, *loc. cit.*

[5] Troost, *Compt. rend.*, 1882, 95, 293.

[6] Besson, *loc. cit.*

[7] Corenwinder, *loc. cit.*; Besson, *loc. cit.*; Fireman, *Amer. Chem. J.*, 1903, 30, 116.

[8] Ogier, *Compt. rend.*, 1881, 92, 83.

[9] Corenwinder, *loc. cit.*

[10] Gautier, *Compt. rend.*, 1874, 78, 286.

[11] Ouvrard, *Compt. rend.*, 1893, 115, 1301.

[12] Corenwinder, *loc. cit.*; Sesteni, *Gazzetta*, 1871, 1, 323; Traxler and Germann, *J. Physical Chem.*, 1925, 29, 1119.

[13] Fireman, *loc. cit.*

[14] Corenwinder, *loc. cit.*; Besson, *loc. cit.*

[15] Berthelot and Luginin, *Ann. Chim. Phys.*, 1878, [5], 15, 185; Ogier, *loc. cit.*

The surface tension of the liquid is 56·5 dynes/cm. at 75·3° C.[1] The dielectric constant is for the solid 3·66, for the liquid 4·12.[2]

Chemical Reactions.—The iodine can be replaced by chlorine, using either the gas itself or chlorides, such as those of mercuric mercury, arsenic, antimony and tin. A sulphoiodide is formed when the triiodide is heated with the trisulphide :—

$$2P_2S_3 + 2PI_3 = 3P_2S_2I_2$$

and the same compound may be produced by the action of hydrogen sulphide on the liquid triiodide :—

$$2PI_3 + 2H_2S = 4HI + P_2S_2I_2$$ [3]

Hydrolysis proceeded in the usual manner giving hydrogen iodide and phosphorous acid, but a solid product was formed at the same time.[4] The reaction with ethyl alcohol gave ethyl phosphorous acid as well as ethyl iodide :—

$$PI_3 + 3C_2H_5OH = 2C_2H_5I + OP(C_2H_5)(OH)_2 + HI$$ [5]

Like the other halides it reacted with anhydrous ammonia. If this was in the liquid form and below − 65° C. an amide was formed :—

$$15NH_3 + PI_3 = P(NH_2)_3 + 3NH_4(NH_3)_3I$$ [6]

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[1] Jager, *Zeitsch. anorg. Chem.*, 1917 101, 173.
[2] Schlundt, *J. Physical Chem.*, 1904, 8, 122.
[3] Ouvrard, *Ann. Chim. Phys.*, 1894, [7], 2, 221.
[4] Besson, *loc. cit.*; Corenwinder, *loc. cit.*
[5] Walker and Johnson, *Trans. Chem. Soc.*, 1905, 87, 1592.
[6] Hugot, *Compt. rend.*, 1905, 141, 1236.

CHAPTER VIII.

OXY- AND THIO-HALIDES.

OXY-HALIDES.

OXYFLUORIDES are the most stable of the oxyhalides, and the stability decreases with increasing atomic weight of the halogen. Special methods are used in the preparation of oxyfluorides, while the other oxyhalides can be prepared by general reactions, such as the partial hydrolysis of the pentahalides, or the oxidation of the trihalides. The compounds fume in the air and readily undergo further hydrolysis giving hydrogen halides and oxyacids of phosphorus.

Phosphorus Oxytrifluoride, POF_3.—The production of this compound by the partial hydrolysis of PF_5 or PF_3Cl_2 has already been mentioned. It may also be made by passing electric sparks through a mixture of PF_3 and oxygen. The first method of preparation consisted in heating phosphorus pentoxide with a fluoride, such as cryolite.[1] It is also produced by the action of hydrogen fluoride on phosphorus pentoxide.

It is best prepared by the action of silver, zinc or lead fluoride on $POCl_3$.[2, 3] The oxychloride is allowed to drop gradually on to anhydrous zinc fluoride in a brass tube at 40° to 50° C. The gas passes out through a lead tube, then through a condenser at $-20°$ C. to retain $POCl_3$, through a tube of zinc chloride to absorb the last traces of oxychloride, and finally is collected over mercury.

It is colourless, with a pungent odour, and fumes slightly in the air. The vapour density is 3·68 to 3·71 (air = 1) and 52·0 (H = 1),[4] the theoretical densities for POF_3 being 3·69 and 52·0 respectively. The gas condenses to a colourless liquid which boils at $-40°$ C. and freezes to a white solid at $-68°$ C. When dry it does not attack glass in the cold, but does so when heated, although not so strongly as phosphorus trifluoride. On the other hand, whilst the trifluoride was absorbed very slowly by water, the oxyfluoride was absorbed very quickly. Neither gas is completely hydrolysed, appearing to form fluooxyacids.

Fluophosphoric Acids.—Fluorine is pre-eminent among the halogens in its power of replacing oxygen of oxyacids to form fluoacids, as is exemplified by such well-known compounds as H_2SiF_6. Examples of fluoacids are also found among the more strongly electronegative elements of Group VI B, *i.e.* sulphur and its congeners.

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[1] Schulze, *Bull. Soc. chim.*, 1881, [2], 35, 173; Thorpe and Hambly, *Trans. Chem. Soc.*, 1889, 55, 759.

[2] Moissan, "*Le Fluor et ses Composés*," Steinheil, Paris, 1900.

[3] Guntz, *Compt. rend.*, 1886, 103, 58.

[4] Thorpe and Hambly, *loc. cit.*

In the case of phosphorus such compounds as $P(OH)_3OK.KF$ may perhaps be regarded as belonging to this type.[1]

It has already been noted that the hydrolysis of phosphoryl fluoride is not at first complete. It reaches a stage at which the addition of "nitron" (see this series, Vol. VI., Part I.) gives a salt, $C_{20}H_{16}N_4HPO_2F_2$ (m.pt. 230·5–232·5° C.), of *difluophosphoric acid*, $POF_2(OH)$. The ammonium salt of this acid has been prepared. The acid is also produced when phosphorus pentoxide is fused with ammonium fluoride, or when the pentoxide is dissolved in aqueous hydrofluoric acid.[2] The last-mentioned solution, when kept at the ordinary temperature, undergoes hydrolysis, and with "nitron" yields the "nitron" salt of *hexafluophosphoric acid*, HPF_6, the ions of which have also been prepared by dissolving phosphorus pentafluoride in cold water. The ions, PF_6^-, are stable towards boiling water. Solutions of the potassium salt do not give precipitates with salts of the alkaline earth metals.[3]

Phosphorus Oxychloride.—Phosphorus oxytrichloride or phosphoryl chloride, $POCl_3$, was early formed during investigations into the action of the pentachloride on substances containing the hydroxyl group.[4] It was also prepared by the oxidation of the trichloride by air, by oxygen, and by many oxidising agents, *e.g.* nitrogen trioxide.[5] It is also produced by the action of water in small proportion or acetic acid on PCl_3Br_2 [5] or by the action of chlorsulphonic acid on red phosphorus.[6]

Two convenient methods of preparation are as follows :—

(i) A current of chlorine is passed through phosphorus trichloride and water is added at the same time, drop by drop. The liquid is kept at its boiling-point, and is distilled at the end of the operation, which is signalised by the appearance of the pentachloride.[7]

(ii) 500 grams of PCl_3 (free from phosphorus) are placed in a tubulated retort having a capacity of 950 c.c. or more. 160 grams of potassium chlorate are added through the tubulure in lots of about 4 grams. The $POCl_3$ is then distilled :—

$$3PCl_3 + KClO_3 = 3POCl_3 + KCl$$ [8]

The $KClO_3$ should be dry and should previously be covered with some $POCl_3$ before adding to the PCl_3.[9] Dried oxalic acid may be used as the oxidising agent, the weight used being half that of the PCl_3.[10]

Phosphoryl chloride may be produced on a large scale by passing a mixture of chlorine and carbon monoxide over an intimate mixture of carbon and calcium phosphate (such as charred bone) at 330° to 340° C. :—[11]

$$Ca_3(PO_4)_2 + 2Cl_2 + 2CO = Ca(PO_3)_2 + 2CO_2 + 2CaCl_2$$
$$Ca(PO_3)_2 + 4Cl_2 + 4CO = 2POCl_3 + 4CO_2 + CaCl_2$$

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[1] Weinland and Alfa, *Zeitsch. anorg. Chem.*, 1899, 21, 43.
[2] Lange, *Ber.*, 1927, 60, [B], 962.
[3] Lange, *Ber.*, 1928, 61, [B], 799.
[4] Wurtz, *Ann. Chim. Phys.*, 1847, [3], 20, 472.
[5] Geuther and Michaelis, *Ber.*, 1871, 4, 766.
[6] Heumann and Köchlin, *Ber.*, 1882, 15, 416.
[7] Vauscheidt and Tolstapiatoff, *J. Russ. Phys. Chem. Soc.*, 1920, 52, 270.
[8] Dervin, *Compt. rend.*, 1883, 97, 576.
[9] Ullmann and Fornaro, *Ber.*, 1901, 34, 2172.
[10] Gerhardt, *Ann. Chim. Phys.*, 1853, [3], 37, 285; 1855, [3], 45, 102.
[11] Riban, *Compt. rend.*, 1882, 95, 1160.

By a similar reaction ferric phosphate is decomposed by carbonyl chloride at 300° to 400° C.[1]

Physical Properties.—Phosphoryl chloride is a colourless fuming liquid which resembles the trichloride in appearance but boils at a higher temperature, 107° C., and can easily be frozen to a solid which melts slightly above 0° C.

Analysis combined with determinations of vapour density led to the formula $POCl_3$.[2] According to the results of many investigators the density of the liquid at ordinary temperatures is slightly below 1·7. The exact experiments of Thorpe and Tutton gave the following results for the density at 0° C., 1·71165 to 1·71185 (1st series) and 1·71185 to 1·71190 (2nd series), and at the boiling-point, 107·23° C., 1·50967.[3] The specific volumes and thermal expansions between these temperatures are summarised by the formula [4]

$$v_t = v_0(1 + 0{\cdot}001064309t + 0{\cdot}0_5112666t^2 + 0{\cdot}0_85299t^3)$$

The liquid boils at 107·22° to 107·33° C. at 760 mm.[4] and at 104·5° to 105·5° C. at 783 mm.[5] It freezes at about −10° C. and the melting-point of the solid was +2° C.,[6] +1·78° C.[7] The critical temperature is 329° C.[8]

The surface tension, as determined by the capillary tube method, was given as 31·91 dynes/cm. at 18° C. and 28·37 at 46·1° C.[8] Hence the change of molar surface energy with the temperature is normal. This physical constant, together with some others, was determined in order to obtain the parachor [*P*]. The sample of $POCl_3$ had a boiling-point of 108·7° C. at 769 mm.

PARACHOR OF PHOSPHORUS OXYCHLORIDE.[9]

t° C. . .	15	49	65
D . .	1·690	1·626	1·596
σ . .	32·77	28·36	26·57
[P] . .	217·1	217·7	218·1

The dielectric constant of the oxychloride is 13·9 at 22° C.[10]

The heat of formation is nearly twice that of the trichloride and also greater than that of the pentachloride according to the equation

$$P\ (\text{solid}) + \tfrac{1}{2}O_2\ (\text{gas}) + 1\tfrac{1}{2}Cl_2\ (\text{gas}) = POCl_3\ (\text{liquid}) + 146{\cdot}0\ \text{Cals.},^{11}\quad 145{\cdot}9\ \text{Cals.}^{12}$$

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[1] du Pont de Nemours Cie, *U.S. Patent*, 1462732, 1923.

[2] Wurtz, *loc. cit.*; Cahours, *Ann. Chim. Phys.*, 1847, 20, 369.

[3] Thorpe, *Trans. Chem. Soc.*, 1880, 37, 141, 327; Thorpe and Tutton, *Trans. Chem. Soc.*, 1890, 57, 572; 1891, 59, 1019.

[4] Thorpe, *loc. cit.* See also under "Surface Tension."

[5] Ullmann and Fornaro, *loc. cit.*

[6] Besson, *Compt. rend.*, 1896, 122, 814.

[7] Oddo, *Atti R. Accad. Lincei*, 1901, [5], 10, i, 452.

[8] Ramsay and Shields, *Trans. Chem. Soc.*, 1893, 63, 1089.

[9] Sugden, Reed and Wilkins, *Trans. Chem. Soc.*, 1925, 127, 1525.

[10] Schlundt, *J. Physical Chem.*, 1902, 5, 157, 503.

[11] Thomsen, "*Therm. Untersuch.*," Leipzig, 1862.

[12] Berthelot, *Ann. Chim. Phys.*, 1879, [5], 16, 442; 1898, [7], 15, 185.

The heat of formation from the trichloride and oxygen is also considerable, thus

$$PCl_3 \text{ (liquid)} + \tfrac{1}{2}O_2 \text{ (gas)} = POCl_3 \text{ (liquid)} + 70{\cdot}66 \text{ Cals.}^1$$

The heat of hydrolysis with water is 74·7 Cals.[2] If much water is used the products are orthophosphoric and hydrochloric acids, but when the compound deliquesces in moist air pyrophosphoryl and metaphosphoryl chlorides (*q.v.*) are formed as intermediate products.[3] It is also hydrolysed by hydroxylated organic compounds and is much used for preparing chlorinated derivatives, *e.g.* C_2H_5Cl and CH_3COCl from C_2H_5OH and CH_3COONa respectively. By this means also alkyl chlorophosphates and alkyl phosphates can be prepared, *e.g.* :—

$$2C_2H_5OH + POCl_3 = POCl(OC_2H_5)_2 + 2HCl$$
$$POCl(OC_2H_5)_2 = C_2H_5Cl + PO_2(OC_2H_5)$$

The alcohol must be added drop by drop to the phosphoryl chloride cooled in an ice-salt mixture.[4] Sodium ethoxide yields triethyl phosphate :—

$$3C_2H_5ONa + POCl_3 = PO(OC_2H_5)_3 + 3NaCl \, ^5$$

The oxychloride is also hydrolysed by orthophosphoric acid, which is dehydrated to the meta-acid, and by phosphorous acid, which is dehydrated and oxidised to metaphosphoric acid, thus :—

$$2H_3PO_4 + POCl_3 = 3HPO_3 + 3HCl$$
$$2H_3PO_3 + 3POCl_3 = 3HPO_3 + 2PCl_3 + 3HCl \, ^6$$

When the oxychloride is treated with potassium chlorate the chlorine of the former is displaced by oxygen, according to the equation

$$2POCl_3 + KClO_3 = P_2O_5 + 3Cl_2 + KCl \, ^7$$

A similar displacement can be effected by sulphur trioxide, thus

$$2POCl_3 + 6SO_3 = P_2O_5 + 3S_2O_5Cl_2 \, ^8$$

Hydrogen sulphide gives a phosphorous oxysulphide, and, when the reaction is carried out at 100° C., an oxychlorosulphide to which the formula $P_2O_2SCl_4$ was assigned, and which could be distilled under reduced pressure.[9]

Phosphorus oxychloride chlorinates the oxides of several non-metals. The chlorides produced may form addition compounds with excess of the oxychloride: thus $SeOCl_2$ gave $SeCl_4$ and P_2O_5;[10] TeO_2 gave $TeCl_4.POCl_3$;[11] B_2O_3 gave $BCl_3.POCl_3$ as well as BPO_4.[12] Other

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[1] Thomsen, *loc. cit.*

[2] Berthelot and Luginin, *Ann. Chim. Phys.*, 1875, [5], 6, 308.

[3] Besson, *Compt. rend.*, 1896, 122, 814; 1897, 124, 151, 763, 1099; 1901, 132, 1556.

[4] Balareff, *Zeitsch. anorg. Chem.*, 1917, 99, 187.

[5] Geuther and Brockhoffs, *J. prakt. Chem.*, 1873, [2], 1, 101.

[6] Geuther, *Annalen*, 1862, 123, 113.

[7] Spring, *Ber.*, 1874, 7, 1584.

[8] Michaelis, *Jena Zeit.*, 1870, [1], 6, 86.

[9] Besson, *loc. cit.*; Carius, *Annalen*, 1858, 106, 326.

[10] Michaelis, *Jena Zeit.*, *loc. cit.*

[11] Lenher, *J. Amer. Chem. Soc.*, 1908, 30, 737.

[12] Gustavson, *Zeitsch. Chem.*, 1871, [2], 7, 417.

addition compounds are as follows :—$SbCl_5.POCl_3$; [1] $TiCl_4.2POCl_3$; [2] $TiCl_4.POCl_3$; [1] $AlCl_3.POCl_3$; [3] $SnCl_4.POCl_3$.[4]

Phosphorus oxychloride is a good solvent for various acid chlorides, bromides and iodides such as those of arsenic and antimony, for $VOCl_3$, S_2Cl_2 and halides of transitional elements such as $FeCl_3$ and $PtCl_4$. For this reason, and on account of its relatively high freezing-point, $POCl_3$ has been much used for the determination of molecular weights by the cryoscopic method.

Combination with dry ammonia in carbon tetrachloride gave a solid product which was said to be the hexammoniate, $POCl_3.6NH_3$,[5] while gaseous ammonia gave a white solid from which amides and aminochlorides were isolated.[6]

Metals with widely different electro-affinities ranging from the alkalies to silver and mercury were not found to be affected much in the cold, but when heated they gave oxides, chlorides and phosphides in various cases.

Addition compounds such as $CaO.2POCl_3$ and $MgO.3POCl_3$ were obtained by heating the constituents together.[7]

Pyrophosphoryl Chloride, *Diphosphorus trioxytetrachloride,* $P_2O_3Cl_4$.—This compound was first prepared by the action of N_2O_3 or N_2O_4 on PCl_3.[8] It is also produced as an intermediate product in the hydrolysis of $POCl_3$. Thus when $POCl_3$ is heated with a tenth of its weight of water in a sealed tube at 100° C. the three phosphoric oxychlorides (phosphoryl, pyrophosphoryl and metaphosphoryl) are present and may be separated by distillation *in vacuo.*[9] Phosphorus pentachloride (2 mols.) and water (3 mols.) also gave this oxychloride when heated to 126° C. under pressure.[10] When separated by fractional distillation under reduced pressure from $POCl_3$, which is more volatile, and PO_2Cl, which is less volatile, the pyro-compound appeared as a colourless fuming liquid which had a much lower freezing-point and a higher boiling-point than $POCl_3$. At ordinary pressures it distilled with decomposition. The analysis agreed with the empirical formula given.[11]

The density is about 1·58.[12] The freezing-point is below $-50°$ C.,[9] the boiling-point 210° to 215° C.[12]

The liquid distils with some decomposition, which may be expressed by the equation

$$3P_2O_3Cl_4 \rightleftharpoons 4POCl_3 + P_2O_5$$

The reaction must be reversible since $P_2O_3Cl_4$ has been obtained by the interaction of the compounds on the right-hand side.[13]

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[1] Weber, *Annalen*, 1867, 132, 452.

[2] Ruff and Ipsen, *Ber.*, 1903, 36, 1783.

[3] Oddo and Tealdi, *Gazzetta*, 1903, 33, ii, 427.

[4] Casselmann, *J. prakt. Chem.*, 1856, [1], 69, 19.

[5] Perpérot, *Compt. rend.*, 1925, 181, 662.

[6] Wurtz, *Compt. rend.*, 1847, 24, 288; Schiff, *J. prakt. Chem.*, 1857, [1], 71, 161; *ibid.*, [1], 72, 331; Gladstone, *Trans. Chem. Soc.*, 1851, 3, 5, 135, 353.

[7] Bassett and Taylor, *Trans. Chem. Soc.*, 1911, 99, 1402.

[8] Geuther and Michaelis, *Ber.*, 1871, 4, 766.

[9] Besson, 1897, *loc. cit.*

[10] Oddo, *Gazzetta*, 1899, 29, ii, 330.

[11] Geuther and Michaelis, *loc. cit.*; Oddo, *loc. cit.*; Huntly, *Trans. Chem. Soc.*, 1891, 59, 202.

[12] Geuther and Michaelis, *loc. cit.*

[13] Huntly, *loc. cit.*

By the action of PCl_5 the ordinary oxychloride is regenerated, thus

$$P_2O_3Cl_4 + PCl_5 = 3POCl_3$$

PBr_5 reacts in a similar manner with the production of an oxychlorobromide, thus

$$P_2O_3Cl_4 + PBr_5 = 2POBrCl_2 + POBr_3$$

Hydrolysis leads to the same final products as are formed in the hydrolysis of $POCl_3$. Pyrophosphoryl chloride also acts in a similar way with organic compounds containing the hydroxyl group giving, *e.g.*, ethyl esters of phosphoric and chlorophosphoric acids.

Addition compounds with lime, magnesia and several other basic oxides were formed in organic solvents such as acetone, or ethyl acetate and other esters, and appeared as crystalline substances, associated usually with two molecules of the solvent, *e.g.* $CaO.P_2O_3Cl_4.2(CH_3)_2CO$.[1]

Metaphosphoryl Chloride, PO_2Cl, was prepared by heating P_2O_5 with $POCl_3$ in a sealed tube at 200° C. for 36 hours, thus

$$P_2O_5 + POCl_3 = 3PO_2Cl$$ [2]

and also by the slight hydrolysis of $POCl_3$ in moist air. Being the least volatile of the chlorides of phosphoric acid it is found in the residues after the others have been fractionally distilled. It has been made in several other ways, including the regulated action of chlorine gas on phosphorous oxide :—

$$4Cl_2 + P_4O_6 = 2POCl_3 + 2PO_2Cl$$ [3]

It is a syrupy liquid which decomposes into P_2O_5 and $POCl_3$ when heated.

Phosphoryl Monochloride, POCl, an oxy-derivative of trivalent phosphorus, is reported as having been produced by the partial hydrolysis of phosphorus trichloride, the excess of which was distilled off under reduced pressure. The residue was a waxy mass with a pungent odour, and dissolved in water with great energy.[4]

Phosphoryl Dichlorobromide, $POCl_2Br$, was made by passing a mixture of HBr and the vapour of $POCl_3$ through a glass tube at 400° to 500° C.,[5] and also by the action of PBr_5 on $P_2O_3Cl_4$ (*q.v.*). A good yield is obtained from the halogenated alkyl derivatives. Phosphoryl ethyl dichloride when treated with bromine gives ethyl bromide and $POCl_2Br$.[6] Phosphoryl ethoxydichloride, which may be obtained from alcohol and $P_2O_3Cl_4$, is acted upon by PBr_5 according to the equation

$$PO(OC_2H_5)Cl_2 + PBr_5 = POCl_2Br + POBr_3 + C_2H_5Br$$ [7]

The formula was established by analysis and by the determination of vapour density.[6] The density is 2·12065 at 0° C. and 1·83844 at the boiling-point, 137·6° C. The coefficient of expansion is expressed by the equation [1]

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[1] Bassett and Taylor, *loc. cit.*

[2] Gustavson, *Ber.*, 1871, 4, 853.

[3] Thorpe and Tutton, *Trans. Chem. Soc.*, 1890, 57, 572.

[4] Besson, *Compt. rend.*, 1897, 125, 171.

[5] Besson, *Compt. rend.*, 1896, 122, 814.

[6] Menschutkin, *Annalen*, 1866, 139, 343.

[7] Geuther and Michaelis, *loc. cit.*; Geuther and Hergt, *Jena Zeit.*, 1876, [2], 3, ii, 104.

$$v_t = v_0(1 + 0{\cdot}00100518t + 0{\cdot}0_6 49053t^2 + 0{\cdot}0_8 44065t^3)$$

The solid melts at 11° to 13° C.[2]

The chemical properties are similar to those of $POCl_3$. When heated the compound dissociates into $POCl_3$ and $POBr_3$.

Phosphoryl Chlorodibromide, $POClBr_2$, was prepared by the action of HBr on $POCl_3$. It melts at about 30° C. and boils at 150° to 160° C. The chemical properties are similar to those of $POCl_2Br$.

Phosphoryl Tribromide, $POBr_3$, is produced by reactions analogous to those which are used in the preparation of phosphorus oxychloride—(*a*) By the gradual hydrolysis of the pentabromide.[3] (*b*) By the oxidation of the tribromide at its boiling-point with oxygen,[4] or in the cold with oxides of nitrogen.[5] (*c*) By the mutual action between P_2O_5 and PBr_5 according to the equation

$$P_2O_5 + 3PBr_5 = 5POBr_3$$ [6]

(*d*) By the oxidation of P_4O_6 with Br_2, thus

$$P_4O_6 + 4Br_2 = 2POBr_3 + 2PO_2Br$$ [7]

Properties.—Phosphoryl bromide is a solid which crystallises in colourless plates. The formula was established by analysis and vapour density.[8] The molecular weight as determined by the cryoscopic method is 300 in benzene.[9] The density of the solid is given as 2·822.[10] The melting-point is given as 45° C.,[11] 56° C.[12] The boiling-point is 193° C. (758 mm.)[13] or 198° C. (760 mm.).[7] As would be expected, the heat of formation from its elements is considerably less than that of $POCl_3$, and is given by the equation

$$\text{P (solid)} + \tfrac{1}{2}O_2 + 1\tfrac{1}{2}Br_2 \text{ (gas)} = POBr_3 \text{ (solid)} + 120 \text{ Cals.}^{14}$$
$$\text{or } +120{\cdot}75 \text{ Cals.}^{6}$$
$$\text{P (solid)} + \tfrac{1}{2}O_2 + 1\tfrac{1}{2}Br_2 \text{ (liquid)} = POBr_3 \text{ (solid)} + 108 \text{ Cals.}^{14}$$
$$\text{or } +109{\cdot}65 \text{ Cals.}^{6}$$

The heat of oxidation of PBr_3 was found to be slightly less than that of PCl_3, and is given by the equation

$$PBr_3 + \tfrac{1}{2}O_2 = POBr_3 \text{ (solid)} + 64{\cdot}88 \text{ Cals.}^{6}$$

Hydrolysis follows the usual course, and the heat evolved per mol of $POBr_3$ hydrolysed was 75 Cals.[1] The action of hydrogen sulphide on the tribromide is described on p. 101.

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[1] Thorpe, 1880, *loc. cit.*

[2] Geuther and Michaelis, *loc. cit.*; Besson, *loc. cit.*

[3] Gladstone, *Phil. Mag.*, 1849, [3], 35, 345.

[4] Demole, *Arch. Sci. phys. nat.*, 1880, [3], 4, 204.

[5] Geuther and Michaelis, *Ber.*, 1871, 4, 766.

[6] Berger, *Compt. rend.*, 1908, 146, 400.

[7] Thorpe and Tutton, *loc. cit.*

[8] Ritter, *Annalen*, 1855, 95, 210; Gladstone, *loc. cit.*; Baudrimont, *Compt. rend.*, 1861, 53, 637; *Ann. Chim. Phys.*, 1864, [4], 2, 58; Berger, *loc. cit.*

[9] Oddo and Tealdi, *Gazzetta*, 1903, 33, ii, 435.

[10] Ritter, *loc. cit.*

[11] Ritter, *loc. cit.*; Thorpe and Tutton, *Trans. Chem. Soc.*, 1891, 59, 1019.

[12] Besson, *Compt. rend.*, 1890, 111, 972; Berger, *loc. cit.*

[13] Walden, *Zeitsch. anorg. Chem.*, 1900, 25, 211.

[14] Ogier, *Compt. rend.*, 1881, 92, 85.

Metaphosphoryl Bromide, PO_2Br, was found as a less volatile part of the products of the action of bromine on phosphorous oxide.[2]

Oxyiodides.—A crystalline substance having the formula $P_3I_6O_8$ was found amongst the residues from the preparation of ethyl iodide. It formed red crystals which melted at 140° C. and were soluble in water and in ether.[3]

THIO-HALIDES.

Phosphorus Thiotrifluoride or *thiophosphoryl fluoride,* PSF_3, was first prepared by heating a mixture of phosphorus and sulphur with an excess of lead fluoride in a lead tube to 250° C. and leading over the mixture a current of dry nitrogen. The gas was purified by standing for about a day over dry lime. It was also prepared by heating arsenic trifluoride in a sealed tube with phosphorus thiotrichloride :—[4]

$$AsF_3+PSCl_3=PSF_3+AsCl_3$$

It is a transparent and colourless gas, which has no action on glass at ordinary temperatures. The formula has been established by analysis and from the vapour density. The compound is decomposed by heat, giving sulphur and fluorides of phosphorus, thus :—

$$PSF_3=PF_3+S$$
$$5PF_3=3PF_5+2P$$

It burns in air with a blue or greyish-green low-temperature flame. The white fumes which are produced contain P_2O_5. The sulphur probably burns first, leaving PF_3, which combines with more oxygen, giving PF_5 and P_2O_5, the whole reaction being summarised by the equation

$$10PSF_3+15O_2=6PF_5+2P_2O_5+10SO_2$$

With moist oxygen in closed vessels the reaction may proceed explosively, but it does not proceed at all when the gas and the oxygen are intensively dried. The gas was slowly absorbed and hydrolysed by water, more rapidly by alkalies, thus :—

$$PSF_3+4H_2O=H_2S+3HF+H_3PO_4$$
$$PSF_3+6NaOH=Na_3PSO_3+3NaF+3H_2O$$

Phosphorus Thiotrichloride or *thiophosphoryl chloride,* $PSCl_3$, has been prepared by many reactions :—

(*a*) The first method, which led to the discovery of this compound, was by the action of H_2S on PCl_5, with elimination of HCl, thus :—

$$H_2S+PCl_5=PSCl_3+2HCl$$ [5]

The H_2S may be supplied in the liquid form.[6]

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[1] Berger, *loc. cit.*
[2] Thorpe and Tutton, *loc. cit.*
[3] Burton, *Amer. Chem. J.*, 1881, 3, 280.
[4] Thorpe and Rodger, *Trans. Chem. Soc.*, 1888, 53, 766; 1889, 55, 306.
[5] Sérullas, *Ann. Chim. Phys.*, 1829, [2], 42, 25.
[6] Ralston and Wilkinson, *J. Amer. Chem. Soc.*, 1928, 50, 258.

(*b*) Some sulphides of the non-metals yield their sulphur to PCl_5 in exchange for chlorine :—

$$CS_2 + 2PCl_5 = 2PSCl_3 + CCl_4 \text{ }^1$$
$$P_2S_5 + 3PCl_5 = 5PSCl_3 \text{ (in a sealed tube at 120°) }^2$$

Compare also :

$$Sb_2S_3 + 3PCl_5 = 2SbCl_3 + 3PSCl_3 \text{ }^3$$

(*c*) Sulphur combines directly with PCl_3 in a sealed tube at 130° C. :—

$$PCl_3 + S = PSCl_3 \text{ }^4$$

(*d*) Sulphur monochloride combines when heated with phosphorus, thus :—

$$2P + 3S_2Cl_2 = 2PSCl_3 + 4S \text{ }^5$$

(*e*) Sulphur monochloride reacts with phosphorus trichloride in the presence of iodine, thus :—

$$3PCl_3 + S_2Cl_2 = 2PSCl_3 + PCl_5 \text{ }^6$$

(*f*) Thionyl chloride when heated with tetraphosphorus decasulphide in a closed tube at 100° to 150° C. reacts according to the equation

$$P_4S_{10} + 6SOCl_2 = 4PSCl_3 + 3SO_2 + 9S \text{ }^7$$

Properties.—Thiophosphoryl chloride is a transparent colourless liquid which fumes in the air and smells of hydrogen sulphide. The formula has been established by analysis and vapour density determination. The density of the liquid is 1·66820 at 0° C. and 1·45599 at the normal boiling-point, 125·12° C.[8] The coefficient of expansion between these temperatures is given by [8]

$$v_t = v_0(1 + 0{\cdot}0_3 99011t + 0{\cdot}0_6 90302t^2 + 0{\cdot}0_8 3825t^3)$$

The melting-point is −35° C.[9]

Thiophosphoryl chloride decomposes when passed through a red-hot tube, giving PCl_3, S and S_2Cl_2.[10] An excess of chlorine combines with both the other elements, according to the equation

$$2PSCl_3 + 3Cl_2 = 2PCl_5 + S_2Cl_2 \text{ }^{11}$$

The compound is reduced slowly by hydrogen iodide, giving PI_3, H_2S, HCl and sulphides of phosphorus.[12] Like other halides of phosphorus it combines with dry ammonia, giving a white solid, which may contain from 30 to 60 per cent. of NH_3. This product is said to contain thio-

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[1] Rathke, *Zeitsch. Chem.*, 1870, [2], 6, 57; Hofmann, *Annalen*, 1860, 115, 264.

[2] Thorpe, *Trans. Chem. Soc.*, 1880, 37, 327; Weber, *J. prakt. Chem.*, 1859, [1], 77, 65.

[3] Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 8.

[4] Henry, *Ber.*, 1869, 2, 638.

[5] Wohler, *Annalen*, 1855, 93, 274.

[6] Kohn and Ostersetzer, *Zeitsch. anorg. Chem.*, 1913, 82, 240.

[7] Prinz, *Annalen*, 1884, 223, 368.

[8] Thorpe, 1880, *loc. cit.*

[9] Besson, *Compt. rend.*, 1896, 123, 884.

[10] Chevrier, *Compt. rend.*, 1869, 68, 1174.

[11] Baudrimont, *loc. cit.*

[12] Besson, *Compt. rend.*, 1896, 122, 1057; 123, 884.

phosphoryl diaminochloride, $P(NH_2)_2ClS$, or thiophosphoryl triamine, $P(NH_2)_3S$.[1]

Thiophosphoryl chloride dissolves sulphur and phosphorus freely when hot, but only sparingly when cold.[2] Since the liquid is immiscible with water the hydrolysis proceeds only on the surface at first, as is usual with phosphorus halides. In this case the products are phosphoric acid, hydrogen chloride and sulphide and a little sulphur. It reacts with ethyl alcohol, giving ethyl chloride and ethyl thiophosphate:

$$3C_2H_5OH + PSCl_3 = (C_2H_5)H_2PSO_3 + 2C_2H_5Cl + HCl$$ [3]

Thiophosphates can also be made from the thiochloride with sodium ethoxide and aqueous alkalies.[3]

Phosphorus Thiotribromide, $PSBr_3$, has been prepared in a number of different ways :—

(i) By the action of phosphorus pentabromide on hydrogen sulphide, according to the equation

$$PBr_5 + H_2S = PSBr_3 + 2HBr$$ [4]

(ii) By distillation of the tribromide with sulphur.

(iii) By combination of the pentabromide with the pentasulphide :—

$$P_2S_5 + 3PBr_5 = 5PSBr_3$$ [5]

The product may be freed from pentabromide by washing with warm water and dried by dissolving in CS_2 and standing over $CaCl_2$.[6]

(iv) By a reaction between ammonium trithiophosphate and hydrogen bromide.[7]

Properties.—The compound crystallised from carbon disulphide in yellow octahedra, having a density of 2·7 to 2·87 and a melting-point of +36·4° to +39° C. It gives off a pungent vapour, and distils at about 212° C. with some decomposition at first into PBr_3, then $PSBr_3$ follows, and finally there is a residue of sulphur and phosphorus.[8] It is only slightly hydrolysed by water even at 100° C., the products being phosphoric acid, hydrogen bromide and some sulphide, together with some sulphur and phosphorous acid. Alcoholysis is said to yield ethyl thiophosphate, $(C_2H_5)_3PSO_3$.[9]

Thiophosphoryl bromide dissolves sulphur and mixes with other halides such as phosphorus trichloride, also with ether, chloroform and carbon disulphide.[10]

Several other thiobromides of phosphorus have been prepared, which can be regarded as derivatives of pyrophosphoric acid. *Diphosphorus monothiohexabromide*, P_2SBr_6, is prepared by distilling $PSBr_3$, and appears as a yellow oil which can be solidified to crystals melting at −5° C. The boiling-point is 205° C. When mixed with water it gives a crystalline hydrate melting at +35° C. $P_2S_3Br_4$ (*diphosphorus*

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[1] Gladstone and Holmes, *Trans. Chem. Soc.*, 1865, 18, 1; Chevrier, *loc. cit.*

[2] Sérullas, *loc. cit.*

[3] Cloez, *Compt. rend.*, 1857, 44, 482.

[4] Gladstone, *Trans. Chem. Soc.*, 1851, 3, 5; Baudrimont, *loc. cit.*

[5] Michaelis, *Annalen*, 1872, 164, 39.

[6] MacIvor, *Chem. News*, 1874, 29, 116; Michaelis, *Ber.*, 1871, 4, 777; *Annalen*, 1872, 164, 44.

[7] Stock, *Ber.*, 1906, 39, 1975, 1998.

[8] MacIvor, Michaelis, Baudrimont, *loc. cit.*

[9] Michaelis, *loc. cit.*

[10] MacIvor, *loc. cit.*

trithiotetrabromide) is prepared by the action of bromine on P_4S_6 dissolved in carbon disulphide. In appearance and properties it is very similar to the other thiobromides.[1]

Mixed Thiotrihalides, $PSClBr_2$ and $PSCl_2Br$, have been prepared by passing a mixture of $PSCl_3$ and HBr over pumice at 400° to 500° C., the products being separated by fractional distillation. Amongst these is also the starting material $PSCl_3$, which is formed in a sealed tube by the reaction:—

$$2PSCl_2Br = PSClBr_2 + PSCl_3$$ [2]

Thioiodides may be obtained by several methods :—

(i) By the interaction of the elements, in their correct proportions, in carbon disulphide.[3]

(ii) By the action of hydrogen sulphide on heated iodides of phosphorus, thus

$$2P_2I_4 + 3H_2S = P_4S_3I_2 + 6HI$$
$$2PI_3 + 2H_2S = P_2S_2I_2 + 4HI$$ [3]

These compounds are soluble in carbon disulphide, from which they may be obtained as orange or yellow crystals. They are only slightly soluble in other organic solvents such as benzene, chloroform, etc. They can be burnt in air, giving oxides of phosphorus, sulphur and iodine. They are decomposed by warm water or moist air, giving first phosphoric and hydriodic acids, then phosphoric acid and hydrogen sulphide.[4]

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[1] Michaelis, *loc. cit.*

[2] Besson, 1896, *loc. cit.*

[3] Ouvrard, *Compt. rend.*, 1902, 135, 1301.

[4] See also Wolter, *Chem. Zeit.*, 1907, 31, 640.

CHAPTER IX.

THE SLOW OXIDATION OF PHOSPHORUS.

The Glow of Phosphorus.—The similarity in appearance between the glow observed on the surface of phosphorus when exposed to air and that observed in the case of substances like commercial calcium and barium sulphides after exposure to light is of course only superficial. While the name " phosphorus " was soon restricted to the element, the term " phosphorescence " in its scientific usage now refers to photoluminescence, while the glow observed on smouldering phosphorus, or fish or wood in certain stages of decay, is called " chemiluminescence." The slow combustion of phosphorus is seen as a pale blue " cold flame " which continually spreads away from the surface and is associated with a peculiar smell. The volatile products are poisonous and consist of phosphorous oxide, and, in the presence of water, phosphorous acid. It was soon discovered that the presence of air was necessary—" the fire and flame of phosphorus have their pabulum out of the air " [1]—but low air pressures, such as remained in the best air pump vacua of the older experimenters, were still sufficient to maintain the glow, whereas the combustion of charcoal was completely extinguished. It follows that in the well-known lecture experiment the oxygen can be removed almost completely from the air by smouldering white phosphorus in the presence of water. The glow, however, is extinguished in pure oxygen at atmospheric pressure. Ozone is produced in the combustion and its presence may be demonstrated by the usual tests (see this Series, Vol. VII., Part I.). Since this striking phenomenon early challenged the attention of chemists it has been the subject of much investigation. Many of the qualitative effects were early demonstrated by Boyle.[2] The increase in luminosity when the air is rarefied was described by van Marum [3] and Davy.[4] A bibliography of the older literature is given in papers by Centnerszwer [5] and Downey.[6]

Effect of Pressure upon the Oxidation of Phosphorus.—At each temperature there is a certain critical pressure below which the glow appears. Also at each pressure (or partial pressure) of oxygen there is a certain critical temperature above which the glow appears.[7]

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[1] Slare, *Phil. Trans.*, 1681, 14, 48, 84.

[2] Boyle, "*Aerial Noctiluca*," London, 1680; "*Icy Noctiluca*," London, 1680.

[3] van Marum, *Ann. Chim. Phys.*, 1799, [1], 21, 158; *Phil. Mag.*, 1800, 8, 193, 313.

[4] J. Davy, *Edin. Phil. J.*, 1826, 15, 48.

[5] Centnerszwer, *Zeitsch. physikal. Chem.*, 1898, 26, 1.

[6] Downey, *Trans. Chem. Soc.*, 1924, 125, 347. See also Schönbein, *loc. cit.* p. 120, and Scharff, " *Ueber das Leuchten des Phosphors und einiger seiner Verbindungen*," Marburg, 1907.

[7] Schweigger, *Schweigger's J.*, 1824, 40, 16.

Thus the pressures had to be reduced below their critical values at the particular temperatures, or the temperatures had to be raised to their critical values at the particular pressures, in order to initiate the slow combustion. Some values of temperature and pressure are:—[1]

t° C. .	1·4	3·0	5·0	8·9	11·5	14·2	19·2
p (mm.) .	355	387	428	519	580	650	760

As already stated, in ordinary moist oxygen or air the glow begins at very low pressures, increases to a maximum with pressure and then decreases, vanishing at an oxygen pressure of 600 to 700 mm.[2]

The limits of pressure within which the glow occurs have also been found by means of a photoelectric counter of the Geiger-Muller type.[3] A quartz tube was coated inside with a thin film of platinum which acted as a photoelectric emitter. Along the axis of the tube ran an insulated tungsten wire which was connected to the earthed positive terminal of a 1200–1500-volt battery. The tube was filled with air at a pressure of 4·7 cm. mercury. The upper threshold of the radiation to which the counter was sensitive was at 2800 Å. As is seen on p. 124 radiations of lower wavelength are emitted by phosphorus glow. Under the influence of these a photoelectron is emitted which ionises the air by collision, causing a drop of potential of the wire, which acts on the grid of an amplifying valve and is recorded as an impulse on a standard recorder of the telephone type. A residual effect of 10–15 impulses per minute due to cosmic ray was constantly present. This number was greatly increased when the wire was surrounded by oxygen and phosphorus vapour at glow pressures, and began to be marked between pressures which gave a yellow and those which gave a bluish glow. The lower limit was found to be 0·3 mm. of mercury and the upper 595 mm. when the oxygen was pure, or 400 mm. when the oxygen was mixed with nitrogen. It was considered that these results were best interpreted by the " chain reaction " theory, as proposed by Semenoff.[4] The oxide is built up by a series of stages, some of which result in the production of an active molecule, thus:—

$$O + P_4 \longrightarrow P_4O', \quad P_4O' + O_2 \longrightarrow P_4O + O + O, \quad P_4O' + O \longrightarrow P_4O_2,$$
$$P_4O_2 + O_2 \longrightarrow P_4O_4 \xrightarrow[+O_2]{} P_4O_6 \xrightarrow[+O_2]{} P_4O_8 \xrightarrow[+O_2]{} P_4O_{10}'$$

In these expressions only some of the active products (marked ′) have been included. Radiation is associated with the spontaneous deactivation of an active product according to (2) below, if it does not happen to activate a molecule of oxygen according to (1):—

$$P_4O_{10}' + O_2 \longrightarrow P_4O_{10} + O + O \quad . \quad . \quad . \quad (1)$$
$$P_4O_{10}' \longrightarrow P_4O_{10} + h\nu \quad . \quad . \quad . \quad (2)$$

h and ν have their usual meaning of Planck's constant and the frequency of the radiation.

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[1] Joubert, *Compt. rend.*, 1874, 78, 1853.
[2] Muller, *Ber.*, 1870, 3, 84; Joubert, *loc. cit.*
[3] Ouellet, *Trans. Faraday Soc.*, 1933, 29, 486.
[4] Semenoff, *Zeitsch. Physik*, 1927, 46, 109.

Velocity of the Reaction.—Quantitative determinations of the velocity of oxidation have been based on the diminution in pressure which follows on absorption of oxygen. This became appreciable, with appearance of glow, at about 700 mm. oxygen pressure.

The rate of oxidation, calculated from the rate of decrease of pressure in a constant volume, at first increases rapidly as the pressure falls, reaches a maximum at about 300 mm., and then falls slowly to 100 mm. Below 100 mm. the rate diminishes rapidly with further decrease of pressure.[1]

The velocity constant K of a unimolecular reaction, *i.e.*

$$K = \frac{1}{t} \log \frac{p}{p_t}$$

(p and p_t are the partial pressures of the oxygen at the beginning and after the lapse of t minutes) is given in the following table:—[2]

RATE OF ABSORPTION OF OXYGEN IN MOIST AIR BY PHOSPHORUS.

Time in Minutes.	Total Pressure in mm. of Mercury.	Partial Pressure of Oxygen.	K.	K_1.
0	773·1	157·8	..	..
25	750·6	135·3	0·00267	42·0
50	729·7	114·0	0·00282	43·1
75	714·3	99·0	0·00271	40·1
100	697·4	82·1	0·00284	42·3
130	682·2	66·9	0·00286	42·1

The constant K increases on the whole with time (although somewhat irregularly), showing that the reaction takes place somewhat faster at a lower pressure than would be expected assuming that it is directly proportional to the partial pressure of the oxygen. Since the reaction takes place between the phosphorus vapour and the oxygen, the reason for the increase in the constant was sought in the increased rate of evaporation of the element at the lower pressures. A correction was introduced for the vapour pressure p_1 of the phosphorus in the form—

$$-\frac{dp}{dt} = K_1 p \times \log \frac{P}{P - p_1} \quad . \quad . \quad . \quad (1)$$

in which P is the total pressure. The integration of this equation gave the corrected constants K_1 in the above table. The results given above refer to air or oxygen in its usual state, *i.e.* slightly moist, and apply also when the air has been partly dried, as by bubbling through concentrated sulphuric acid, which still leaves enough water vapour for the continuance of slow oxidation.[1] If, however, the air or oxygen is carefully dried, the velocities at all pressures are much lower, and are between 0 and 70 mm. proportional to the square roots of the oxygen pressures. The maximum velocity of oxidation is also attained at a lower pressure (about 100 mm. of oxygen) and the upper limit of chemiluminescence is found at lower pressures, *i.e.* at about 200 mm. of oxygen.[2] If the oxygen is quite dry, no combustion takes place, no glow is seen and no ozone is formed—the production of ozone and hydrogen peroxide is due to the presence of moisture.[3]

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[1] Ewan, *Zeitsch. physikal. Chem.*, 1895, 16, 315; idem, *Phil. Mag.*, 1894, [5], 38, 305, 512.

[2] Ikeda, *J. Coll. Sci. Imp. Univ. Japan*, 1893, 6, 43; "*Studies in Chemical Dynamics*," van't Hoff-Cohen, translated by Ewan, Williams & Norgate, 1896.

The results in the table may be summarised in the statement that from low pressures up to a certain limiting pressure the velocities are proportional to the oxygen pressure and are also a function of the rate of supply of vapour from the surface of the phosphorus. In fact, if in the equation on p. 118, $\frac{dp/dt}{\log P/(P - p_1)}$ is plotted against p, the graph is rectilinear from the lowest value of oxygen pressure up to 520 mm., then rapidly decreases to zero at 700 mm.

Low Pressures.—The velocity of oxidation of phosphorus vapour at low pressures has been further investigated by Semenoff,[4] who found that an inert gas increases the reaction velocity and lowers the lower critical oxidation pressure. The subject was taken up at this point by Melville.[5]

According to Semenoff[6] "if p_{P_4}, p_{O_2} and p_x are the pressures of phosphorus, oxygen and inert gas respectively, then, at the lower explosion limit

$$p_{P_4} \times p_{O_2}\left(1 + \frac{p_x}{p_{P_4} + p_{O_2}}\right) = \text{constant} \quad . \quad . \quad (1)$$

provided that the explosions are confined to a vessel of a given size. Now (1) indicates that the inert gas effect should be independent of the nature of the gas. Subsequent work[7] has shown that (1) does not describe exactly the effect of gases on the lower critical oxidation limit of phosphorus. From (1) it is seen that if $1/p_{O_2}$ is plotted against $1 + p_x/(p_{P_4} + p_{O_2})$, a straight line is obtained. The slope A of this line is, however, dependent on the nature of x."

The critical pressure or glow pressure is affected by the presence of inhibitors (see p. 121).

The explanation why such a complicated reaction as the slow oxidation of phosphorus appears to be unimolecular is one which has often been brought forward in similar cases. The slowest part of the process is a diffusion, either of oxygen molecules to the reaction surface, or of phosphorus molecules from the surface, or of the inhibiting molecules of phosphorus oxide from the surface. According to the theory of diffusion the rates will follow the unimolecular law. Since the vapour pressure of phosphorus is low at ordinary temperatures, the concentration of oxygen molecules is many times greater than that of phosphorus molecules, even at the lower oxygen pressures.[1]

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[1] Russell, *Trans. Chem. Soc.*, 1903, 83, 1263.

[2] van't Hoff-Cohen, *loc. cit.*

[3] Baker, *Phil. Trans.*, 1888, 179, A, 571; Baker and Dixon, *Proc. Roy. Soc.*, 1889, 45, 1.

[4] Semenoff, *Zeitsch. Physik*, 1927, 46, 109; *Zeitsch. physikal. Chem.*, 1929, 2, B, 161.

[5] Melville, *Trans. Faraday Soc.*, 1932, 28, 308.

[6] *Loc. cit.*

[7] Melville and Ludlam, *Proc. Roy. Soc.*, 1931, 132, A, 108.

Phosphorus vapour when apparently inactive in an atmosphere of oxygen may really be combining with the oxygen at isolated centres, but the combination does not spread, on account of the inhibitory effect of the enormous excess of oxygen molecules.[2] The combination has obvious similarities to the combustion of hydrocarbons, etc., in air or oxygen, which, as is well known, is limited and finally inhibited by an excess either of the combustible substance or of oxygen. An excess of oxygen probably hinders the diffusion of phosphorus across the solid-gas interface on which a layer of vapour is continually being formed and removed. If the rate of formation of oxide (especially in a dry atmosphere) exceeds that of evaporation of the phosphorus, a protective coating of oxide will also inhibit further action.[3]

The products of oxidation have been investigated.[4] When the oxidation was carried out in moist air or oxygen the partial pressures of which were varied between 100 and 1200 mm. the product was a nearly constant mixture of the tetroxide and pentoxide. The empirical composition $PO_{2 \cdot 10}$ is nearly the same as that of the corresponding product derived from P_4O_6. It is considered that the phosphorus trioxide is formed as an intermediate stage which does not accumulate in the system.

Effect of Temperature.—The pressures corresponding to the maxima of chemiluminescence diminish with fall of temperature; at 0° C. the maximum oxygen pressure is 320 mm., while by extrapolation this pressure would become zero, and the effect vanish, at $-13 \cdot 8°$ C. The pressures at which the glow first appears also decrease with fall and increase with rise of temperature. At 27° C. the glow appeared in oxygen at atmospheric pressure.[3] At higher temperatures the velocity, as is usual, increases greatly, until at about 60° C. (or at lower temperature if pressure is reduced) the combustion changes its character, and the phosphorus ignites.[5]

Production of Ozone.—In the first definite description of ozone by Schönbein in 1840 the discoverer noted that this gas is produced by the slow oxidation of phosphorus [6] (see "Ozone," this Series, Vol. VII., Part I.).

It was observed later that half an atom of oxygen is activated for every atom of phosphorus which is oxidised.[7] This may be explained on the supposition that the reaction takes place in stages, thus :—[8]

$$2P + O_2 = P_2O + O$$
$$O + O_2 = O_3$$
$$P_2O + O_2 = P_2O_3$$

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[1] Chariton and Waltoa, *Zeitsch. Physik,* 1926, 39, 547.

[2] Rayleigh, "*Royal Institution Discourse,*" *Nature,* 1924, 114, 30; idem, *Proc. Roy. Soc.,* 1922, 104, A, 322.

[3] Weiser and Garrison, *J. Physical Chem.,* 1921, 25, 61, 349, 473.

[4] Miller, *Trans. Chem. Soc.,* 1929, p. 1829.

[5] Weiser and Garrison, *loc. cit.*; Eydmann, *Rec. Trav. chim.,* 1901, 19, 401.

[6] Schönbein, *J. prakt. Chem.,* 1868, 105, 226; 1864, 93, 25; and many references back to 1845; Macleod, *Trans. Chem. Soc.,* 1880, 37, 188; Kingzett, *ibid.,* 1880, 37, 392; Leeds, *Chem. News,* 1881, 43, 97; Chappuis, *Bull. Soc. chim.,* 1881, [2], 35, 419.

[7] Ostwald, *Zeitsch. physikal. Chem.,* 1900, 34, 248.

[8] Downey, *Trans. Chem. Soc.,* 1924, 125, 347.

The amount of ozone formed is proportional to the intensity of the glow, and is 0·5 to $5·0 \times 10^{-6}$ gram per c.c. of gas which passes over the phosphorus. The radiation from the glow has been proved capable of producing ozone.[1]

The effect of ozone is to raise the upper critical explosion limit for phosphorus and oxygen and to lower the lower limit.[2] The effect is much greater than that for an ordinary neutral gas (equation, p. 119). The presence of 5 per cent. of ozone in phosphorus vapour and oxygen diminishes the lower critical pressure by about 20 per cent., whereas the normal effect for an inert gas at this concentration would be 1 to 2 per cent.[3]

Inhibition of the Glow.—The following substances diminish or destroy the glow at ordinary temperatures, or allow it to appear only at higher temperatures—chlorine, iodine, nitrous and nitric oxides, hydrogen sulphide, sulphur dioxide, turpentine, alcohol, benzene, chloroform, aniline, ethylene, acetylene and other unsaturated hydrocarbons, and lead tetraethyl.[4, 5, 6] The glow is not diminished by nitrogen, sulphur, acetic acid, hydrogen chloride or ammonia in small quantities. Some of the inhibitors will combine with ozone, but it has been stated that their relative activity in inhibiting the glow is not the same as that shown in destroying ozone.[7]

The diminution in the rate of propagation of the glow was shown by measuring the velocity of an air current which was just sufficient to carry the glow to a point marked in a tube.[7] This method was also used in examining the effect of varying the partial pressures of oxygen in nitrogen.[8] In the presence of 0·16 per cent. of ethylene this velocity was 140 cm. per second, and when the percentage was increased to 0·43 the velocity required fell to 1 cm. per second. The temperature at which the glow is first seen increases with increasing concentration of ethylene, etc., and can be raised to well over 60° C., the normal ignition point of the phosphorus. When air containing 8 and 26 per cent. of ethylene was heated for long periods in contact with phosphorus a certain amount of non-luminous oxidation did occur. It has been shown further [9] that the partial pressure of the ethylene which will just inhibit the glow is proportional to the partial pressure of the phosphorus over the range 60° to 97° C.

Phosphorus trioxide itself inhibits the glow of phosphorus, being about three times as powerful in this respect as ethylene. The ratio of the partial pressure of trioxide to that of ethylene which just stops the glow [9] is about 145.

The inhibitory effect may also be expressed as a function of the "glow pressure" at which the glow can just be detected. An empirical equation was used by Tausz and Görlacher—[10]

$$p_x(x+a)=K$$

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[1] Downey, *loc. cit.*; Weiser and Garrison, *loc. cit.*

[2] Kowalski, *Zeitsch. physikal. Chem.*, 1929, 4, B, 288.

[3] Melville, *loc. cit.*

[4] v. Vogel, *Annalen*, 1814, 48, 375; *J. prakt. Chem.*, 1840, [1], 19, 394.

[5] Deschamps, *Compt. rend.*, 1861, 52, 355.

[6] Tyer, *Chem. News*, 1923, 127, 321; Chappuis, *loc. cit.*

[7] Emeléus, *Trans. Chem. Soc.*, 1926, p. 1336.

[8] Bloch, L. and E., *Compt. rend.*, 1908, 147, 842.

[9] Miller, *Trans. Chem. Soc.*, 1929, p. 1926.

[10] Tausz and Görlacher, *Zeitsch. anorg. Chem.*, 1930, 190, 95.

in which p_x represents the partial pressure of oxygen at which the glow appears, x is the percentage by volume of the inhibitor or anticatalyst and a and K are empirical constants for each substance. This equation holds for certain percentage admixtures in the case of each inhibitor—thus for 0·1 to 0·9 per cent. sulphur dioxide; for 2 to 10 per cent. benzene; for 0·01 to 0·1 per cent. isoprene; for 0·0$_4$6 to 0·0$_4$7 per cent. iron carbonyl. The corresponding values of the constants are as follows :—

	Sulphur Dioxide.	Benzene.	Isoprene.	Iron Carbonyl.
a	23	21	0·025	0·0033
K	13520	10805	20	1·7
$1/K$	0·0$_4$74	0·0$_4$93	0·05	0·59

The maximum pressure at which the glow will persist is lowered by these substances, and their activity in this respect is proportional to $1/K$. It is noteworthy that lead tetraethyl (p. 121) and iron carbonyl, which are known as "anti-knock" additions to petrol, are both very active inhibitors.

The results of these experiments lend support to the theory that oxidation probably takes place only in the gaseous phase and is catalysed by the active oxygen produced in the reaction.

Nature of the Chemiluminescence.—Many observations lead to the conclusion that the glow is produced by the combination of gases only. The glowing zone may be removed from the surface of the phosphorus by a current of air, leaving a dark space in the immediate neighbourhood of the phosphorus.[1]

The glow is exhibited by ordinary phosphorus trioxide,[2] but is then really due to small quantities of dissolved phosphorus. The oxide when purified as described on p. 126 gave only a momentary glow at the commencement of the oxidation (by oxygen), which afterwards proceeded without emission of light. The glow of phosphorus, which actually is inhibited by the trioxide, is restored continuously as this is hydrated by small amounts of water vapour.[3] The inhibitory effect of P_4O_6 is also removed by ozone.

Ionisation by the Glow.—Air which has been drawn over smouldering phosphorus is rendered electrically conducting, so that it allows an electroscope to discharge itself[4] whether it is positively or negatively charged; therefore gaseous ions of both signs are produced. These may be charged atoms, O^+ and O^-, one of which may combine with the phosphorus and the other form ozone.[5] The conductivity is not due to the ozone itself, since after removal of this, conductivity is retained.[1]

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[1] Bloch, L. and E., *Compt. rend.*, 1908, 147, 842.

[2] Scharff, *Zeitsch. physikal. Chem.*, 1908, 62, 179.

[3] Miller, *Trans. Chem. Soc.*, 1928, p. 1847

[4] Matteuci, *Compt. rend.*, 1851, 32, 145; 33, 663; Christomanos, *Zeitsch. anorg. Chem.*, 1905, 45, 132.

[5] See also Brodie, *Phil. Trans.*, 1850, 1862, 1863, 152, 407; Clausius, *Annalen*, 1858, 103, 644; 1864, 121, 250; Schönbein, *loc. cit.*; v. Helmholtz and Richarz, *Wied. Annalen*, 1890, 40, 161; Elster and Geitel, *Wied. Annalen*, 1890, 40, 191; *Physikal. Zeitsch.*, 1903, 16, 457; "*The Conduction of Electricity through Gases*," J. J. Thomson, Cambridge, 1903; Bloch, E., "*Récherches sur la conductibilité electrique de l'air produite par le phosphore et sur les gaz récemment préparés*," Paris, 1904; Bloch, E., *Ann. Chim. Phys.*, 1905, [8], 4, 25.

The fact that below 100 mm. the rate of oxidation is proportional to the square root of the partial pressure of oxygen suggests that the active atoms of oxygen are produced before the combination.[2] The difficulty in this supposition is that there is no apparent source of the high energy of activation required, which could, however, be drawn from a coupled reaction such as that formulated on p. 120, or from the formation and decomposition of a peroxide.[3]

It has been shown by numerous investigators that the connection between ionisation, oxidation and chemiluminescence is a close one. If air or oxygen is mixed with the vapours of turpentine, etc., the conductivity of the mixture after passing over the phosphorus is only slight, corresponding to the suppression of the glow.[4]

The mobilities of the positive and negative ions were found to be equal at first, but the mobilities and sizes change with time. Maxima and minima were found at different temperatures, including a maximum mobility just below the ignition temperature, at 40° C.[5]

Moisture is favourable, perhaps even essential, to the ionisation, which leads to the opinion that the conducting ions may be those of an acid.

The gases in flames are ionised as a rule, and it has been stated that the vivid combustion of phosphorus also gives rise to ionisation.[6]

One cause of the ionisation is indicated by the observation that the light from glowing phosphorus when transmitted through a window of fluorite, is capable of ionising air on the other side.[7] This proves that the light contains ultraviolet radiations.[8] This light also produces ozone.[9] Under otherwise similar conditions ozone is produced from oxygen in greater amount by light transmitted through a window of fluorite than by that transmitted through a window of quartz.[10] Now it is known that quartz (2 mm. thick) is weakly transparent to light of wavelength lower than 200 mμ and opaque to that of wavelength below 160 mμ; while fluorite is opaque to light of wavelength below 125 mμ. This, taken in conjunction with the observation[11] that light of wavelength 120 to 180 mμ is a strong ozonising agent, while that of wavelength 230 to 290, especially 257, decomposes ozone, explains the effect mentioned above.

The Emission Spectrum.—A spectroscopic examination of the light emitted by glowing phosphorus reveals a number of narrow bands in the ultraviolet at

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[1] Schmidt, H., *Physikal. Zeitsch.*, 1913, 14, 120.

[2] Loew, *Zeitsch. Chem.*, 1870, [2], 6, 65; Fudakowsky, *Ber.*, 1873, 6, 108.

[3] Ostwald, *loc. cit.*; Bach, *Compt. rend.*, 1897, 124, 951.

[4] Schenck, Banthien and Mihr, *Ber.*, 1906, 39, 1506; Richarz and Schenck, *Sitzungsber. K. Akad. Wiss. Berlin*, 1903, p. 1102; Schenck, *ibid.*, 1904, p. 37; Schenck and Breuning, *Ber.*, 1914, 47, 2601.

[5] Harries, *Physikal. Zeitsch.*, 1904, 5, 93; Busse, *Ann. Physik*, 1927, [4], 82, 873; 83, 80.

[6] Schmidt, G. C., *Ber. Deut. physikal. Ges.*, 1906, 4, 640; *Ann. Physik*, 1903, [4], 10, 704.

[7] Downey, 1924, *loc. cit.*

[8] Lenard, *Ann. Physik*, 1900, [4], 1, 486; Hughes, *Proc. Cam. Phil. Soc.*, 1910, 15, 483.

[9] Downey, *loc. cit.*; Weiser and Garrison, *loc. cit.*

[10] Downey, *loc. cit.*

[11] Regener, *Ann. Physik*, 1906, [4], 20, 1033.

$\lambda=3270$	2600	2530	2470	2390 Å.[1]
$\lambda=3275$	2630	2530	2475	2390 Å.[2]

The same bands are shown when phosphorus burns under reduced pressure with a flame which has a temperature of 125° C.[2] and in the glow of phosphorous oxide.[3] The broader bands which have been reported as present in the light from glowing phosphorus [4] have been shown to be due to incipient combustion ; [2] they are the same as those shown by phosphorus burning in air enriched with oxygen at a flame temperature of 800° C.[2] and by phosphine burning in air at reduced pressure with a flame temperature of 160° to 230° C., and also in oxygen at atmospheric pressure.[3] The bands have, in reality, a complex structure. Such spectra are associated with molecular rather than atomic vibrations. There must therefore be some excited system common in all these kinds of combustion. In this connection it was noted by Emeléus and Purcell [5] that the band at about $\lambda=3270$ had already been observed in the light emitted by phosphorus pentoxide when volatilised in an oxyhydrogen flame.[6]

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[1] Centnerszwer and Petrikaln, *Zeitsch. physikal. Chem.*, 1912, 80, 235.
[2] Emeléus and Downey, *Trans. Chem. Soc.*, 1924, 125, 2491.
[3] Emeléus, *ibid.*, 1925, 127, 1364.
[4] Petrikaln, *Zeitsch. Physik*, 1924, 22, 119.
[5] Emeléus and Purcell, *Trans. Chem. Soc.*, 1927, p. 788.
[6] Hartley, *Phil. Trans.*, 1894, 185, 168.

CHAPTER X.

THE OXIDES OF PHOSPHORUS.

PHOSPHORUS forms two well-defined oxides, namely, diphosphorus trioxide and diphosphorus pentoxide, having the empirical formulæ P_2O_3 and P_2O_5 respectively; an intermediate oxide, diphosphorus tetroxide, P_2O_4, and possibly the suboxides P_4O and P_2O, are known.

The Suboxides.—A solid substance said to be tetraphosphorus monoxide, or phosphorus tetritoxide, P_4O, has been prepared by a number of reactions, amongst which may be mentioned the slow oxidation of phosphorus in ether, and the reduction of phosphorus pentoxide with ammonia, followed by treatment to remove other oxides, namely, washing and evacuation.[1] The removal of water from hypophosphorous acid is said also to yield this product, thus

$$4H_3PO_2 = P_4O + O + 6H_2O$$ [2]

Acetic anhydride in the presence of glacial acetic acid has been used as the dehydrating agent.[3] A solution of phosphorus in 10 per cent. aqueous caustic soda with twice its volume of alcohol yielded on acidification a greenish-yellow solid to which the same composition was assigned.[2] The substance prepared by various methods has a red or orange colour and a density of about 1·9. It is a mixture, the composition of which may be inferred from the facts that it retains hydrogen and moisture, that it gives phosphorus and phosphorus pentoxide when heated in an indifferent gas, and that when distilled in chlorine it yields phosphorus oxychloride as well as the pentachloride.[4]

The supposed compound P_2O [5] is also a mixture of finely divided phosphorus with phosphorous acid.[6]

Phosphorus Trioxide.—The formation of an oxide by the slow combustion of phosphorus had already been noticed in the eighteenth century,[7] and the existence of such a compound was known to Lavoisier and Davy, while the conditions of formation and the composition were established by Dulong.[8]

The method of preparation by the slow oxidation of white phosphorus has already been described (Chap. IX.). When a current of dry air, or of oxygen, the pressure of which lies between certain limits, is passed over solid white phosphorus, this oxide is formed at a slow rate. At higher temperatures, at or above the melting-point of white phosphorus, the rate of formation is sufficiently great, but the product may contain less than 10 per cent. of phosphorous oxide, with nearly 80 per cent. of phosphoric oxide, and variable quantities of phosphorus remain unburnt in the form of the white mixed with the red element.[1] It is possible to separate the phosphorus pentoxide, as is done in the standard method due to Thorpe and Tutton,[2] according to which a rapid stream of dry air is passed over liquid phosphorus in a hard glass tube, which is connected with a brass tube containing a glass wool filter and maintained at about 60° C. by an external current of water. This tube retains the phosphorus pentoxide, while the trioxide passes on and is condensed in a U-tube which is immersed in a freezing mixture. The phosphorous oxide is melted and filtered into another U-tube. The further purification is described below.

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[1] Leverrier, *Ann. Chim. Phys.*, 1837, [2], 65, 257; Biltz, *Ber.*, 1894, 27, 1258.

[2] Michaelis and Pitsch, *Annalen*, 1900, 310, 45.

[3] Michaelis and von Arend, *Annalen*, 1901, 314, 259.

[4] Chapman and Lidbury, *Trans. Chem. Soc.*, 1899, 75, 973; Burgess and Chapman, *ibid.*, 1901, 79, 1235; Stock and Rudolph, *Ber.*, 1910, 43, 157.

[5] Besson, *Compt. rend.*, 1901, 132, 1556.

[6] Chalk and Partington, *Trans. Chem. Soc.*, 1927, p. 1930.

[7] le Sage, *Mém. Acad.*, 1777, p. 321.

[8] Dulong, *Ann. Chim. Phys.*, 1816, [2], 2, 141; *Phil. Mag.*, 1816, 48, 271.

Phosphorous oxide has also been prepared by the action of the trichloride on phosphorous acid, thus

$$H_3PO_3 + PCl_3 = P_2O_3 + 3HCl$$ [3]

It is also produced when phosphorus trichloride is used to replace the hydroxyl group of anhydrous acetic acid, thus

$$3CH_3COOH + 2PCl_3 = P_2O_3 + 3HCl + 3CH_3COCl$$ [4]

The trioxide sublimes as a mist of solid particles which are difficult to condense completely. The condensate forms a snow-like mass of minute crystals, or large feathery crystals, or a wax-like mass which is very fusible, deliquescent and inflammable. The vapour smells of garlic and is poisonous. The material contains small quantities, up to about 1 per cent., of phosphorus, droplets of which may appear in the later stages of the distillation. The complete removal is difficult, but the amount may be greatly reduced by the following method.[5] The trioxide is crystallised from dry carbon disulphide in an atmosphere of carbon dioxide at $-18°$ C. The crystals are filtered off on a perforated porcelain disc, washed with petroleum ether and recrystallised from carbon disulphide. These operations are carried out in an atmosphere of dry carbon dioxide. The purified oxide is analysed by melting under water at 40° to 50° C. It is completely absorbed, whereas the usual preparation, which is saturated with phosphorus at 25° C., shows a small residue of undissolved phosphorus under the same conditions. The solubility of phosphorus in the purified oxide at 25° C. is 1·7 grams in 100 grams. The solution on solidifying assumes the opaque waxy appearance characteristic of the ordinary preparation.

Physical Properties.—Most of the available data refer to the ordinary preparation.

Solid Phosphorus Trioxide.—The density ($D^{21°}_{4°}$) is 2·135.[6] The melting-point is 22·5° C.[1] The crystalline system is monoclinic.[2] When large crystals are examined in polarised light they may show pinacoid, prism and complementary pairs of pyramid faces. When the oxide is freed from all except traces of the dissolved phosphorus as just described, it appears as a transparent crystalline solid [3] and the physical properties are slightly modified; in particular, the melting-point was 23·8° C. instead of 22·4°.

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[1] Cowper and Lewes, *Trans. Chem. Soc.*, 1883, 43, 224; 1884, 45, 10.
[2] *Trans. Chem. Soc.*, 1890, 57, 543; 1891, 59, 1019.
[3] Kraut, *Annalen*, 1871, 158, 332; Gautier, *Compt. rend.*, 1873, 76, 49, 173.
[4] Thorpe, *Trans. Chem. Soc.*, 1880, 37, 186.
[5] Miller, *Trans. Chem. Soc.*, 1928, p. 1847.
[6] Thorpe and Tutton, *loc. cit.*

Liquid Phosphorus Trioxide.—The density of the slightly super-cooled liquid at 21° C. ($D^{21°}_{4°}$) is 1·9431 and that of the liquid at its boiling-point, 173·1° C., 1·6897. The smoothed values of the specific volume as derived from measurements in a dilatometer from 27·10° to 140·30° C. are as follows, and give the coefficient of expansion of the liquid up to its boiling-point:—

RELATIVE SPECIFIC VOLUMES OF PHOSPHORUS TRIOXIDE.[1]

t° C. .	25	30	50	75	100	125	150	170	173·1
v .	1·000	1·0046	1·0228	1·0459	1·0695	1·0941	1·1200	1·1419	1·1454

The vapour pressures of the liquid are as follows:—[4]

VAPOUR PRESSURES OF PHOSPHORUS TRIOXIDE.

t° C. .	22·4	30·8	40·8	50·0	64·4	72·7	91·2
p (mm.) .	2·7	4·1	6·0	9·5	18·4	50·8	297·9

A straight line is obtained by plotting log p against $1/T$ up to $T=336°$, and if this is produced it leads to a boiling-point under normal pressure of $T=458°$ C. abs. (*cf.* 446° above). The corresponding graph above 336° is also a straight line which, however, leads to a boiling-point of $T=374°$. It is considered that the measurements at higher temperatures are defective, probably owing to interaction of the trioxide and moisture, with production of phosphine.[5]

The refractive index of the liquid has been determined for several of the standard wavelengths in the visible spectrum:—

λ	670·5	589·2	434·0 mμ
n	1·5350	1·5403	1·5616

These and other results are represented by the dispersion formula [1]

$$n=1{\cdot}5171+817670\lambda^{-2}-31659070_7\lambda^{-4}$$

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[1] Thorpe and Tutton, *loc. cit.*

[2] Cabell, *Chem. News*, 1884, 50, 209; Thorpe and Tutton, *loc. cit.*

[3] Miller, *loc. cit.*

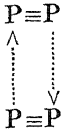
[4] Schenck, Banthien and Mihr, *Ber.*, 1906, 39, 1506.

[5] Miller, *Trans. Chem. Soc.*, 1929, p. 1823.

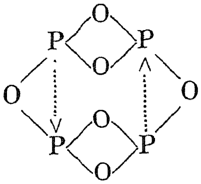
The dielectric constant at 22° C. is 3·2.

Composition and Structure.—The molecular weight and structure have been deduced in the usual manner from physical constants. The vapour density, as determined by Hofmann's method, varied between 7·67 and 7·83 (air = 1) at temperatures between 132° and 184° C., which corresponds to a molecular weight which is represented by the formula P_4O_6.[1] This agrees with the molecular weight calculated from the lowering of the freezing-point of benzene.

The molar volume at the boiling-point, 130·2, minus the atomic volumes of six singly-linked oxygen atoms (—O—) leaves 83·4, which is very nearly equal to four times the atomic volume of elementary phosphorus at its boiling-point, *i.e.* 4 × 20·9. It is concluded that the molecule P_4 in P_4O_6 occupies the same volume as the molecule P_4 of the liquid element. Now the atomic volume of phosphorus in its trivalent combination, as in PCl_3, etc., is certainly greater than that of elementary phosphorus at the same vapour pressure (see p. 51). Whence it follows that elementary phosphorus, as well as phosphorus in P_4O_6, is exerting its highest valency, *i.e.*, according to p. 52, is tercovalent with a mixed bond. The respective structural formulæ for the element and the trioxide would therefore be



and



A somewhat similar formula involving the transfer of electrons has been suggested by Henstock.[2]

Decomposition.—Phosphorus trioxide turns yellow and then red on exposure to sunlight, and slightly yellow in ordinary diffused light. After months of exposure red phosphorus is formed.[1] The change may be represented by the equation

$$5P_2O_3 = 4P + 3P_2O_5$$

When the oxide was heated to about 200° C. in a sealed tube it became turbid, then yellow and finally red. These changes proceeded still further at higher temperatures, and at 445° C. the whole was converted into solid products according to the equation

$$2P_4O_6 = 3P_2O_4 + 2P \text{ }^1$$

The oxide is unaffected by molecular hydrogen.

The liquid ignites in air or oxygen at about 50° C. and burns with a vivid flame to the pentoxide. Like phosphorus itself phosphorous oxide undergoes slow combustion with the emission of a glow, which may be due in part to the small quantities of the element already mentioned. This combustion, however, differs from that of phosphorus in several respects. Ozone is produced only in small quantities, if at all, and may be due to the action of light of wavelength $\lambda = 120$ to 180 $m\mu$ on the oxygen.[3] Hydrogen peroxide is not produced by the oxidation of phosphorous oxide. Dry oxygen combines with the oxide with increasing speed from about 10° C., and over a certain range the speed varies as the square root of the oxygen pressure. Glowing oxidation in the presence of water vapour has been connected with the intermediate formation of phosphine.[1] Ozonised air gives a strong glow, close to the surface of the oxide.

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[1] Thorpe and Tutton, *loc. cit.*

[2] Henstock, *Chem. News*, 1923, **127**, 259.

[3] Downey, *loc. cit.*

Products of oxidation vary according to the conditions. Dry oxygen at ordinary temperatures, and especially under reduced pressure, gave phosphorus pentoxide, while moist oxidation at atmospheric pressure gave tetroxide.[2] Further experiments have shown that (*a*) the pure trioxide, (*b*) the ordinary trioxide (p. 126), when oxidised either by air or oxygen or ozonised oxygen, gives a mixture of P_2O_4 and P_2O_5 in the constant proportions which correspond to an empirical formula $PO_{2 \cdot 19}$. The equation suggested for this oxidation is

$$8P_4O_6 + 4O_3 + 5O_2 = 5P_4O_8 + 3P_4O_{10}$$ [3]

Phosphorous oxide ignites spontaneously in chlorine, burning with a greenish flame and forming a clear liquid which on distillation yielded phosphoryl trichloride and a residue of metaphosphoryl chloride :—

$$P_4O_6 + 4Cl_2 = 2POCl_3 + 2PO_2Cl$$ [2]

The oxide also inflames in bromine. Slow combination yields the pentabromide and pentoxide, thus

$$5P_4O_6 + 20Br_2 = 8PBr_5 + 6P_2O_5$$

Combination with iodine is less vigorous, but when the oxide and iodine in carbon disulphide are heated in a sealed tube, orange-red P_2I_4 is deposited.

The oxide does not mix with sulphur, but when heated together in an inert atmosphere to about 160° C. the two combine with the production of diphosphorus dithiotrioxide, $P_4O_6S_4$.

The liquid oxide slightly above the melting-point does not mix with water, but combines with it slowly to give phosphorous acid :—

$$P_4O_6 + 6H_2O = 4H_3PO_3$$

Hot water reacts explosively giving phosphine and red phosphorus.

Hydrogen chloride dissolves in phosphorous oxide and reacts with it in a manner which is the reverse of that by which the oxide can be formed, this reverse equation being

$$P_4O_6 + 6HCl = 2PCl_3 + 2H_3PO_3$$

Such a mixture may also give phosphoric acid and phosphorus, according to the equation

$$4H_3PO_3 + PCl_3 = 3H_3PO_4 + 2P + 3HCl$$ [4]

Ammonia reacts violently with the oxide, reducing it to red phosphorus. When, however, the ammonia is passed into a solution of the oxide in ether, it gives a diamide of phosphorous acid, $HOP(NH_2)_2$.

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[1] Rinde, *Arkiv. Chem. Min. Geol.*, 1917, 7, No. 7; Miller, *Proc. Roy. Soc. Edin.*, 1926, 46, 76, 239.

[2] Thorpe and Tutton, *loc. cit.*

[3] Miller, 1929, *loc. cit.*

[4] Geuther, *J. prakt. Chem.*, 1873, [2], 8, 359.

The oxide acts vigorously upon ethyl alcohol, and by the regulation of this reaction diethyl phosphite has been obtained :—

$$P_4O_6 + 8C_2H_5OH = 4HOP(OC_2H_5)_2 + 2H_2O$$ [1]

The chemical properties of the purified oxide differ in some respects from those of the ordinary preparation. It has a pungent acid smell which does not recall the smell of phosphorus. When exposed to light, either in an evacuated bulb or in one filled with carbon dioxide, it does not turn red. It does not absorb oxygen at pressures of about 100 to 80 mm. even at 25° C. and in the presence of water vapour. When heated in a sealed tube containing dry oxygen at 300 mm. it shows no glow below 200° C., and the oxygen is only slowly absorbed at 220° C.

Phosphorus Dioxide, $[PO_2]_n$, or Tetroxide, P_2O_4.—The formula P_2O_4 is sometimes assigned to this oxide by analogy with N_2O_4, but by analogy with the other oxides of phosphorus the formula would be P_4O_8.

The formation of this oxide by the decomposition of P_4O_6 has been described already (p. 129). By heating in a sealed evacuated tube the products of the slow combustion of phosphorus, a crystalline sublimate is obtained,[2] which was shown by Thorpe and Tutton [3] to be a distinct new oxide, probably formed according to the equation

$$P_4O_6 = 3PO_2 + P$$ [4]

The oxide may also be formed directly by slow oxidation of phosphorus in oxygen at a pressure of 600 mm. and containing water vapour (0·1 mm.).

It sublimes at about 180° C. in colourless crystals which are of rhombic appearance. The density, $D^{22\cdot6°}_{14°}$, is 2·537.[5] The vapour density, determined at a temperature above 1400° C., corresponded to a molecular weight of 458·6, and therefore to the formula P_8O_{16}.[5] This oxide is stable in oxygen at the ordinary temperature, but is oxidised to pentoxide at 350° to 400° C.[6]

As the tetroxide has been shown to have the formula of a " mixed anhydride," it should yield phosphorous and phosphoric acids on treatment with water. Actually, the solution, after neutralisation with sodium hydroxide, showed the reactions of phosphites and metaphosphates. The hydration may therefore be represented by an equation

$$2PO_2 + 2H_2O = H_3PO_3 + HPO_3$$

Phosphorus Pentoxide.—Vigorous combustion of phosphorus in air produces a voluminous white powder which is very deliquescent and hisses when dropped into water, evolving much heat and giving a liquid of acid reaction. These salient facts were observed by the early workers on phosphorus, *e.g.* by Robert Boyle in 1681. The compound was analysed by many of the leading chemists at the beginning of the nineteenth century, and the empirical formula P_2O_5 was established.

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[1] Thorpe and North, *Trans. Chem. Soc.*, 1890, 57, 634.

[2] Hautefeuille and Perrey, *Compt. rend.*, 1884, 99, 33.

[3] *Loc. cit.*

[4] Miller, *loc. cit.*; Russell, *Trans. Chem. Soc.*, 1903, 83, 1263.

[5] West, *Trans. Chem. Soc.*, 1902, 81. 923.

[6] Miller, 1929, *loc. cit.*

This oxide is formed by combustion, in a full supply of air or oxygen, of white phosphorus (ignition temperature about 60° C.), of phosphorous oxide (50°–70° C.), of red phosphorus (about 260° C.), and of the phosphines and other combustible compounds. The white powder prepared in the laboratory or technically by these methods is always impure, containing a little phosphorous oxide, metaphosphoric acid, etc., while a part of the phosphorus usually escapes combustion and remains as red phosphorus. The preparation of a pure product requires further treatment. Thus the pentoxide may be thrown into a red-hot porcelain basin and stirred in a current of oxygen.[1] The crude oxide may also be resublimed in a current of oxygen and passed over platinised asbestos or platinum sponge.[2] The product used by Baker in experiments on intensive drying was also distilled, without the aid of a catalyst, in a current of oxygen at 180° to 210° C. The yield was about 10 per cent. A convenient apparatus for this preparation was described by Finch and Peto.[3] The ordinary pentoxide was pushed continually through a glass tube down the vertical limb of a heated iron T-piece which was traversed by a current of oxygen. The product, which was collected in a wide-mouthed glass bottle, was partly crystalline and partly amorphous.[4]

The purified oxide should be devoid of any alliaceous odour or odour of phosphine, and should not reduce a boiling solution of mercuric chloride. When dissolved in water and the solution neutralised with alkali (to methyl orange) it should give a white precipitate with silver nitrate which should not darken after boiling for five minutes.

Properties.—The pentoxide exists in crystalline and vitreous forms, the transformation temperature of which has been given as 440° C.[5] Sublimation proceeds with moderate speed between 180° and 250° C.[6] and the vapour pressure may reach 760 mm. at 360° C.[7] When it is sublimed at 360° C. in a current of oxygen the oxide forms brilliant crystals together with some of the amorphous material which is considered to be a product of polymerisation. The crystalline form, by X-ray examination, is that of the rhombohedral system with $12P_2O_5$ in a unit cell; the lengths of the axes are $a = 11{\cdot}12$, $b = 1{\cdot}12$ Å.[8]

The melting-point was found to vary between 560° and 570° C. according to the time of heating.[7]

The vapour density indicated a molecular weight of 336 at a red heat[9] and 300 at 1400° C.[10] At the higher temperature, therefore, the molecule approximates to P_4O_{10} ($M = 284$).

The inconsistent behaviour on sublimation suggests that phosphorus pentoxide, like sulphur trioxide and phosphorus itself (*q.v.*), contains at least two crystalline forms, a metastable form with a higher and a stable form with a lower vapour pressure. These are present as a mixture below 300° C., at which temperature the vapour pressure of the metastable form becomes appreciable and then increases rapidly, reaching 3·5 atm. at 400° C. From this temperature upwards the pressure of the stable form becomes appreciable and equilibrium conditions are more easily obtained.[1] The more volatile form may be sublimed away; consequently an abrupt fall of pressure above 400° C. has been observed.[2] A stable vapour pressure curve has been obtained up to and beyond the triple point.[1] Pure dry oxygen was passed over English P_2O_5 [3] which was heated to 270° C. The sublimate was received directly in the tensimeter, which was contained in an electric furnace wound with nichrome wire which gave temperatures above 400° C., which were controlled within ±2° C. The pressures were measured by a glass manometer with quartz thread indicator.[4] The following typical values are taken from the tabulated results :—

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[1] Travers, "*Experimental Study of Gases,*" Macmillan, 1901, etc.

[2] Threlfall, *Phil. Mag.*, 1893, [v], 35, 1; Shenstone and Beck, *Trans. Chem. Soc.*, 1893, 63, 475.

[3] Finch and Peto, *Trans. Chem. Soc.*, 1922, 121, 692.

[4] See also Finch and Fraser, *Trans. Chem. Soc.*, 1926, p. 117.

[5] Thorpe and Tutton, *loc. cit.*; Tilden and Barnett, *Trans. Chem. Soc.*, 1896, 69, 154.

[6] Kempf, *J. prakt. Chem.*, 1908, [2], 78, 228.

[7] Hoeflake and Scheffer, *Rec. Trav. chim.*, 1926, 45, 191.

[8] Sanfourche, Hernette and Fair, *Bull. Soc. chim.*, 1930, [4], 47, 273.

[9] Tilden and Barnett, *loc. cit.*

[10] West, *Trans. Chem. Soc.*, 1902, 81, 923.

VAPOUR PRESSURES OF PHOSPHORUS PENTOXIDE.

	Solid.			Liquid.			
t° C. . .	449	522·5	557·5	596·5	613·5	656	700
p cm. mercury	2·3	12·6	32·7	68·7	83·9	135·6	216

The triple point is found at 55·5 cm. of mercury and 580° C.

The affinity of formation of P_2O_5 evidently is very great, since no dissociation was observed at the highest temperatures mentioned above. When heated in the oxyhydrogen flame the oxide gives a continuous spectrum.[5] In respect of this great stability P_2O_5 differs markedly from its congeners N_2O_5 and As_2O_5.

The heat of formation is also by far the highest in the Group and is higher than the heat of oxidation per atom of any other non-metal. The value per mol of solid P_2O_5 from solid white phosphorus and gaseous oxygen is given as 369·9 Cals.,[6] 369·4 Cals.[7] As already mentioned (p. 37) the heats of formation from red phosphorus are rather lower.

Phosphoric oxide has also an exceptionally high affinity of hydration, on which account it is universally used, where its chemical properties permit, as the most powerful drying agent for neutral or acid gases and liquids and also in desiccators. The heat of hydration of crystalline P_2O_5 is given as 44·6 Cals.,[8] 40·8 Cals.[9] The amorphous variety when dissolved in much water evolved 33·8 Cals. and the vitreous variety 29·1 Cals.[10] Hence heat is evolved when the crystalline variety is transformed into the amorphous variety.

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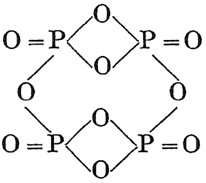
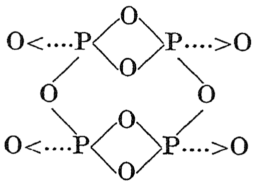
[1] Smits, *Zeitsch. physikal. Chem.*, 1930, 149, 337.
[2] Smith and Rutgers, *Trans. Chem. Soc.*, 1924, 125, 2573.
[3] Hopkin and Williams, Manufacturers.
[4] Jackson, *Trans. Chem. Soc.*, 1911, 99, 1906.
[5] Hartley, *Chem. News*, 1893, 67, 279.
[6] Thomsen, "*Thermochemischen Untersuchungen*," 1882, Leipzig.
[7] Giran, *Compt. rend.*, 1903, 136, 550, 677.
[8] Hautefeuille and Perrey, *loc. cit.*
[9] Giran, *loc. cit.*, and *Ann. Chim. Phys.*, 1903, [7], 30, 203.
[10] Giran, *loc. cit.*

Structure.—Many possible structures may be assigned to the molecule. Whichever of these is adopted the phosphorus must be quinquevalent according to the old representation, or quadrivalent with a semipolar bond according to the " octet " theory. Thus



or



Chemical Properties.—Phosphorus pentoxide was reduced by hydrogen at a red heat in the presence of nickel,[1] and by carbon at high temperatures, but not by silicon.[2]

The alkali and alkaline earth metals react with great energy when heated with the oxide, giving oxides and phosphides.[3]

When heated with halides of phosphorus the two molecules give oxyhalides, the change being represented by the equation[4]

$$P_4O_{10} + 6PCl_5 = 10POCl_3$$

or

$$P_4O_{10} + 6PBr_5 = 10POBr_3$$

The pentoxide also gives the oxychloride when heated with the halides of other non-metals, although the other non-metal does not necessarily give oxyhalide also. Thus with boron trichloride

$$P_2O_5 + 2BCl_3 = POCl_3.BCl_3 + BPO_4$$

and with carbon tetrachloride in a sealed tube between 200° and 300°

$$P_2O_5 + 2CCl_4 = COCl_2 + CO_2 + 2POCl_3$$

With an excess of P_2O_5

$$2P_2O_5 + 3CCl_4 = 3CO_2 + 4POCl_3$$ [5]

Oxyhalides of phosphorus are also produced when the pentoxide is heated with fluorides or chlorides of the alkali and alkaline earth metals; thus POF_3 is produced with calcium fluoride[6] and $POCl_3$ with sodium chloride.[7]

When brought into contact with water under various conditions phosphorus pentoxide forms one or more of differently hydrated acids. Metaphosphoric acid (*q.v.*) probably is the first product.

The pentoxide has a powerful dehydrating effect upon oxyacids and is therefore used in preparing anhydrides from these (see under " Nitrogen Pentoxide," this Volume, Part I.). It also removes halogen from halogen hydracids under some conditions, giving oxyhalides, *e.g.*

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[1] Neogi and Adlucary, *Zeitsch. anorg. Chem.*, 1910, 69, 209.
[2] Kahlenberg and Trautmann, *Trans. Amer. Electrochem. Soc.*, 1921, 39, 377.
[3] Davy, *Phil. Trans.*, 1818, 108, 316.
[4] Berger, *Compt. rend.*, 1908, 146, 400.
[5] Gustavson, *Ber.*, 1871, 4, 853; 1872, 5, 30.
[6] Thorpe and Hambly, *Trans. Chem. Soc.*, 1889, 55, 759.
[7] Kolbe and Lautemann, *Annalen*, 1860, 113, 240.

POF_3 from HF.[1] Hydrogen chloride is completely absorbed by the oxide and gives a liquid from which $POCl_3$ can be distilled.[2]

Phosphorus pentoxide cannot be oxidised further by ordinary oxidising agents, except to compounds of the " peracid " type. The oxygen is displaced by metathesis as just shown, but not by anhydrous halogens, except fluorine, which at a dull red heat gives PF_5 and POF_3.[3]

Dry ammonia gives amido- or imido-phosphoric acids (*q.v.*), and also salts such as diammonium amidopyrophosphate.[4]

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[1] Gore, *Trans. Chem. Soc.*, 1869, 22, 368.
[2] Bailey and Fowler, *Trans. Chem. Soc.*, 1888, 53, 755.
[3] Moissan, *Bull. Soc. chim.*, 1891, [3], 5, 458.
[4] Sanfourche, Hernette and Fair, *loc. cit.* See also Schiff, *Annalen*, 1857, 103, 168.

CHAPTER XI.

THE OXYACIDS OF PHOSPHORUS—UNSATURATED.

THE numerous oxyacids of phosphorus may be regarded as derived from three prototypes, namely, hypophosphorous acid, H_3PO_2, phosphorous acid, H_3PO_3, and orthophosphoric acid, H_3PO_4, in all of which phosphorus probably has the co-ordination number 4 (see p. 59).

In the hypophosphorous and phosphorous series the phosphorus undoubtedly is in a lower state of oxidation, and may be wholly in the trivalent state, which corresponds to a symmetrical structure of the molecules. More probably, however, these acids consist of a mixture containing the more symmetrical molecules in tautomeric equilibrium with less symmetrical molecules which contain hydrogen directly united to phosphorus. In either form the unsaturated acids and their salts are powerful reducing agents and are easily oxidised to the stable phosphate series.

Hypophosphorous Acid.—The alkali salts of this acid were discovered among the products of the decomposition of phosphides by water.[1] A method of preparing hypophosphites by boiling milk of lime with phosphorus was also discovered early in the nineteenth century. The resulting solution of calcium hypophosphite could then be decomposed by oxalic acid.[2] Hypophosphite was also prepared by heating the phosphorus with a solution of baryta.[3] The barium salt, $Ba(H_2PO_2)_2$, is easily recrystallised, and from it the free acid may be prepared by double decomposition of a fifth molar solution with the calculated amount of 20 to 25 per cent. sulphuric acid.[4] The filtered solution may be evaporated first to one-tenth of its volume and then until the temperature rises to 105° C. It is filtered hot and then further evaporated to a temperature of 110° C., and this evaporation by stages is continued until the temperature rises to 130° or even 138° C. without decomposition. The liquid should then be poured into a closed flask and cooled to 0° C., when it nearly all solidifies to a mass of crystals. Crystallisation may be induced if necessary by seeding with a crystal of the acid.[5] The commercial acid usually contains calcium salts. These may be removed by the addition of alcohol and much ether to the evaporated solution, when the salts are precipitated. The alcohol and ether are removed by distillation and the acid is further concentrated as above.[6]

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[1] Dulong, *Phil. Mag.*, 1816, 48, 271.

[2] Rose, *Annalen*, 1843, 58, 301.

[3] Dulong, *loc. cit.*; *Ann. Chim. Phys.*, 1816, [2], 2, 141.

[4] Thomsen, *Ber.*, 1874, 7, 994; *Annalen*, 1871, 143, 354, 497.

[5] Marie, *Compt. rend.*, 1904, 138, 1216.

[6] Michaelis and von Arend, *Annalen*, 1901, 314, 266.

Properties.—The density of the crystallised acid is given as 1·4625.[1] The melting-point, 17·4° C.[2] or 26·5° C.,[3] no doubt varies with small variations in the proportion of water present.

The latent heat of fusion (heat absorbed) is 2·4 Cals., the latent heat of solution of the crystals from −0·2 to −0·17 Cals., and of the fused acid from +2·2 to +2·14 Cals. (per mol in each case).

The heats of formation (heat evolved) from the elements

$$P \text{ (solid)} + O_2 \text{ (gas)} + 1\tfrac{1}{2}H_2 \text{ (gas)}$$

are +137·7 Cals. (liquid acid), +140·0 Cals. (solid acid), +139·8 Cals. (dissolved acid).[4]

The pure acid decomposes rapidly when heated above 130° C. and below 140° C. mainly according to the equation

$$3H_3PO_2 = PH_3 + 2H_3PO_3$$

while between 160° and 170° C. the main decomposition (consecutive reaction) is symbolised as

$$4H_3PO_3 = PH_3 + 3H_3PO_4 \;^{3}$$

Aqueous Solutions of Hypophosphorous Acid.—The effect of dilution on the molar conductivity of hypophosphorous acid shows that the acid is moderately strong, but however obeys the law of mass or concentration action sufficiently well to give a "constant" (*K* below) which remains of the same order although it diminishes steadily with increasing dilution.

MOLAR CONDUCTIVITIES OF HYPOPHOSPHOROUS ACID AT 25° C.[5]

V . .	2	4	8	16	32	64	128
μ . .	140	172	207	245	281	312	335
K . .	0·1012	0·0876	0·0757	0·0670	0·0587	0·0508	0·0417
K' .	. .	. .	0·1015	0·1014	0·1017	0·1014	0·1019

V . .	256	512	1024	2048	∞
μ . .	352	361	367	368·3	389
K . .	0·0336	0·0234	0·0154	0·0082	. .
K' .	0·1024	0·1008	0·1014	0·1028	. .

The values of α ($=\mu/\mu_\infty$) in the expression $\alpha^2/(1-\alpha)V = K$ were calculated from $\mu_\infty = 389$ based on the work of Arrhenius.[6] The ionic conductivity L_∞ of $H^+=347$, which gives L_∞ of $H_2PO_2^-$ as 42·0, in agreement with the value 41·8 deduced from the sodium salt.[1]

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[1] Michaelis and von Arend, *loc. cit.*

[2] Thomsen, *loc. cit.*

[3] Marie, *loc. cit.*

[4] Thomsen, *loc. cit.*, and *Ber.*, 1870, 3, 187, 593; 1871, 4, 308, 586; *J. prakt. Chem.*, 1875, [2], 11, 133.

[5] Ostwald, "*Lehrbuch der Allgem. Chem.*," 1903, 2, Leipzig.

[6] Arrhenius, *Zeitsch. physikal. Chem.*, 1889, 4, 96.

These values have been recalculated to the newer units [2] and an empirical constant K' (see table) has been found which shows a better constancy, *i.e.*: [2]

$$K'=\frac{\alpha^2}{(1-\alpha)V}+\frac{1}{35}\log V$$

The constant K has been redetermined by Kolthoff [3] as 0·01 at $V=1000$ and 0·062 at $V=20$. In another series of results the values of α and K were derived from $\lambda_\infty=392{\cdot}5$, which was based on the limiting conductivity of NaH_2PO_2 (at 25° C.):—[4]

c mols/litre	0·5004	0·2502	0·1251	$0{\cdot}0625_5$	0·03128
μ . .	137·1	168·5	205·0	242·9	279·5

whence K may be calculated in the usual manner.

The conductivity increases at first with the temperature as is usual; the rate of increase then diminishes and the conductivity reaches a maximum at about 50° C., the exact temperature varying with the concentration and being 57° C. in the case of normal acid.[5] The conductivity then decreases. It is supposed that the effect of the normal increase in ionic mobility with temperature is diminished and finally reversed by the opposite effect of decreasing dissociation. Since the dissociation constant decreases with rise of temperature the dissociation into ions must take place with evolution of heat, *i.e.* the heat of ionisation is positive. Therefore the neutralisation of the acid with alkali must result in a production of heat greater than the heat of formation of water from its ions, which may be taken as 13·52 Cals. per mol. If the heat of dissociation is Q_d Cals. per gram-ion and the undissociated portion of the free acid is $1-\alpha$, then the total heat of neutralisation Q_n will be given by the equation

$$Q_n=13{\cdot}52+(1-\alpha)Q_d \text{ Cals.}$$

At 21·5° C. α is 0·449 at a certain concentration and $(1-\alpha)Q_d$ has the value +1·769 Cals. Therefore Q_n is 15·289 Cals. by calculation, while the experimental value was 15·316 Cals.[6]

The transport number of the anion was found to be 41·8.[1]

Basicity.—The results of conductivity measurements indicate that only one of the hydrogens is dissociable as ion, the dissociation taking place according to the equation

$$H_3PO_2 \rightleftharpoons H^+ + H_2PO_2^-$$

In the process of neutralisation also only one hydrion takes part, as is shown by the fact that the heat evolved practically reaches a limit when one equivalent of alkali has been added to one mol of the acid. Thus when 2, 1 and 0·5 mols of the acid were added to one equivalent of NaOH the heats observed were 15·4, 15·2 and 7·6 Cals.[1]

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[1] Bredig, *Zeitsch. physikal. Chem.*, 1894, 13, 191.
[2] Mitchell, *Trans. Chem. Soc.*, 1920, 117, 957.
[3] Kolthoff, *Rec. Trav. chim.*, 1927, 46, 350.
[4] Ramstedt, *Meddel. Vet. Akad. Nobelinstitut*, 1915, 3, No. 7.
[5] Ostwald, *loc. cit.*; Wegelius, *Zeitsch. Elektrochem.*, 1908, 14, 514.
[6] Thomsen, *loc. cit.*

The monobasicity is confirmed by the formulæ of all the known salts.

Oxidation in Solution.—Hypophosphorous acid and its salts are strong reducing agents and are oxidised to phosphorous acid or finally to phosphoric acid and their salts. The self-oxidation and -reduction to phosphine and phosphorous acid is described on p. 136. A similar reaction is brought about by hydrogen iodide :—

$$3H_3PO_2 + HI = 2H_3PO_3 + PH_4I$$ [2]

Hypophosphorous acid is also oxidised to phosphorous acid by sulphur dioxide with deposition of sulphur,[3] and by phosphorus trichloride with deposition of phosphorus, thus :—

$$3H_3PO_2 + PCl_3 = 2H_3PO_3 + 2P + 3HCl$$ [4]

It is oxidised by alkali with evolution of hydrogen :—

$$NaH_2PO_2 + NaOH = Na_2HPO_3 + H_2$$ [5]

The velocity constant of this reaction has been measured at temperatures slightly below 100° C. It is slightly greater for KOH than for NaOH at equivalent concentration, and increases faster than the concentration of the alkali.[6]

Salts of the noble metals are reduced by hypophosphorous acid or hypophosphites, and in many cases phosphorous acid can be isolated among the products. The reduction of silver nitrate was noticed by the early workers.[7] Phosphoric acid was formed with or without the evolution of hydrogen, thus :—

$$2NaH_2PO_2 + 2AgNO_3 + 4H_2O = 2H_3PO_4 + 2NaNO_3 + 3H_2 + 2Ag$$

or the nascent hydrogen gave more silver :—

$$2H + 2AgNO_3 = 2HNO_3 + 2Ag$$ [8]

The formation of phosphorous acid is represented by the equation

$$2AgNO_3 + H_3PO_2 + H_2O = 2Ag + H_3PO_3 + 2HNO_3$$

Copper sulphate is reduced to copper with the production of an acid solution :—

$$4CuSO_4 + Ba(H_2PO_2)_2 + 4H_2O = 2H_3PO_4 + 4Cu + BaSO_4 + 3H_2SO_4$$ [9]

It has also been stated that copper hydride is first produced, which decomposes with evolution of hydrogen.[1] It appears further that, with excess of the hypophosphite, hydrogen also is evolved, while with excess of copper salt copper only is precipitated.[2] The spongy copper appears to act as a catalytic agent in liberating hydrogen from excess of hypophosphorous acid. Cuprous oxide probably is first formed, and the substance first precipitated from an acid solution may contain this with hydride and phosphate.[3]

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[1] Thomsen, *loc. cit.*

[2] Poundorf, *Jena Zeit. Suppl.*, 1876, [2], 3, 45.

[3] Poundorf, *loc. cit.*; Rother, *Pharm. J.*, 1879, [3], 10, 286.

[4] Geuther, *J. prakt. Chem.*, 1874, [2], 8, 366.

[5] Loessner, "*Ueber reakt. d. unterphosphor. Säure, etc.*," Weida i Thurm, 1911.

[6] Loessner, *loc. cit.*; Sieverts and Loessner, *Zeitsch. anorg. Chem.*, 1912, 76, 10; Major, "*Zur Kenntnis der phosph. u. unterphosph. Säure*," Weida i Thurm, 1908.

[7] Dulong, *loc. cit.*

[8] Sieverts, *Zeitsch. anorg. Chem.*, 1909, 64, 29; Sieverts and Loessner, *loc. cit.*

[9] Rose, *Annalen*, 1827, 9, 225; 1828, 11, 92; 1828, 12, 77, 288; 1834, 32, 467; 1843, 58, 301.

Mercuric chloride is reduced to mercurous chloride and mercury.[4] In this case also phosphorous acid was produced, and by a reaction which was quicker than that which led to phosphoric acid, thus :—

$$H_3PO_2 + 2HgCl_2 + H_2O = H_3PO_3 + Hg_2Cl_2 + 2HCl$$ [5]

Palladous salts oxidise the acid to phosphoric acid with deposition of palladium.[6]

The velocities of some oxidations have been determined. Thus in the reaction

$$H_3PO_2 + I_2 + H_2O = H_3PO_3 + 2HI$$

the velocity was independent of the concentration of iodine if this was more than 0·004N, and unimolecular with respect to H_3PO_2.[7] The hypothesis has been advanced that the reducing agent is an active form H_5PO_2, which is produced with a measurable velocity (catalysed by hydrogen ions) when the equilibrium amount is diminished.[8]

The Hypophosphites.—Hypophosphites of most of the metals have been prepared by a few general reactions :—

(1) By heating aqueous solutions of the alkali or alkaline earth hydroxides with white phosphorus.
(2) By the double decomposition of barium hypophosphite with the sulphate of the required metal.
(3) By dissolving the hydroxide or carbonate of the metal in hypophosphorous acid.

The hypophosphites are all soluble. Those of barium and calcium, which are the least soluble, dissolve in 2·5 to 3·5 and 6 to 7 parts of water respectively. Those of the alkali metals and ammonium dissolve also in alcohol. Solutions of hypophosphites of the alkali metals are fairly stable, especially in the absence of air, and the salts generally may be obtained in well-crystallised forms by evaporation. More concentrated solutions often decompose, especially if alkaline, with evolution of phosphine. The dry salts are also fairly stable in the cold, but when heated decompose giving phosphine and hydrogen and leaving the pyro- or meta-phosphate.

The electrical conductivities of the sodium salt [9] and of the barium salt [10] give the mobility of the $H_2PO_2^-$ ion.

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[1] Wurtz, *Ann. Chim. Phys.*, 1844, [3], 11, 250; 1846, [3], 16, 190.
[2] Sieverts, *loc. cit.*; Muthmann and Mawrow, *ibid.*, 1896, 11, 268.
[3] Firth and Myers, *Trans. Chem. Soc.*, 1911, 99, 1329.
[4] Rose, *loc. cit.*
[5] Mitchell, *Trans. Chem. Soc.*, 1921, 119, 1266.
[6] Sieverts, Sieverts and Loessner, *loc. cit.*
[7] Steele, *Trans. Chem. Soc.*, 1907, 91, 1641.
[8] Kolthoff, *Pharm. Weekblad*, 1916, 53, 909; 1924, 61, 954; Mitchell, *Trans. Chem. Soc.*, 1920, 117, 1322.
[9] Ramstedt, *Meddel. Vet. Akad. Nobelinstitut*, 1915, 3, No. 7.
[10] Walden, *Zeitsch. physikal. Chem.*, 1887, 1, 529.

The formulæ of some typical hypophosphites are as follows :—

$LiH_2PO_2.H_2O$, monoclinic prisms ; $NaH_2PO_2.H_2O$, monoclinic prisms ; KH_2PO_2, hexagonal plates ; $NH_4H_2PO_2$, rhombic tables ; $Mg(H_2PO_2)_2.6H_2O$, tetragonal ; $Ca(H_2PO_2)_2$, monoclinic leaflets ; $Ba(H_2PO_2)_2.H_2O$, monoclinic needles or prisms ; $Cu(H_2PO_2)_2$, white precipitate ; $Pb(H_2PO_2)_2$, rhombic prisms ; $Fe(H_2PO_2)_2.6H_2O$, green octahedra ; $Fe(H_2PO_2)_3.xH_2O$, white precipitate ; $Co(H_2PO_2)_2.6H_2O$, red tetragonal ; $Ni(H_2PO_2)_2.6H_2O$, green crystals.

The hexahydrated salts of magnesium and the iron group are said to be isomorphous. Further details about each salt are given under the metal in the appropriate volume of this Series.

Ammonium and hydroxylamine hypophosphites have been prepared by double decomposition between the sulphates and barium hypophosphite. The ammonium salt, $NH_4H_2PO_2$,[1] was crystallised from water or alcohol. When heated to about 200° C. it melted and decomposed, giving off ammonia, phosphine and hydrogen and leaving a mixture of pyro- and meta-phosphoric acids. Hydroxylamine hypophosphite, $NH_2OH.H_3PO_2$, has also been prepared by reaction between KH_2PO_2 and $NH_2OH.HCl$, and was extracted with hot absolute alcohol.[2] Solutions of this salt must be evaporated in an atmosphere of CO_2, etc. in order to avoid oxidation. The crystals obtained were very deliquescent. They began to decompose at about 60° C., melted below 100° C. and exploded at a higher temperature.[3]

The detection, estimation and structure of hypophosphites are discussed under " Phosphites " (*q.v.*).

In contradistinction to phosphorus itself and the products of its slow oxidation, hypophosphorous acid and the hypophosphites do not appear to be toxic.[4] Calcium hypophosphite appears to be completely eliminable from the system.[5] Hypophosphites of calcium, sodium and iron have been prescribed in medicine, but although in some cases they appear to have done good there is no conclusive evidence of the value of the hypophosphite radical apart from the basic radical or other constituent of the mixture.

Phosphorous Acid, H_3PO_3.—The production of an acid liquid by the slow combustion of phosphorus in the presence of water was observed by le Sage in 1777.[6] The acid was prepared by Pelletier by drawing a slow current of air over phosphorus enclosed in fine tubes which dipped into water.[7] The distinction between this acid and phosphoric acid was recognised in the early nineteenth century, as also was the fact that the slow combustion of phosphorus could yield a mixture of the two acids.[8]

The method of preparation just mentioned is not a good one. Phosphorous oxide dissolves only slowly in cold water and phosphoric acid is continuously produced from the first, while hot water gives a variety of products. A better method is that recommended by Davy,[1] namely, by the hydrolysis of phosphorus trichloride. Some white phosphorus is placed in a deep cylinder and covered with water. The element is melted and chlorine is passed in through a tube which dips well into the phosphorus.[2] Large quantities may be quickly obtained by this method, but the product contains phosphoric acid. Regulated action of PCl_3 on water may be effected by passing a current of dry air through the trichloride kept at 60° C. and then through two wash-bottles containing water.[3] The action is also much less violent if an acid such as concentrated aqueous hydrochloric acid is used in place of the water. Oxalic acid is most suitable, since it is dehydrated with decomposition when heated in a flask with phosphorus trichloride. The flask is furnished with a reflux condenser. Much of the HCl is evolved and a concentrated solution of phosphorous acid remains :—

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[1] Dulong, *loc. cit.*, and *Ann. Phil.*, 1818, 11, 134; Rammelsberg, *Annalen*, 1867, 132, 491; *Trans. Chem. Soc.*, 1873, 26, 1, 13; Michaelis and von Arend, *loc. cit.*

[2] Hofmann and Kohlschutter, *Zeitsch. anorg. Chem.*, 1898, 16, 469.

[3] Sabaneeff, *Ber.*, 1897, 30, 287; *Zeitsch. anorg. Chem.*, 1898, 17, 483; 1899, 20, 21.

[4] Paquelin and Joly, *Compt. rend.*, 1878, 86, 1505; *J. Pharm. Chim.*, 1878, [4], 28, 314; Polk, *Pharm. J.*, 1874, [3], 5, 425.

[5] Pauzer, *Zeitsch. Nahr. Genuss-m.*, 1902, 5, 11.

[6] le Sage, *Mém. Acad.*, 1777, p. 321.

[7] Pelletier, *Ann. Chim. Phys.*, 1792, [1], 14, 113.

[8] Davy, *Phil. Trans.*, 1812, 102, 405; 1818, 108, 316; Dulong, *Ann. Chim. Phys.*, 1816, [2], 2, 141; *Phil. Mag.*, 1816, 48, 271; Sommer, *J. Soc. Chem. Ind.*, 1885, 4, 574.

$$PCl_3 + 3H_2C_2O_4 = H_3PO_3 + 3CO + 3CO_2 + 3HCl$$ [4]

In these preparations it is usually necessary to remove the hydrochloric acid which is produced ; this may be done by distilling the solution up to a temperature not exceeding 180° C. A syrupy liquid is then obtained which, after cooling, crystallises quickly, or at any rate within a few hours. The process may be hastened as usual by seeding.

Physical Properties.—The crystalline acid was found to melt at 70·1° C.,[5] 74° C.[6] The density of the liquid supercooled at 21° C. was 1·651.[5] The latent heat of fusion of the acid was found to be 7·07 Cals.[5] The heat of solution of the acid per mol dissolved in 400 mols or more of water was +233 Cals.[5] The heat of formation of the crystallised acid has been given as +227·7 Cals.[5]

Aqueous Solutions.—The conductivities of phosphorous acid are lower than those of hypophosphorous acid at corresponding dilutions, showing that the former acid is less dissociated, as appears from the following values :—[7]

MOLAR CONDUCTIVITIES OF PHOSPHOROUS ACID AT 25° C.

V .	2	4	8	16	32	64	128	256	512	1024
μ .	129	156	187	222	252	292	318	337	351	358

Since phosphorous acid is dibasic, the dissociation constant was not calculated from the conductivities, but from the hydrogen-ion concentrations set up during neutralisation, which may be expressed by a neutralisation curve. This[8] gave $K_1 = 0{\cdot}05$ and $K_2 = 2{\cdot}4 \times 10^{-5}$ or[9] $K_1 = 0{\cdot}016$ at $c = 0{\cdot}001$ to $K_1 = 0{\cdot}062$ at $c = 0{\cdot}1$ and $K_2 = 0{\cdot}7 \times 10^{-6}$.

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[1] *Loc. cit.*

[2] Droquet, *J. Chim. Méd.*, 1828, [1], 4, 220.

[3] Grosheintz, *Bull. Soc. chim.*, 1877, [2], 27, 433.

[4] Hurtzig and Geuther, *J. prakt. Chem.*, 1859, [1], III, 170.

[5] Thomsen, *loc. cit.*

[6] Hurtzig, "*Einige Beiträge zur näheren Kenntnis der Saüren des Phosphors und Arseniks,*" Göttingen, 1859.

[7] Ostwald, "*Lehrb. d. Allgemein. Chem.,*" 1903, Leipzig.

[8] Blanc, *J. Chim. phys.*, 1920, 18, 28.

[9] Kolthoff, *Rec. Trav. chim.*, 1927, 46, 350.

As in the case of hypophosphorous acid, the molar conductivity, while increasing at first with temperature, reached a maximum at about 70° C. and then diminished.[1]

The lowering of the freezing-point, $-\Delta t$, and the elevation of the boiling-point, $+\Delta t$, of water, which is made c-normal with respect to phosphorous acid, are taken as proving that polymerisation had taken place as well as electrolytic dissociation.

LOWERING OF FREEZING-POINT OF WATER BY H_3PO_3.

c . .	1·186	0·539[*]	0·296	0·148
$-\Delta t$, ° C.	2·941	1·538	0·835	0·455
i . .	1·128	1·143	1·515	1·650

RAISING OF THE BOILING-POINT OF WATER BY H_3PO_3.

c . .	0·976	0·488	0·244	0·122
$+\Delta t$, .	0·51	0·28	0·16	0·13
i . .	0·969	1·063	1·215	1·972

The factors or activity coefficients i are calculated on the assumption that the original molecules dissociating are the simplest, *i.e.* H_3PO_3.[2]

Basicity.—In the neutralisation of the acid by NaOH in dilute solution it was found that

$$H_3PO_3 + NaOH = NaH_2PO_3 + H_2O + 148 \text{ Cals.}$$
$$H_3PO_3 + 2NaOH = Na_2HPO_3 + 2H_2O + 2 \times 142 \text{ Cals.}$$
$$H_3PO_3 + 3NaOH = Na_2HPO_3 + 2H_2O + NaOH + 3 \times 96 \text{ Cals.}$$

whence only two of the hydrogens are ionisable.[3] So far as the formulæ of phosphites are known (*v. infra*, p. 146), they contain a maximum of two equivalents of a base combined with 1 mol of the acid. Attempts to prepare Na_3PO_3 have not been successful.[4] Dibasicity is also confirmed by a study of the neutralisation curves.

Oxidation in Solution.—Phosphorous acid and the phosphites are not quite such strong reducing agents as hypophosphorous acid and the hypophosphites. The free acid undergoes self-oxidation and -reduction at a higher temperature than hypophosphorous acid (see p. 138).

Atmospheric oxygen does not oxidise the acid at ordinary temperatures, nor is such oxidation catalysed by iodine in the dark. In the light, however, hydrogen iodide is formed according to the equation

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[1] Ostwald, *loc. cit.*

[*] Probably should be 0·593.

[2] Italiener, "*Beiträge zur Kenntnis der phosphorigen Saüre und ihrer Salze,*" 1917, Freiburg i. Br.

[3] Thomsen, *loc. cit.*; Amat, *Ann. Chim. Phys.*, 1891, [6], 24, 319; *Compt. rend.*, 1890, 111, 676.

[4] Amat, *loc. cit.*, and *Compt. rend.*, 1888, 106, 1351; 1889, 108, 404.

$$H_3PO_3 + I_2 + H_2O = H_3PO_4 + 2HI$$

being reoxidised rapidly by oxygen, thus

$$2HI + \tfrac{1}{2}O_2 = I_2 + H_2O$$ [1]

The oxidation of phosphites by iodine was found to proceed to completion in neutral solution[2] (see "Estimation," p. 149). Over a narrow range of concentrations the reaction was found to be unimolecular with respect to iodine and phosphorous acid.[3] It is said to be catalysed by hydrogen ions which are formed as the reaction proceeds.[4] A further study of the velocity constants showed that the mechanism was more complicated than had previously been supposed, and that the two tautomeric forms participated in different ways.[5] A solution of iodine in potassium iodide contains the ions I^- and I_3^-, and also molecular iodine, I_2. The latter reacts directly with the normal form of phosphorous acid and this reaction is repressed by hydrogen ions. Simultaneously, the phosphorous acid changes into another form with which the I_3^- ion reacts. This second reaction is accelerated by hydrogen ions either directly or, more probably, because they accelerate the tautomeric change.

General Reactions.—Various products were obtained when phosphorous acid was heated with halogens in a sealed tube. Iodine gave phosphoric and hydriodic acids, phosphonium iodide and an iodide of phosphorus, whilst bromine gave phosphoric acid, phosphorus tribromide and hydrobromic acid.[6] A dry ether solution of the acid was not oxidised by bromine or dry palladium black, but oxidation proceeded readily in the presence of moisture.[7]

Phosphorous acid also reduced sulphurous acid, the end products being sulphur and phosphoric acid, thus :—

$$2H_3PO_3 + H_2SO_3 = 2H_3PO_4 + S + H_2O$$ [8]

Sulphuric acid, which dissolved phosphorous acid in the cold, was reduced to sulphur dioxide on heating.[9]

Salts of the noble metals, including copper and mercury, were found to oxidise phosphorous to phosphoric acid. The metal was precipitated from silver salts[10] and also from gold salts.[11] It is generally agreed that copper is precipitated from copper sulphate,[1] while cuprous oxide or hydrogen may also be liberated, according to the conditions :—

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[1] Luther and Plotnikoff, *Zeitsch. physikal. Chem.*, 1908, 61, 513.
[2] Rupp and Finck, *Ber.*, 1902, 35, 3691.
[3] Federlin, *Zeitsch. physikal. Chem.*, 1902, 41, 365.
[4] Steele, *Trans. Chem. Soc.*, 1909, 95, 2203.
[5] Mitchell, *Trans. Chem. Soc.*, 1923, 123, 2241; and *loc. cit.*
[6] Gustavson, *J. prakt. Chem.*, 1867, [1], 101, 123.
[7] Wieland and Wingler, *Annalen*, 1923, 434, 185.
[8] Wohler, *Annalen*, 1841, 39, 252; Cavazzi, *Gazzetta*, 1886, 16, 169.
[9] Wurtz, *Compt. rend.*, 1844, 18, 702; 1845, 21, 149, 354; Adie, *Trans. Chem. Soc.*, 1891, 59, 230.
[10] Sieverts, *Zeitsch. anorg. Chem.*, 1909, 64, 29; Vanino, *Pharm. Zentr.-h.*, 1899, 49, 637.
[11] Balard, *Ann. Chim. Phys.*, 1834, [2], 57, 225; Wurtz, *loc. cit.*; Sieverts, Major, "*Zur Kenntnis der phosphorigen und unterphosphorigen Säure,*" Weidai Th., 1908.

$$3H_3PO_3 + CuSO_4 + 3H_2O = Cu + 2H_2 + 3H_3PO_4 + H_2SO_4$$
$$H_3PO_3 + CuSO_4 + H_2O = Cu + H_3PO_4 + H_2SO_4$$

The reduction of mercuric chloride gave mercurous chloride when the mercuric chloride was in excess, and mercury when the phosphorous acid was in excess,[2] while the total reaction can be represented by the equations

$$2HgCl_2 + H_3PO_3 + H_2O = H_3PO_4 + 2HgCl + 2HCl \quad . \quad (1)$$

or

$$HgCl_2 + H_3PO_3 + H_2O = H_3PO_4 + Hg + 2HCl \quad . \quad . \quad (2)$$

The mechanism has not been completely elucidated and may be very complex. The reaction has been classified as of the third order in dilute solution, and as of the first order with respect to $HgCl_2$.[3] But it has also been stated that the reaction which is chiefly responsible for the observed velocity is the conversion of a first or normal form of H_3PO_3 into a second or active form, which then reacts according to equation (2) above. In the absence of extraneous chloride ions these are produced by another reaction, thus

$$HgCl^+ + H_3PO_3\ (\text{normal}) + H_2O = H_3PO_4 + Hg + 2H^+ + Cl^-$$ [4]

Many other oxidising agents are capable of oxidising phosphorous acid. The reaction with potassium persulphate is very slow, but in the presence of hydriodic acid it is much accelerated. This is a good example of a coupled reaction.[5]

Phosphorous acid forms esters by direct union with several alcohols.[6] With ethyl alcohol it gave diethyl phosphite.[7] Ethyl derivatives of phosphorous and phosphoric acids have been made by the action of bromine on sodium diethyl phosphite in ligroin. They are separated by fractional distillation.[8]

The Phosphites.—Two series of phosphites are known, the primary phosphites, MH_2PO_3, and the secondary, M_2HPO_3, M being a univalent metal. Crystalline salts have also been prepared containing an excess of phosphorous acid. The phosphites of the alkali metals and ammonia are soluble, those of the alkaline earths sparingly soluble, while those of other metals are only very slightly soluble. They may be prepared by the usual methods :—

(1) By neutralising phosphorous acid to the appropriate end point with alkali hydroxides and evaporating to crystallisation.

(2) By neutralising a solution of phosphorous acid, or one made from PCl_3, with ammonia and adding a salt of the required metal.

(3) By dissolving the hydroxide of the base in phosphorous acid.

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[1] Rammelsberg, *Annalen*, 1867, 131, 263, 359; 132, 481; Sieverts, *loc. cit.*; Major, *loc. cit.*

[2] Balard, *loc. cit.*; Wurtz, *loc. cit.*

[3] Linhart, *Amer. J. Sci.*, 1913, [4], 35, 353.

[4] Mitchell, *Trans. Chem. Soc.*, 1924, 125, 1013.

[5] Federlin, *Zeitsch. physikal. Chem.*, 1902, 41, 570.

[6] Sachs and Levitsky, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 211.

[7] Thorpe and North, *Trans. Chem. Soc.*, 1890, 57, 634.

[8] Arbusov, *J. prakt. Chem.*, 1931, [2], 131, 103.

The phosphites are fairly stable in the absence of oxidising agents and dilute solutions may even be boiled without decomposition. More concentrated solutions may decompose, giving hydrogen; thus

$$Na_2HPO_3 + NaOH = Na_3PO_4 + H_2$$

The solid salts decompose when heated, giving phosphine or hydrogen or both, and leaving the ortho- or pyro-phosphate of the metal; thus

$$2BaHPO_3.H_2O = Ba_2P_2O_7 + 2H_2$$
$$5PbHPO_3 = Pb_2P_2O_7 + Pb_3(PO_4)_2 + PH_3 + H_2$$

The formulæ of typical phosphites are as follows :—

LiH_2PO_3 ; $Li_2HPO_3.H_2O$, four-sided plates ; $NaH_2PO_3.2\frac{1}{2}H_2O$, monoclinic prisms ; $Na_2HPO_3.5{\cdot}5H_2O$, rhombic bipyramidal needles ; KH_2PO_3, monoclinic prisms ; K_2HPO_3 ; $NH_4H_2PO_3$, monoclinic prisms ; $(NH_4)_2HPO_3.H_2O$, four-sided prisms ; Ag_2HPO_3, white crystalline precipitate ; $2CaHPO_3.2H_2O$, white precipitate ; $Ba(H_2PO_3)_2$; $BaHPO_3.\frac{1}{2}H_2O$, white crystals ; $Ba_2(H_2PO_3)_3.5H_2O$; $Mg(H_2PO_3)_2$; $MgHPO_3.6H_2O$; $CuHPO_3.2H_2O$, blue crystals ; $ZnHPO_3.2\frac{1}{2}H_2O$; $MnHPO_3.H_2O$, reddish-white precipitate ; $Pb(H_2PO_3)_2$; $PbHPO_3$; nFeO.P_2O_3, crystalline mineral ; $CoHPO_3.2H_2O$, red crystals, blue when dried ; $(NH_4)_2[Co_3(HPO_3)_4].18H_2O$, and a corresponding nickel compound.

Ammonium phosphite in its hydrated form, $(NH_4)_2HPO_3.H_2O$, or as the anhydrous salt, has been made by saturating phosphorous acid with ammonia,[1] or by passing ammonia over the hydrogen phosphite at 100° C.[2] It easily loses both water and ammonia when heated or kept in a vacuum.[3]

The hydrogen phosphite $NH_4H_2PO_3$ is rather more stable, and has been prepared by the neutralisation of phosphorous acid with ammonia to methyl orange, followed by careful evaporation.[4] It melts at about 120° C. and decomposes at about 140° C., giving ammonia, phosphine and phosphorous acid. The form and constants of the crystals have been described.[5]

Hydroxylamine phosphite, $(NH_2OH)_2.H_3PO_3$, was prepared by double decomposition of one mol of Na_2HPO_3 with two mols of $NH_2OH.HCl$. The sodium chloride was crystallised out by evaporation *in vacuo*, and the very soluble hydroxylamine salt crystallised from alcohol. It melts easily, is inflammable and is a strong reducing agent. Hydrazine phosphite, $N_2H_4.H_3PO_3$, has also been prepared, from barium phosphite and hydrazine sulphate.[6]

Structure of the Hypophosphites and Phosphites.—The monobasicity of hypophosphorous acid points to the unsymmetrical formula. The probable existence also of a proportion in the symmetrical form may be indicated by the ease with which the acid undergoes self-oxidation and -reduction on heating, thus

$$HO-PO=\boxed{H_2 \quad H-P}=(OH)_2 \longrightarrow PH_3 + HO-PO=(OH)_2$$

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[1] Rose, *Annalen*, 1827, 9, 28, 33, 215; Fourcroy and Vauquelin, *Journ. Polyt.*, 1795, 4, 655.

[2] Amat, *loc. cit.*, and "*Sur les phosphites et les pyrophosphites*," 1891, Paris.

[3] Wurtz, *Ann. Chim. Phys.*, *loc. cit.*

[4] Amat, *loc. cit.*

[5] Dufet, *Bull. Soc. min. de France*, 1891, 14, 209.

[6] Sabaneeff, *Zeitsch. anorg. Chem.*, 1898, 17, 488; 1899, 20, 22.

Hypophosphorous acid easily adds on benzaldehyde, and the product, di[oxybenzene] phosphorous acid, must have the unsymmetrical formula

$$HO-PO=[CH(OH)C_6H_5]_2$$ [1]

Alkylphosphinic acids should also be considered as compounds in which the alkyl is directly attached to phosphorus, since they have been obtained by the oxidation of primary alkylphosphines with fuming nitric acid. $(CH_3)_2=PO-OH$ is hardly an acid, but rather resembles a higher aliphatic alcohol in its waxy appearance and melting-point (76° C.). This compound sublimes without decomposition.

Ester acids of phosphorous acid are known, such as $CH_3.PO(OH)_2$ (m.pt. 105° C.) and $C_2H_5.PO(OH)_2$ (m.pt. 44° C.), which are capable of giving mono- and di-ethyl esters.[2]

The tautomerism of phosphites has been proved by the preparation of two triethyl phosphites.[3] The one, prepared by the action of phosphorus trichloride on sodium ethoxide, was probably the symmetrical ester, being formed according to the equation

$$PCl_3+3NaOC_2H_5=P(OC_2H_5)_3+3NaCl$$

Its density, $D^{17°}_{0°}$, was 0·9605, it boiled at 156° C., was insoluble in water, soluble in many organic solvents, and had a molecular weight of 154 in benzene. It reduced mercuric chloride. The other, prepared by the action of lead phosphite on ethyl iodide, or phosphorous oxide on ethyl alcohol, had a density, $D^{21°}_{0°}$, of 1·028, boiled at 198° C. and did not reduce mercuric chloride. This was probably diethylethyl phosphite, having the formula $C_2H_5-PO=(OC_2H_5)_2$. A diethyl ester has also been prepared which boils at 187°–188° C. and may have either formula

$$HO-P(OC_2H_5)_2 \quad \text{or} \quad H-PO(OC_2H_5)_2$$

The unsaturated character of these trialkyl esters was shown by the ease with which they were attacked by nitric acid, but still more clearly by the formation, with evolution of heat, of stable crystalline addition compounds when they were mixed with cuprous halides. Thus $CuCl.P(OC_2H_5)_3$ was described as consisting of colourless crystals melting at 190° to 192° C. and soluble in organic solvents.[4] This property they share with phosphine, alkylphosphines and phosphorus trihalides. The phosphoric esters were quite indifferent to cuprous halides. Nor were such addition compounds formed either by phosphorous acid itself or by the dialkyl esters, which may show that the latter compounds have the unsymmetrical formula. Phosphorous acid probably exists in both forms, but first as $P(OH)_3$, *i.e.* when produced from PCl_3 and H_2O.[5] This may be transformed into the unsymmetrical form through an addition compound $HCl.P(OH)_3$,[4] and probably also exists in the form of complex molecules, such as

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[1] Ville, *Ann. Chim. Phys.*, 1891, [6], 23, 291.

[2] Thorpe and North, *Trans. Chem. Soc.*, 1890, 57, 545, 634. See also Palazzo and Maggiacomo, *Atti R. Accad. Lincei*, 1908, [5], 17, i, 432.

[3] Railton, *Trans. Chem. Soc.*, 1855, 7, 216; Thorpe and North, *loc. cit.*; Michaelis and Becker, *Ber.*, 1897, 30, 1003.

[4] Arbusov, *J. Russ. Phys. Chem. Soc.*, 1905, 38, 161.

[5] Mitchell, *Trans. Chem. Soc.*, 1925, 127, 336.

$H_4(H_2P_2O_6)$, the existence of which was demonstrated by the freezing-points of concentrated solutions.[1]

The X-ray K absorption spectra of phosphorous acid and the phosphites of Na, Al, Mn, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, Ca, Ni and Cd were nearly the same, the head of the absorption band lying at $\lambda = 5754{\cdot}1$ X-ray units. The band of silver diethyl phosphite was at 5760·4. The values for phosphorus in the elementary state and in different forms of combination were as follows :—

Hypophosphites.	Phosphites.	Phosphates.	Violet Phosphorus.	White Phosphorus.
5757·5	5754·1	5750·7	5771·5	5776·9 [2]

It was stated that the wavelengths of the absorption bands of elements are higher than those of their compounds, and that the bands pass to shorter wavelengths as the valency rises, provided that the successively attached atoms or radicals are the same. The general results showed that the structural formulæ of the phosphorous diesters, triphenylmethylphosphorous acid and ferric monopropyl phosphite were $(RO)_2{=}PO-(H)$, sodium diethyl phosphite $(EtO)_2PO(Na)$, silver diethyl phosphite $(EtO)_2P(OAg)$, monoacetylphosphorous acid $(HO)_2PO(Ac)$. In solution, the diesters and metal esters contained a mixture of tautomeric forms.[3]

Meta- and Pyro-phosphorous Acids.—The acids HPO_2 and $H_4P_2O_5$ may be regarded as partly dehydrated forms of orthophosphorous acid. In their modes of preparation and properties they recall somewhat the meta- and pyro-phosphoric acids.

Metaphosphorous Acid was produced during the spontaneous combustion of dry phosphine in dry oxygen at a low pressure, probably according to the equation

$$PH_3 + O_2 = H_2 + HPO_2$$

It was deposited on the walls of the vessel in feathery crystals,[4] which were readily hydrated by water giving H_3PO_3.

Pyrophosphorous Acid has been made by treating PCl_3 with a little water, or by shaking the syrupy acid with a slight excess of PCl_3 and evaporating in a desiccator over KOH and P_2O_5. The crystalline acid was very deliquescent.[5] Secondary phosphites when heated gave pyrophosphites with loss of water, thus

$$2BaHPO_3 = Ba_2P_2O_5 + H_2O$$

By the addition of the theoretical quantity of sulphuric acid the unstable $H_4P_2O_5$ was obtained.

Sodium dihydropyrophosphite was prepared by heating sodium hydrogen phosphite in a vacuum at 160° C. :—

$$2NaH_2PO_3 = Na_2H_2P_2O_5 + H_2O$$ [6]

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[1] Rosenheim and Italiener, *Zeitsch. anorg. Chem.*, 1923, 129, 196.

[2] Stelling, *Zeitsch. anorg. Chem.*, 1923, 131, 48.

[3] Stelling, *Zeitsch. physikal. Chem.*, 1925, 117, 194.

[4] van de Stadt, *Zeitsch. physikal. Chem.*, 1898, 12, 322.

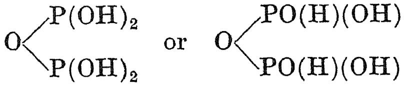
[5] Auger, *Compt. rend.*, 1903, 136, 814.

[6] Amat, "*Sur les phosphites et les pyrophosphites*," Paris, 1891; *Compt. rend.*, 1888, 106, 1400; 1889, 109, 1056; 1890, 110, 191; 1890, 111, 676; 1891, 112, 527, 614.

The free acid was hydrated to phosphorous acid in solution with evolution of 4·9 Cals. per mol of $H_4P_2O_5$. Hydration was accelerated by strong acids. The dihydrogen pyrophosphite of sodium, $Na_2H_2P_2O_5$, similarly gave NaH_2PO_3. The acid appears to be dibasic, the salt $Na_2H_2P_2O_5$ being formed by neutralisation, with evolution of 14·3 Cals. per mol of water formed in the equation

$$H_4P_2O_5 + 2NaOH = Na_2H_2P_2O_5 + 2H_2O$$

Other salts of this acid have been prepared. As in the case of phosphorous acid the structure may be symmetrical or unsymmetrical, thus



$$O\left\langle\begin{matrix}P(OH)_2\\P(OH)_2\end{matrix}\right. \quad \text{or} \quad O\left\langle\begin{matrix}PO(H)(OH)\\PO(H)(OH)\end{matrix}\right.$$

Detection and Estimation of Phosphites and Hypophosphites.—Solutions of hypophosphorous and phosphorous acids, as well as their salts, when evaporated to dryness and heated, give spontaneously inflammable phosphine and a residue of phosphoric acid or phosphate respectively. The reduction of salts of copper and silver, and of mercuric chloride, by these acids may also be used as tests. When the alkali salts are boiled with concentrated alkali hydrogen is evolved and a phosphate is found in solution, thus

$$KH_2PO_2 + 2KOH = K_3PO_4 + 2H_2$$
$$K_2HPO_3 + KOH = K_3PO_4 + H_2$$

Nascent hydrogen, from zinc and sulphuric acid, reduces both acids to phosphine, which may be detected by the yellow stain which it produces on silver nitrate :—

$$PH_3 + 6AgNO_3 = PAg_3.3AgNO_3 + 3HNO_3$$

This is similar to the stain given by arsine and, like $AsAg_3.3AgNO_3$, is hydrolysed and blackened by moisture :—

$$PAg_3.3AgNO_3 + 3H_2O = H_3PO_3 + 3HNO_3 + 6Ag$$

Hypophosphites are all soluble in water and therefore the solutions give no precipitates with the ions of the alkaline earths, silver, etc. Silver salts, however, are rapidly reduced to metallic silver, and phosphoric acid is found in the solution :—

$$2NaH_2PO_2 + 2AgNO_3 + 4H_2O = 2H_3PO_4 + 2NaNO_3 + 2Ag + 3H_2$$

When hypophosphites are heated with copper sulphate solution to 55° C. a reddish-black precipitate of Cu_2H_2 is produced, which decomposes at 100° C. into hydrogen and copper. Permanganates are immediately reduced by hypophosphites. The effect of other oxidising agents is mentioned under "Estimation."

Phosphites may be distinguished from hypophosphites by several tests. The ions of barium and lead give white precipitates with solutions of phosphites. Silver nitrate gives a white precipitate in the cold, from which black metallic silver is quickly deposited on warming :—

$$Na_2HPO_3 + 2AgNO_3 = Ag_2HPO_3 + 2NaNO_3$$
$$Ag_2HPO_3 + H_2O = 2Ag + H_3PO_4$$

Copper sulphate is reduced to brown metallic copper with evolution of hydrogen, but without intermediate formation of a hydride. Permanganates are reduced more slowly by phosphites than by hypophosphites under similar conditions.

Estimation.—The course of the neutralisation curves of hypophosphorous and phosphorous acids can be deduced from the values of the dissociation constants. The curves have also been determined with the aid of the glass electrode.[1] The curve for hypophosphorous acid is that of a strong acid with only one inflection. That of phosphorous acid has two inflections, at $pH = 3{\cdot}4$ to $4{\cdot}5$ and at $pH = 8{\cdot}4$ to $9{\cdot}2$. The first " end-point " can be located with dimethylaminoazobenzene or methyl orange, and the second with phenolphthalein or thymol blue. The first gives the sum of H_3PO_2, H_3PO_3 and H_3PO_4 if present together, while the difference between the first and second " end-points " gives the sum of H_3PO_3 and H_3PO_4. From these data the equivalents of H_3PO_2 can be obtained.

Hypophosphite and phosphite may also be determined by oxidation with iodine. In *alkaline* bicarbonate solutions phosphites are oxidised quickly to phosphates, while hypophosphites are hardly affected, *i.e.* they do not use any measurable amount of decinormal iodine after standing for two hours at ordinary temperatures. In *acid* solution hypophosphorous acid is slowly oxidised to phosphorous acid, but no further, according to the equation

$$H_3PO_2 + I_2 + H_2O = H_3PO_3 + 2HI$$ [2]

On these reactions is based a method for determining the acids separately or in the same solution.

A *phosphite* solution of about $M/10$ concentration is placed in a stoppered flask with an excess of sodium bicarbonate saturated with carbonic acid and an excess of decinormal iodine solution and allowed to stand for about an hour. It is then acidified with acetic acid and the excess of iodine is back-titrated with decinormal bicarbonate-arsenite.

$$1 \text{ c.c. of decinormal iodine solution} \equiv 0{\cdot}004103 \text{ gram of } H_3PO_3$$

A *hypophosphite* solution is acidified with dilute sulphuric acid, treated with a known amount, in excess, of decinormal iodine solution and allowed to stand for 10 hours at ordinary temperatures. A cream of $NaHCO_3$ is then added until CO_2 evolution ceases, then fifth-normal $NaHCO_3$ solution, saturated with CO_2, whereby oxidation goes through the next stage, to phosphate. After addition of acetic acid the excess of iodine is titrated with standard arsenite as before.

$$1 \text{ c.c. decinormal iodine solution} \equiv 0{\cdot}00165 \text{ gram of } H_3PO_2$$

Phosphite, which usually is present in small amounts in hypophosphite, will be included and must be titrated separately in bicarbonate solution as before.[3]

Acid dichromate and alkaline permanganate may also be used as oxidising agents, the excess being determined iodometrically and with ferrous sulphate solution respectively.

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[1] Morton, *Quart. J. Pharm.*, 1930, 3, 438.

[2] Rupp and Finck, *Ber.*, 1902, 35, 3691; *Arch. Pharm.*, 1902, 240, 663.

[3] Wulf and Jung, *Zeitsch. anorg. Chem.*, 1931, 201, 347.

Either of these acids may also be determined by weighing the mercurous chloride which is produced by reaction with mercuric chloride in slightly acid solution, according to the equations

$$H_3PO_2 + 2H_2O + 4HgCl_2 = 2Hg_2Cl_2 + 4HCl + H_3PO_4$$
$$H_3PO_3 + H_2O + 2HgCl_2 = Hg_2Cl_2 + 2HCl + H_3PO_4$$

The mercurous chloride is washed with water and dried at 110° C., or with alcohol and ether and dried at 95° C.[1]

Hypophosphoric Acid.—This acid, together with phosphorous and phosphoric acids, was first produced by the slow oxidation of phosphorus in the air and in the presence of water at a moderately low temperature (5° to 10° C.); it was isolated through the formation of a sparingly soluble sodium salt.[2]

It was also produced by the slow oxidation of phosphorus with silver nitrate in neutral or ammoniacal solution.[3]

Oxidation of yellow phosphorus by copper nitrate in the presence of nitric acid at about 60° C. also yielded hypophosphoric acid along with phosphoric acid and copper phosphide.[4] These reactions have been expressed by the equations

$$4P + 5Cu(NO_3)_2 + 8H_2O = Cu_3P_2 + 2Cu + 10HNO_3 + 2H_3PO_4$$
$$4P + 4Cu(NO_3)_2 + 6H_2O = Cu_3P_2 + Cu + 8HNO_3 + H_4P_2O_6$$ [5]

Better yields were obtained by the electrolysis of 1 to 2 per cent. sulphuric acid using anodes of copper or nickel phosphide.[6]

The conditions for obtaining a good yield by the oxidation of phosphorus have been worked out by a number of investigators.[7] In the method of Cavalier and Cornec [8] glass rods are placed parallel to one another in a photographic dish and sticks of phosphorus laid across them, each pair of sticks being separated by a glass rod, which is also of course laid transversely to the supporting rods. Water is added until the sticks of phosphorus are half-immersed and the whole is covered with a glass plate resting on wadding at its edges. The air is thus filtered as it enters round the edges. A temperature of 5° to 10° C. is the most favourable. Below 5° C. the oxidation is too slow, while above 10° C. undue quantities of meta- and ortho-phosphoric acids are produced. In winter about 12 per cent. of the phosphorus is oxidised to hypophosphoric acid. The solution may then be treated with saturated sodium acetate, when the acid salt $NaHPO_3.3H_2O$ separates on cooling. Or the boiling solution of the acids may be neutralised to methyl orange with sodium carbonate and concentrated by evaporation, when $NaHPO_3.3H_2O$ crystallises and may be recrystallised from boiling water. The sodium salt dissolved in hot water may be treated with lead acetate and the sparingly soluble lead hypophosphate filtered off. This is then suspended in water and a current of hydrogen sulphide is passed, which liberates the acid. The filtered solution is concentrated somewhat by heat in the open and finally in a vacuum over concentrated sulphuric acid. Alternatively the dilute solution of the free acid may be prepared from barium hypophosphate and dilute sulphuric acid.

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[1] Mitchell, *Trans. Chem. Soc.*, 1924, 125, 1024.

[2] Salzer, *Annalen*, 1878, 194, 28; 1882, 211, 1; 1886, 232, 114.

[3] Sänger, *Annalen*, 1886, 232, 14.

[4] Rosenheim and Pinsker, *Ber.*, 1910, 43, 2003; Corne, *J. Pharm. Chim.*, 1882, [5], 6, 123.

[5] Tauchert, "*Untersuch. über Unterphosphorsäure*," 1913, Munich; idem, *Zeitsch. anorg. Chem.*, 1913, 79, 350.

[6] Rosenheim and Pinsker, *loc. cit.*

[7] Joly, *Compt. rend.*, 1885, 101, 1058, 1150; 1886, 102, 110, 259, 760, 1065; Rosenheim, Stadler and Jacobsohn, *Ber.*, 1906, 39, 2838; Bausa, *Zeitsch. anorg. Chem.*, 1894, 6, 128.

[8] Cavalier and Cornec, *Bull. Soc. chim.*, 1909, [4], 5, 1058.

General Properties.—The evaporated solution prepared as above deposited crystals of the hydrate $H_2PO_3.H_2O$ which had the form of four-sided rectangular plates and melted at 70° C.[1] They were very deliquescent, but when kept over sulphuric acid effloresced giving the anhydrous acid, which melted at 55° C. A half-hydrate, $H_2PO_3.\frac{1}{2}H_2O$, which melted at about 80° C. was also obtained by evaporation over sulphuric acid.

When the anhydrous acid was kept above its melting-point it suddenly decomposed with considerable evolution of heat, thus

$$2H_2PO_3 = H_3PO_3 + HPO_3$$

Phosphine was evolved at about 180° C.

The molar heat of fusion of the anhydrous acid was 3·85 Cals.[2] The hydrate dissolved with absorption of heat.

Aqueous Solutions of Hypophosphoric Acid.—The electrical conductivity of this acid shows that its first hydrion is largely dissociated.

THE MOLAR CONDUCTIVITIES OF HYPOPHOSPHORIC AND PHOSPHOROUS ACIDS.[3]

V	16	32	64	128	256	512	1024
μ H_2PO_3 at 25·6° C. .	184	199	222	246	275	304	370
μ H_3PO_3 at 25·0° C. .	222	252	292	318	337	351	358

The molar conductivities of H_3PO_3 at dilutions up to, and including, 512 were greater than those of H_2PO_3, and this difference would have increased if the latter conductivities had been determined at 25° C. The ions HPO_3^- and $H_2PO_3^-$ probably have practically the same mobility, so that the difference is to be attributed rather to the smaller second dissociation of HPO_3^- (into H^+ and $PO_3^=$) as compared with that of $H_2PO_3^-$ into H^+ and $HPO_3^=$. A very low second constant would also be ascribed to H_2PO_3 on account of the high alkalinity of solutions containing two equivalents of alkali (see "Neutralisation," p. 152).

The change in the conductivity of the salt $NaHPO_3$ or $Na_2H_2P_2O_6$ with dilution shows no effect due to dissociation of a second hydrogen until a dilution is reached between 256 and 512 litres, as is seen from the following table :—

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[1] Joly, *loc. cit.*; Rosenheim and Pritze, *Ber.*, 1908, 41, 2710.

[2] Joly, *loc. cit.*

[3] Rosenheim and Pinsker, *loc. cit.*; Parravano and Marini, *Gazzetta*, 1907, 37, 268; van Name and Huff, *Amer. J. Sci.*, 1918, [4], 45, 91, 103.

V	16	32	64	128	256	512	1024
μ (25° C.)	78·8	81·6	88·1	94·5	100·2	105·9	111·9 [1]
μ (25° C.)	78·8	86·1	92·2	95·9	98·1	100·7	101·6 [2]

Basicity.—The heats of neutralisation indicate a dibasic acid (per atom of phosphorus) as will be seen from the following figures :—[3]

Equivalents of NaOH per mol H_2PO_3	0·5	1	1·5	2·0	3·0
Heat evolved, Cals.	7·57	15·05	21·36	27·11	27·65

During the neutralisation with alkali a sharp end-point was obtained (to methyl orange) when one equivalent of alkali had been added, while phenolphthalein gradually changed between 1·5 and 2·0 equivalents, showing that the second dissociation constant is lower than that of the majority of organic acids (see also "Electrical Conductivity," p. 151).

These facts can be explained equally well on the assumption that the acid is tetrabasic, with two atoms of phosphorus, *i.e.* $H_4P_2O_6$, and this view is in accordance with the existence of four salts—$MH_3P_2O_6$, $M_2H_2P_2O_6$, $M_3HP_2O_6$ and $M_4P_2O_6$.[4]

Further evidence is collected under "Molecular Weight" (p. 153).

The molecular weight as deduced from the freezing-points of aqueous solutions corresponded with doubled molecules, $H_4P_2O_6$, which are highly dissociated, giving one hydrogen ion,[5] or to the acid H_2PO_3 which is very slightly dissociated even in fiftieth-normal solution.

Chemical Properties.—The proof of the individuality of hypophosphoric acid rests largely upon the great differences which exist between it and a mixture of phosphorous and phosphoric acids. These acids were formed irreversibly when hypophosphoric acid was allowed to stand in aqueous solution, especially when this was concentrated and the temperature was 30° C. (or above). A 5 per cent. solution after 3 years contained only phosphorous and phosphoric acids. These acids, on the other hand, showed no tendency to condense together when kept under ordinary conditions. The freezing-point curves of mixtures of the anhydrous acids showed no intermediate maximum and only one eutectic at $-13·0°$ C. and 39 mols per cent. of H_3PO_3.[6]

Decomposition of hypophosphoric acid may be represented as an hydrolysis, thus

$$H_4P_2O_6 + H_2O \longrightarrow H_3PO_3 + H_3PO_4$$

This reaction is catalysed by hydrogen ions and was found to be unimolecular in normal hydrogen-ion concentrations. The values of the constants were 0·000186 at 25° C. and 0·00631 at 60° C.[1] The sodium salt, $NaHPO_3$, having only a low hydrogen-ion concentration (*ca.* 1×10^{-4}), could be kept for long periods without much change, and alkaline solutions containing Na_2PO_3, etc., were still more stable.

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[1] Rosenheim, Stadler and Jacobsohn, *Ber.*, 1906, 39, 2839.
[2] Rosenheim and Reglin, *Zeitsch. anorg. Chem.*, 1921, 120, 103.
[3] Joly, *loc. cit.*
[4] Salzer, *loc. cit.*
[5] Rosenheim and Pinsker, *loc. cit.*
[6] Rosenheim, Stadler and Jacobsohn, 1906, *loc. cit.*

Cold solutions of the acid did not precipitate the metals from gold, silver or mercurous solutions. The acid was not oxidised by iodine, hydrogen peroxide or chromic acid in the cold, but was slowly oxidised by potassium permanganate. Hot concentrated solutions were more easily oxidised. When the neutral salts were heated they gave phosphate and phosphine, or pyrophosphate, elemental phosphorus and phosphine. Reducing agents such as hydrogen sulphide or sulphur dioxide had no effect, and even nascent hydrogen, from zinc and acid, gave no phosphine.

Molecular Weight.—Much investigation has been carried out with a view to ascertaining whether the molecule should be formulated as H_2PO_3 or $H_4P_2O_6$. The evidence of electrical conductivity does not lead to a definite conclusion. Molar weights of some esters are known. Thus dimethyl and diethyl hypophosphates (from the silver salt and alkyl iodide) gave elevations of boiling-point in ethyl iodide, chloroform, etc., which corresponded to the formulæ $(CH_3)_2PO_3$, etc.[2] On the other hand molecules such as $(CH_3)_4P_2O_6$ were indicated in benzene solution at its freezing-point. If, as seems probable, the free acid in concentrated solution has the formula $H_4P_2O_6$, the constitution and hydrolysis of this would be represented by

$$(HO)_2OP-PO(OH)_2+H_2O=(HO)_2HPO+(HO)_3PO$$

Hypophosphoric acid was not formed by any ordinary dehydration of a mixture of phosphorous and phosphoric acids, neither was it produced by the hydration of P_2O_4, which yielded only a mixture of equal mols of H_3PO_3 and H_3PO_4.

Hypophosphates.—The salts of the alkali, alkaline earth and some other metals were prepared and studied by Salzer, Rammelsberg, Schuh, Joly, Palm, Bausa and others.[3] The alkali salts prepared from excess of alkali were soluble, whilst those of the alkaline earths, silver and other metals were only sparingly soluble.

The formulæ of some typical hypophosphates are as follows [solubilities in grams per 100 grams of water] :—

$Li_2H_2P_2O_6.2H_2O$, crystalline, sparingly soluble ; $Li_4P_2O_6.7H_2O$, solubility 0·83 ; $Na_2H_2P_2O_6.6H_2O$, monoclinic, solubility 2·0 ; $Na_3HP_2O_6.9H_2O$, tabular monoclinic ; $Na_4P_2O_6.10H_2O$, six-sided monoclinic, solubility 1·5 ; $K_3H_5(P_2O_6)_2.2H_2O$, rhombic, solubility 40 ; $K_2H_2P_2O_6.2H_2O$, monoclinic plates ; $K_4P_2O_6.8H_2O$, rhombic pyramids, solubility 25 ; $(NH_4)_2H_2P_2O_6$, granular or needles, stable in air, solubility 7·1 ; $(NH_4)_4P_2O_6.H_2O$, prismatic, efflorescent, solubility 3·3 ; $Ag_4P_2O_6$, insoluble ; $CaH_2P_2O_6.6H_2O$, monoclinic prisms ; $Ca_2P_2O_6.2H_2O$, gelatinous, insoluble ; $BaH_2P_2O_6$, monoclinic prisms ; $Ba_2P_2O_6$, white precipitate; $Mg_2P_2O_6.12H_2O$, gelatinous, slowly crystalline, solubility 0·0067; $Zn_2P_2O_6.2H_2O$, white precipitate; $Cu_2P_2O_6.6H_2O$, insoluble; $Pb_2P_2O_6$, insoluble; $Ni_2P_2O_6.12H_2O$, prismatic crystals.

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[1] van Name and Huff, *loc. cit.*

[2] Rosenheim and Pinsker, *loc. cit.*; Rosenheim and Reglin, *loc. cit.*; Rosenheim, Stadler and Jacobsohn, *loc. cit.*; Cornec, *Bull. Soc. chim.*, 1909, [4], 5, 1081.

[3] Salzer, *loc. cit.*; Rammelsberg, *J. prakt. Chem.*, 1892, [2], 45, 153; Schuh, "*Beiträge z. Kenntn. d. Unterphosph. Säure,*" Munich, 1911; Joly, *loc. cit.*; Bausa, *loc. cit.*; Palm, "*Neue Verbind. d. Unterphosph. Säure,*" Elberfeld, 1890; Drawe, "*Einige neue Salze der Unterphosphorsäure,*" Rostock, 1888; *Ber.*, 1888, 21, 3401.

A number of double hypophosphates of manganese, cobalt and nickel with the alkali metals have been prepared, such as $K_2NiP_2O_6.6H_2O$ and $3K_2H_2P_2O_6.CoH_2P_2O_6.15H_2O$.

Hypophosphites of hydroxylamine resemble those of ammonia. Thus $(NH_2OH)_2.H_4P_2O_6$ is a crystalline salt, very soluble in water and melting with decomposition. Hydrazine dihydro- and trihydro-hypophosphates, $(N_2H_5)_2H_2P_2O_6$ and $(N_2H_5)H_3P_2O_6$, were both obtained in the crystalline state. The latter is isomeric with ammonium dimetaphosphate, $(NH_4PO_3)_2$.[1]

Detection and Estimation.—The distinctive tests which distinguish hypophosphates from phosphites have already been pointed out (p. 153). One of the most useful is the sparing solubility of sodium hypophosphate. Also, a sparingly soluble guanidine salt (1 per cent. at 28·5° C.) is precipitated when guanidine carbonate is added to a solution of the acid.[2] The acid may be titrated with alkali and phenolphthalein; 3 mols of NaOH correspond to 2 mols of H_2PO_3, *i.e.* the salt $Na_3HP_2O_6$ is formed.[3] The acid may be estimated in the presence of phosphoric and phosphorous acids by precipitation of the silver salt at $pH = 1$ to 2.[4]

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[1] Sabaneeff, *Zeitsch. anorg. Chem.*, 1898, 17, 488; 1899, 20, 22.

[2] Rosenheim and Pinsker, *loc. cit.*

[3] Pinsker, "*Zur anal. Bestimm. der Unterphosphorsaure und phosphorige Säure,*" Berlin, 1909.

[4] Wolf and Jung, *Zeitsch. anorg. Chem.*, 1931, 201, 347.

CHAPTER XII.

PHOSPHORIC ACIDS.

Historical and General.—The production of an acid solution by dissolving in water the products of the combustion of phosphorus was demonstrated by Boyle,[1] and the acid was prepared in a similar manner by Marggraf, who described its properties.[2] It was extracted from the calcium phosphate of bones by Scheele.[3] Lavoisier [4] obtained it from phosphorus and nitric acid. Three forms differing in their properties and in their mode of preparation were recognised early in the nineteenth century.

The usual form, as prepared by Boyle and others, when partly neutralised by soda gave a yellow precipitate with a solution of silver nitrate. When a solution of this ordinary acid was heated in a gold crucible until water ceased to be evolved, a thick pasty mass was left [5] which gave a white silver salt and coagulated albumin. When ordinary sodium phosphate, Na_2HPO_4, was heated to 240° C. it was converted into a salt which gave a white precipitate with silver nitrate.[6] It was also shown by Graham [5] that phosphoric acid could be obtained as a vitreous mass by long heating at 215° C., and that this; when dissolved in water, did not coagulate albumin or give a precipitate with barium chloride in acid solution. When the acid was still more strongly heated it gave a tough vitreous mass, a solution of which coagulated albumin and gave a precipitate with barium chloride.[7] Salts of the same acid were obtained by heating sodium biphosphate, namely, NaH_2PO_4. A vitreous mass was left which was known as " Graham's salt," and is now known as metaphosphate, $NaPO_3$ (*q.v.*), in a polymerised condition. The acid itself was prepared by decomposing the lead salt with H_2S, and also by heating the ortho- or pyro-acid to over 300° C.,[8] and later by several other methods (*q.v.*).[9]

Graham proved that the three acids, ortho-, H_3PO_4, pyro-, $H_4P_2O_7$, and meta-, HPO_3, differed by the quantity of combined water. This water determined the basicity of the acid. The hydrogen could be replaced in stages by a metal, and *e.g.* in the case of orthophosphoric acid different salts, the primary, secondary and tertiary phosphates, could be produced (see also "Basicity," p. 163).

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[1] Boyle, *Phil. Trans.*, 1680, 13, 196.

[2] Marggraf, " *Chemischen Schriften*," 1762, 1, Berlin.

[3] Scheele, "*Chem. Abhandl. v. der Luft u. Feuer*," Upsala, 1777.

[4] Lavoisier, "*Opuscules physiques et chymiques*," Paris, 1774.

[5] Graham, *Phil. Trans.*, 1833, 123, 253.

[6] Clark, *Edin. J. Science*, 1827, 7, 298.

[7] Berzelius, *Gilbert's Annalen*, 1816, 53, 393; 1816, 54, 31; *Ann. Chim. Phys.*, 1816, [2], 2, 151, 217, 329.

[8] Gregory, *Annalen*, 1845, 54, 94; Maddrell, *Phil. Mag.*, 1847, [3], 30, 322.

[9] See Graham, "Researches on the Arsenates, Phosphates and Modifications of Phosphoric Acid," *Phil. Trans.*, 1833, 123, 253.

ORTHOPHOSPHORIC ACID, H_3PO_4.

The acid which is produced finally by the oxidation of phosphorus in the presence of sufficient water and after heating has probably the constitutional formula $OP(OH)_3$ (see p. 59). The term "ortho," in accordance with Graham's description, was applied to "ordinary" phosphoric acid. Later, on the hypothesis of the quinquevalent nature of phosphorus, it was considered that the hypothetical acid $P(OH)_5$ would, strictly speaking, be the "ortho" acid. However, the present theories of valency do not indicate the possible existence of such an acid, but rather that $OP(OH)_3$ should be the most highly hydroxylated compound.

Preparation.—The acid may be made by means of a great variety of reactions, some of which are referred to under the "Oxides," "Halides" and "Phosphoric Acid (p. 224)." Only a few methods, of technical or historical importance, will be described here.

(1) The decomposition of naturally occurring phosphates. From this source the original supplies both of technical and refined phosphoric acid are derived. The decomposition is effected by sulphuric acid, supplied in the quantities required by the equation

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

The decomposition may be carried out in a large vat of pitch pine saturated with tar oil, and provided with a vertical wooden shaft bearing arms or paddles and rotating on a pivot which is protected with cast-iron. In the vat are placed weak liquors from a previous decomposition and steam is blown in through a leaden pipe. Stirring is then commenced, and a charge of 6 cwt. of finely-ground high-grade phosphate (at least 70 per cent. $Ca_3(PO_4)_2$) is added alternately with 5 carboys of "chamber acid" of density 1·5 to 1·6 (free from arsenic). After the reaction is completed the whole charge is run on to slightly inclined filter-beds made of ashes supported on clinkers and contained in rectangular wooden tanks. The phosphoric acid which runs off first has a density of 1·150. The deposited gypsum is kept covered with water supplied as a spray until the density of the effluent falls to 1·010. The gypsum sludge, containing small amounts of free phosphoric acid and phosphate of lime, is dried by waste heat and used for mixing with superphosphate and for other purposes. The solution of phosphoric acid is concentrated by evaporation in lead-lined wooden tanks which are heated by lead pipes carrying superheated steam, concentration being continued up to a density of 1·325 to 1·50. Calcium sulphate deposited in this part of the process is removed and washed.

(2) The preparation of the acid by the combustion of phosphorus and solution of the "flowers of phosphorus" in water has an historical interest only. It is obviously too expensive for large-scale work, nor does it yield a pure product.

(3) Oxidation of red phosphorus by nitric acid was used before the end of the eighteenth century.[1] An excess of nitric acid of density

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[1] Lavoisier, *Mém. Acad.*, 1780, 343; Martres, *Ann. Chim. Phys.*, 1810, [1], 73, 98.

1·20 to 1·25, namely, about 16 parts, is added to 1 part of phosphorus in a flask carrying a reflux condenser which is fitted in by a ground-glass joint. The phosphoric acid may be concentrated in a platinum or gold dish and is then free from most of the impurities mentioned later, with the possible exception of arsenic derived from the red phosphorus. [In process (1) arsenic, if present, is generally introduced with the sulphuric acid.] In both cases it will be converted into arsenic or arsenious acid. It may be removed by saturation with sulphur dioxide, which reduces arsenic to arsenious acid, followed by boiling to remove the excess of SO_2, precipitation of the arsenic as sulphide by hydrogen sulphide, filtration and removal of the excess of H_2S by means of a current of air.

Concentrated phosphoric acid may be further purified by crystallisation (see p. 158).

(4) *Furnace Methods.*—Phosphoric acid can be prepared from the pentoxide, which is sublimed at high temperatures from a mixture of calcium phosphate, sand and coke. Phosphorus is first produced and then burns to the pentoxide. Reduction proceeds according to the equation

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C = 3CaSiO_3 + 2P + 5CO$$

An electrically-heated furnace (p. 8) or an oil-fired furnace built of carborundum bricks and kept at a temperature of 1500° to 1700° C. is suitable. A regenerative system of heating is used. The mixture of carbon, sand and phosphate is introduced at the top of a slanting flue and meets the ascending heated gases in its descent to the hearth, where it melts and reacts according to the equation given above. The escaping gases are taken round and burnt in a set of channels which surround the furnace.[1]

If phosphorus is burnt in air to the pentoxide, the absorption of this in water is rather difficult. Oxidation by steam according to the equation

$$2P + 5H_2O = P_2O_5 + 5H_2$$

gives hydrogen as a by-product which may be converted into ammonia and combined with the phosphoric oxide (Liljenroth process).[2]

Impurities.—The acid prepared by commercial methods contains numerous impurities, some of which are difficult to remove. They include bases such as Na, K, Ca, Al, Fe, Mn totalling 0·5 to 3·0 per cent., Pb up to 14 parts per million, Ag from 1 to 2·5 parts per million, H_2SO_4 from 0·1 to 1·0 per cent., HF in about the same amount, and HCl from 0·01 to 0·04 per cent.[3]

Preparation of the Crystalline Acid.—Two compounds have been crystallised from concentrated solutions of phosphoric acid—the anhydrous acid, H_3PO_4, and the hemi-hydrate $2H_3PO_4.H_2O$.[1] According to Joly[1] a solution having the composition $H_3PO_4 + 0{\cdot}3H_2O$, when inoculated with a crystal of H_3PO_4, deposits the hemi-hydrate. The mother liquor then has the composition $2H_3PO_4.H_2O$ and solidifies to a mass of crystals when inoculated with this hydrate. Another method of obtaining the crystalline acid has been described in the following terms: "Crystals of anhydrous phosphoric acid were prepared by maintaining the ordinary C.P.* acid in an open vessel at a temperature of about 95° C. until it reached a specific gravity of approximately $D^{25°}_{4°}$ 1·85. The solution was then cooled below 40° C., inoculated with a crystal of orthophosphoric acid, allowed to stand until crystallisation was complete and the mother liquor then separated from the crystals by centrifuging in a porcelain-lined centrifuge. The crystals recovered in this way were then melted at a temperature of about 50°, sufficient water was added to bring to a specific gravity of $D^{25°}_{4°}$ 1·85, the solution inoculated as before and the process repeated thrice. The crystals were finally dried by allowing them to stand for several months over phosphorus pentoxide. Crystals of the semi-hydrate were prepared by adding the proper amount of water to a weighed portion of fused anhydrous phosphoric acid, cooling below 29° and inoculating with a crystal of the hydrate."[2]

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[1] Thomas, *British Patents*, 2414, 2196 (1879); Albert, *German Patent*, 12501 (1880); Rose, *German Patent*, 12372 (1880); Thomas and Twymann, *British Patent*, 438 (1883); Adair and Thomlinson, *British Patent*, 747 (1883); Lomax, *British Patent*, 9611 (1900); Fairweather, *British Patent*, 191630 (1922). Kendall, Booge and Andrews, *J. Amer. Chem. Soc.*, 1917, 39, 2303; Carpenter, *Chem. Age*, 1922, 6, 830; Waggaman and Turley, *J. Ind. Eng. Chem.*, 1920, 12, 646; Waggaman, *ibid.*, 1924, 16, 176; Ross, Durgin and Jones, *ibid.*, 1922, 14, 533; *ibid.*, 1925, 17, 1081; Ross, Mehring and Jones, *ibid.*, 1924, 16, 563; Jacob, *Chem. Trade J.*, 1925, 77, 353.

[2] *Chem. Age*, 1927, 17, 232, 252; "*Annual Reports of the Progress of Applied Chemistry*," 1926.

[3] Ross, Durgin and Jones, *loc. cit.*

Physical Properties of the Solid Hydrates of P_2O_5.—The melting-points, as registered by different investigators, are in fair agreement, thus:

H_3PO_4 . .	38·6[3]	41·75[4]	42·30[5]	42·35° C.[2]
$2H_3PO_4.H_2O$.	27·0[6]	29·0[7]	29·35[5]	29·32° C.[2]

The thermal diagram of H_3PO_4 and H_2O is shown in fig. 4,[2] on which there are two melting-points, m_1 that of H_3PO_4 and m_2 that of $2H_3PO_4.H_2O$, and two eutectics, e_1 that of H_3PO_4 and $2H_3PO_4.H_2O$ and e_2 that of $2H_3PO_4.H_2O$ and ice. The solubilities according to Smith and Menzies are marked in the table opposite by an asterisk. These investigators reported also a distinct solubility curve corresponding to a hydrate $10H_3PO_4.H_2O$, which started from the eutectic e_1 and ended with a transition point at 25·85° C.

Phosphoric acid crystallises in four- or six-sided prisms belonging to the rhombic system.[6]

The determination of the molecular weight by depression of the freezing-point indicates some electrolytic dissociation.[8] A value of 93 has been found for the molecular weight.[9] The acid apparently

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[1] Joly, *Compt. rend.*, 1885, 100, 447; 1886, 102, 316.

* C.P. = Commercial pure.

[2] Ross and Jones, *J. Amer. Chem. Soc.*, 1925, 47, 2165.

[3] Thomsen, *Ber.*, 1874, 7, 997.

[4] Berthelot, *Ann. Chim. Phys.*, 1878, [5], 14, 441.

[5] Smith and Menzies, *J. Amer. Chem. Soc.*, 1909, 31, 1183.

[6] Joly, *Compt. rend.*, *loc. cit.*

[7] Giran, *Compt. rend.*, 1908, 146, 1270; idem, *Ann. Chim. Phys.*, 1908, [8], 14, 565.

[8] Kendall, Booge and Andrews, *loc. cit.*; Jones, H. C., "*Hydrates in Solution*," Washington, 1907.

[9] Holt and Myers, *Trans. Chem. Soc.*, 1911, 99, 384; *ibid.*, 1913, 103, 532.

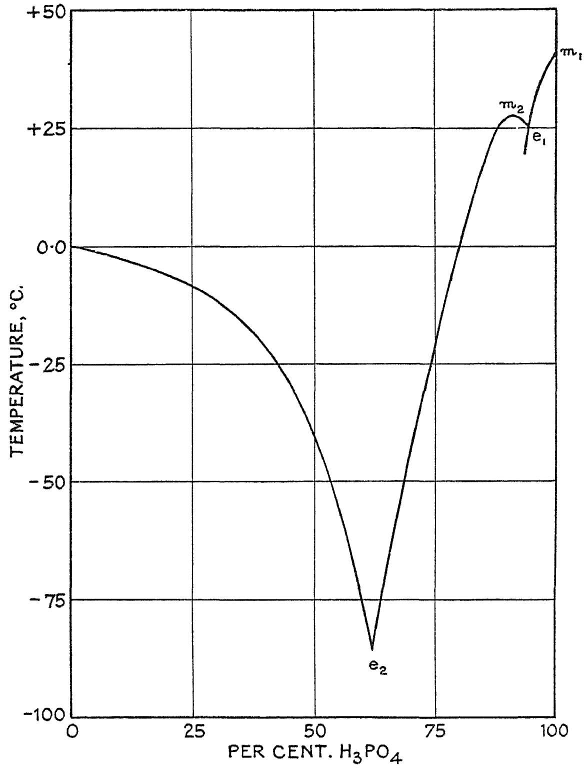

Fig. 4.—Hydrates of Phosphoric Acid.

SOLUBILITIES, MELTING-POINTS AND EUTECTICS OF THE SYSTEM H_3PO_4—H_2O.

Temperature, ° C.	Grams H_3PO_4 per 100 Grams Solution.	Solid Phase.	Temperature, ° C.	Grams H_3PO_4 per 100 Grams Solution.	Solid Phase.
e_2, −85·0	62·5	Ice + $2H_3PO_4.H_2O$	28·28	92·72	$2H_3PO_4.H_2O$
'$_2$, −81·0*	63·0	,,	27·36	93·33	,,
−57·0	67·5	$2H_3PO_4.H_2O$	26·08	93·24	,,
−43·0	70·0	,,	e_1, 23·50	94·75	$2H_3PO_4.H_2O$ + H_3PO_4
−29·0	72·5	,,	25·41*	94·1	$2H_3PO_4.H_2O$
−17·5	75·0	,,	25·88	95·22	H_3PO_4
−16·3*	76·7	,,	26·23*	95·90	,,
0·0	78·75	,,	27·30	95·56	,,
+ 0·5*	78·7	,,	28·38	95·86	,,
18·92	84·07	,,	29·90	96·18	,,
23·41	85·93	,,	31·96	96·80	,,
25·24	87·05	,,	34·06	97·40	,,
27·0*	87·7	,,	36·15	98·00	,,
27·3	88·51	,,	40 02	99·27	,,
28·75	90·0	,,	m_1, 42·30*	100·0	,,
m_2, 29·32	91·60	,,	m_1, 42·35	100·0	,,
m_2, 29·35*	91·60	,,			,,

forms double molecules in glacial acetic acid which dissociate in process of time.[1]

The molar heat of fusion of H_3PO_4 is 2·52 Cals.,[2] that of $2H_3PO_4.H_2O$ 7·28 Cals.[3] The heat of solution was found to be positive,[4] 2·69 Cals. per mol of the crystalline acid dissolved[2] and 5·21 Cals. per mol of the liquid acid.

The heat of dilution was found to be—[5]

Mols water per mol H_3PO_4	11·19	13·88	19·88	29·99
Heat of dilution, Cals. .	33·13	19·93	12·26	8·23

The heat of formation from the elements includes that of water, and was found to be—[2]

H_3PO_4 crystalline, 302·56 Cals.	H_3PO_4 fused, 300·04 Cals.	H_3PO_4 dissolved, 305·29 Cals.

The following tables summarise the principal determinations of the densities at certain definite temperatures. If the percentages of H_3PO_4 are divided by 1·38 the quotient gives percentages of P_2O_5.

DENSITIES OF AQUEOUS SOLUTIONS OF PHOSPHORIC ACID.

At 15° C.[6]

Per cent. H_3PO_4 .	5	10	20	30	40	50	60
Density . .	1·0276	1·0567	1·1196	1·1889	1·2651	1·3486	1·4395

At 17·5° C.[7]

Per cent. P_2O_5	5	10	20	30	40	50	60	68
Density . .	1·037	1·079	1·169	1·271	1·383	1·521	1·677	1·809

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[1] Giran, *Ann. Chim. Phys.*, 1908, [8], 14, 565.

[2] Thomsen, "*Thermochemische Untersuchungen,*" transl. Traube, Stuttgart, 1906.

[3] Joly, *loc. cit.*

[4] Giran, *Compt. rend.*, 1902, 135, 961; 1903, 136, 552.

[5] Rümelin, *Zeitsch. physikal. Chem.*, 1907, 58, 460.

[6] Schiff, *Annalen*, 1860, 113, 183, 192.

[7] Hager, "*Kommentar zur Pharm. germ.,*" Berlin, 1884.

At 25° C.[1]

Per cent. H_3PO_4 .	5	10	15	20	25	30	35	40
Density . .	1·027	1·055	1·085	1·116	1·149	1·183	1·219	1·256
Per cent. H_3PO_4 .	45	50	55	60	65	70	75	80
Density . .	1·294	1·336	1·381	1·429	1·477	1·527	1·579	1·633
Per cent. H_3PO_4 .	85	90	91	..	..	..	..	..
Density . .	1·690	1·753	1·766	..	..	..	..	..

The vapour pressures of solutions at 0° C. are—[2]

Grams H_3PO_4 in 100 grams H_2O	0·945	22·32	124·9	390·2
p_{H_2O} . .	4·612	4·377	2·710	0·636 mm.

Vapour pressures of water at 100° C. were lowered in a high ratio by phosphoric acid, as appears from the following data :—[3]

Grams H_3PO_4 in 100 grams H_2O .	20·75	149·16	330·52
Lowering of vapour pressure .	30·1	290·9	507·3 mm.

The crystalline acid has an appreciable specific conductivity of about 1×10^{-4} reciprocal ohms (mhos), while the fused acid at the same temperature has a conductivity of 1×10^{-2} mhos.[4] Specific conductivities of the more concentrated solutions show a maximum at about 43 per cent., as appears from the following data :—[5]

CONDUCTIVITIES OF CONCENTRATED SOLUTIONS OF PHOSPHORIC ACID.

H_3PO_4, per cent. .	1·4	2·87	5·28	16·09	30·71
Specific conductivity, κ	0·014	0·02533	0·04245	0·08064	0·12816
H_3PO_4, per cent. .	43·26	52·83	71·29	92·07	100·0
Specific conductivity, κ	0·14916	0·13750	0·07876	0·02203	0·01406

The molar conductivity $(=1000\kappa/c)$ thus varies from 97·50 in the 1·4 per cent. solution to 26·28 in the 43·26 per cent. solution and 1·31 in the 92·07 per cent. solution. Degrees of ionisation are low in the concentrated acids.

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[1] Knowlton and Mounce, *J. Ind. Eng. Chem.*, 1921, 13, 1158.
[2] Dieterici, *Wied. Annalen*, 1891, 42, 513; 1893, 50, 47; 1897, 62, 616.
[3] Tammann, *Mém. Acad. St Petersburg*, 1888, [7], 35, 9.
[4] Rabinovitch, *Zeitsch. anorg. Chem.*, 1923, 129, 60.
[5] Phillips, *Trans. Chem. Soc.*, 1909, 95, 59.

The conductivities of the more dilute solutions up to 0·1 molar have been determined to 156° C.

EQUIVALENT CONDUCTIVITIES OF DILUTE SOLUTIONS OF PHOSPHORIC ACID.[1]

H_3PO_4, mols per litre .	0	0·0002	0·002	0·010	0·0125	0·050	0·080	0·100
λ at 18° C. .	338	330·8	283·1	203	191·2	122·7	104	96·5
λ at 25° C. .	378	367·2	311·9	222	208·1	132·6	112·4	104·0

The temperature coefficient was positive as usual at ordinary temperatures and reached a maximum at temperatures which varied with the ion concentration. Thus, in the case of the 0·0002 molar solutions, the maximum had not been reached at 156° C. ($\lambda = 804{\cdot}7$), while in the 0·1 molar solution it occurred at about 75° C. Other results were expressed by the formula—[2]

$$\lambda = \lambda_0 e^{-0{\cdot}0822t}(1 + 0{\cdot}01455t)$$

It is clear that the degree of dissociation is less at the higher temperatures; thus for a 0·1 molar solution it is estimated as 38·5 per cent. at 18° C. and 11·5 per cent. at 156° C.[1]

The viscosities of concentrated solutions of phosphoric acid are high; those of moderately concentrated solutions are given below :—

VISCOSITIES OF SOLUTIONS OF PHOSPHORIC ACID.

H_3PO_4, mols per litre . .	0·25	0·50	1·00	2·00 [3]
η relative at 18° C. (water = 1)	1·064	1·143	1·311	1·739
H_3PO_4, equivalents per litre .	0·125	0·25	0·50	1·00 [4]
η relative at 25° C. (water = 1)	1·0312	1·0656	1·1331	1·2871

The refractive index of a solution of the acid of density 1·180 was at 7·5° C.—

Spectral line .	A	D	H
n . . .	1·3584	1·3630	1·3746

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[1] Noyes, "*The Electrical Conductivities of Aqueous Solutions*," Washington, 1907; Noyes, Melcher, Cooper and Eastman, *Zeitsch. physikal. Chem.*, 1910, 70, 335. See also Kohlrausch and Holborn, "*Leitvermogen der Elektrolyte*," Teubner, Leipzig, 1898.

[2] Arrhenius, *Zeitsch. physikal. Chem.*, 1892, 9, 339.

[3] Moore, *Phys. Review*, 1896, [1], 3, 321.

[4] Reyher, *Zeitsch. physikal. Chem.*, 1888, 2, 744.

The molar refraction was 23·6.[1] The equivalent refracting power of the $H_2PO_4^-$ ion has been calculated as 21·6.[2] Refractivities may conveniently be used in determining the concentration of aqueous solutions and also in testing for freedom from the meta- and pyro-acids.[3]

Basicity and Neutralisation of the Phosphoric Acids.—The crystalline forms and other properties of the different phosphates of sodium were described by Graham.[4] The ordinary phosphate of soda "is a highly alkaline salt, although generally viewed as neutral in composition. Mitscherlich found that a solution of this salt required the addition of half as much acid as it already possesses to deprive it of an alkaline reaction." [4] By heating, the salt was found to contain 25·2 molecules of water to 1 molecule of phosphoric oxide. One of these molecules was retained to a higher temperature than the others. "The phosphate of soda contains 3 atoms base; namely, 2 atoms soda and 1 atom water. When this last atom was lost the sodium salt changed into that of a different acid, namely, a pyrophosphate." [5] In modern symbols—

$$Na_2HPO_4.12H_2O \longrightarrow Na_2HPO_4 + 12H_2O$$
$$2Na_2HPO_4 \longrightarrow Na_4P_2O_7 + H_2O$$

Sodium biphosphate was known as a dimorphous salt ". . . of the 4 atoms of water which the crystals contain, they lose, I find, 2 atoms at the temperature of 212° (F.), and not a particle more till heated up to about 375°." After heating to 212° "it contains 3 atoms base, namely, one atom soda and 2 atoms water united to a double atom of phosphoric acid. The salt cannot sustain the loss of any portion of this water without assuming a new train of properties." Several other forms were obtained by heating to higher temperatures, and at a low red heat a glass was obtained which was deliquescent, not crystallisable from solution, and which gave the reactions of "phosphoric acid ignited *per se*." In modern symbols—

$$2NaH_2PO_4.2H_2O \longrightarrow 2NaH_2PO_4 + 2H_2O \text{ at } 212^\circ \text{ F.}$$
$$2NaH_2PO_4 \longrightarrow Na_2H_2P_2O_7 + H_2O \text{ at } 400^\circ \text{ F.}$$
$$2NaH_2PO_4 \longrightarrow 2NaPO_3 + 2H_2O \text{ at dull red heat}$$

When at least half as much alkali as it already contained was added to ordinary phosphate of soda and the solution was concentrated, tufts of slender prismatic needles appeared. This salt was highly alkaline in reaction. "It is a fact of extraordinary interest that the acid of this sub-phosphate is not convertible into pyrophosphoric acid by the action of heat on the salt." In modern terms Na_3PO_4 is unchanged on ignition.

The heat of neutralisation, Q_n, of phosphoric acid (1 mol) with NaOH (n mols) in dilute solution has been determined with the following results:—

---

[1] Gladstone, *Trans. Chem. Soc.*, 1870, 23, 101. See also Cornec, *Ann. Chim. Phys.*, 1913, [8], 29, 490; 30, 63.

[2] Pope, *Trans. Chem. Soc.*, 1896, 69, 1530.

[3] Blake, *Amer. Chem. J.*, 1902, 27, 72.

[4] Graham, *Phil. Trans.*, 1833, 123, 253; "*Researches on the Arseniates, Phosphates, etc.*," Alembic Club Reprints, No. 10, Clay, Edinburgh, 1895.

[5] Clark, 1827, *loc. cit.*

n	0·5	1·0	2·0	3·0	6·0 mols
Q_n	7·3	14·8	27·1	34·0	35·3 Cals.

Thus heat was evolved in a uniform manner as the alkali increased from 0 to 0·5 and 0·5 to 1·0 in the neutralisation of the first hydrogen. It was also evolved in a uniform manner but at a lower rate between 1·0 and 2·0 alkali, showing that the affinity of dissociation of the second hydrogen is lower than that of the first, and at a lower rate still during the neutralisation of the third hydrogen, showing that this has an even lower dissociation affinity (see "Constants," p. 165).[1] Heats corresponding to the neutralisation of the first, second and third hydrogens were 14·8, 12·3 and 6·9 Cals. Heats of neutralisation by the alkaline earths in very dilute solution were in the same order, *e.g.* for $\frac{1}{2}Ca(OH)_2$, etc., 14·8, 9·7 and 5·3 Cals. respectively.[2]

The heat of dissociation, Q_d, probably is positive, since dissociation diminished with rise of temperature. This agrees with the fact that the heat of neutralisation, Q_n, of the first hydrogen ion, viz. 14·8 Cals., is somewhat greater than that of a completely dissociated strong monobasic acid, viz. 13·5 Cals. The following calculation also shows a quantitative agreement :—[3]

$$Q_d = -RT^2\frac{d \log x}{dt}$$

in which x is the electrical conductivity and $Q_d = 1{\cdot}530$ Cals. at 21·5° C. Therefore $(1-\alpha)Q_d = 1{\cdot}242$, in which the value of the amount of undissociated phosphoric acid, $(1-\alpha)$, has been introduced. Now $Q_n = 13{\cdot}520 + (1-\alpha)Q_d$. Therefore $Q_n = 14{\cdot}76$ Cals. calculated.

The heat of dissociation of the first hydrogen as calculated from the change of the constant with temperature was found to be 2·00 Cals. at 25° to 37·5° C.,[4] which, when combined with the preceding value of α, gives $Q = 15{\cdot}14$ Cals.

The molar refractivities during neutralisation, $M(\mu-1)/D$, when plotted against the percentage of alkali added gave curves which showed discontinuities at the points corresponding to primary and secondary salt.

Most important confirmation of the discontinuities at these points was obtained by plotting the static acidities (H^+) expressed as their negative logs (pH) against the alkali added. The discontinuities in these graphs were clearly marked. Parts of these neutralisation curves were obtained first by the physiological chemists on account of the use of phosphates as mixtures of regulated acidity (" buffers ") for comparison with the acidities and alkalinities of physiological fluids.[5]

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[1] Thomsen, "*Thermochemistry*," translated by Burke (Longmans, 1908); Favre and Silbermann, *Compt. rend.*, 1847, 24, 1081; Berthelot and Luginin, *Ann. Chim. Phys.*, 1876, [5], 9, 26; de Forcrand, *Compt. rend.*, 1892, 115, 610.

[2] Berthelot, *Compt. rend.*, 1878, 87, 575.

[3] Arrhenius, *Medd. gr. Vet. Akad. Nobelinst.*, 1911, [27], 8; *Zeitsch. physikal. Chem.*, 1889, 4, 96; 1892, 9, 339.

[4] Jowett and Millett, *J. Amer. Chem. Soc.*, 1929, 51, 1004.

[5] Ringer, *Verlag. Physiol. Lab. te Utrecht*, 1909, 10, 109; Sørensen, *Biochem. Zeitsch.*, 1909, 21, 131; 1909, 22, 352; Salm, *Zeitsch. physikal. Chem.*, 1906, 57, 471; Prideaux, *Trans. Chem. Soc.*, 1911, 99, 1224.

Other series of results within the range which is suitable for " buffer " mixtures have been determined.[1] The points of inflection were also determined by the conductivity method.[2]

The neutralisation curves have been expressed by three constants corresponding to the first, second and third dissociations, viz. :—

$$K_1=\frac{[H^+][H_2PO_4^-]}{[H_3PO_4]},\qquad K_2=\frac{[H^+][HPO_4^=]}{[H_2PO_4^-]},\qquad K_3=\frac{[H^+][PO_4^{\equiv}]}{[HPO_4^=]}$$

The value of the first constant was determined as $1{\cdot}1\times10^{-2}$ by measurements of the conductivity of the free acid.[3] The second constant was determined as $1{\cdot}95\times10^{-7}$ by conductivity measurements in solutions of NaH_2PO_4.[3] This value was confirmed by calculations from the neutralisation curve as determined by means of the hydrogen electrode.[4] The value of the third constant, viz. $3{\cdot}6\times10^{-13}$, was first determined by measurements of the conductivity of ammonium phosphates and also by the distribution of the ammonia between water and chloroform.[3] It was shown that this result was incompatible with the observed values of hydrion concentration during the later stages of neutralisation by a strong alkali. A calculation based on these values gave $K_3=3{\cdot}0\times10^{-12}$ in decimolar solutions.[4]

A review of all the data revealed a slight drift in the constants of this acid (as of others) with changes in concentration, etc. The constants were corrected for alterations in the " activities " of the $HPO_4^=$ and other ions in the more dilute solutions for which ionic strengths could be calculated. These corrections, applied to the results of Michaelis and Garmendia,[5] and to new results, gave constants which were hardly affected by changes in concentration,[6] namely $K_2=5{\cdot}9\times10^{-8}$, $K_3=1\times10^{-12}$. The value of K_1, corrected for ionic strength, was $0{\cdot}9\times10^{-2}$ at $c=0{\cdot}1$ and $0{\cdot}8\times10^{-2}$ at limiting (low) concentration.[7] A redetermination,[8] with the aid of the quinhydrone electrode, in solutions of $c=0{\cdot}06$ down to $c=0{\cdot}005$ molar gave $K_1=0{\cdot}8\times10^{-2}$, $K_2=7{\cdot}4\times10^{-8}$, $K_3=0{\cdot}8\times10^{-12}$.

Other values of (uncorrected) constants obtained in moderately dilute solutions are : $K_1=0{\cdot}94\times10^{-2}$, $K_2=1{\cdot}4\times10^{-7}$, $K_3=2{\cdot}7\times10^{-12}$;[9] $K_2=8\times10^{-7}$, $K_3=2{\cdot}3\times10^{-12}$;[10] $K_3=5{\cdot}0\times10^{-13}$.[11]

It is suggested that the following rounded constants will represent pH values in phosphate solutions of concentrations from 0·1 molar downwards with sufficient accuracy for many purposes :—

$$K_1=1{\cdot}0\times10^{-2}\,;\qquad K_2=1{\cdot}5\times10^{-7}\,;\qquad K_3=2{\cdot}0\times10^{-12}$$

---

[1] Clark and Lubs, *J. Bacteriol.*, 1917, [2], 1, 109, 191; Clark, "*The Determination of Hydrogen Ions*," Baltimore, 1920, and later edition, 1928 ; Michaelis and Kruger, *Biochem. Zeitsch.*, 1921, 119, 307.

[2] Kuster, Gruters and Geibel, *Zeitsch. anorg. Chem.*, 1904, 42, 225.

[3] Abbott and Bray, *J. Amer. Chem. Soc.*, 1909, 31, 729, 1191.

[4] Prideaux, *loc. cit.*

[5] Michaelis and Garmendia, *Biochem. Zeitsch.*, 1914, 67, 431.

[6] Prideaux and A. J. Ward, *Trans. Chem. Soc.*, 1924, 125, 423.

[7] Sherrill and Hughes, *J. Amer. Chem. Soc.*, 1926, 48, 1861.

[8] Jowett and Millett, *J. Amer. Chem. Soc.*, 1929, 51, 1004.

[9] Britton, *Trans. Chem. Soc.*, 1927, p. 614.

[10] Blanc, *J. Chim. phys.*, 1920, 18, 28.

[11] Kolthoff, *Rec. Trav. chim.*, 1927, 46, 350.

The complete titration tabulated was obtained by means of the hydrogen electrode in a 0·01277 molar solution of phosphoric acid to which was added 0·0919 normal sodium hydroxide at 20° C., the titration to NaH_2PO_4 requiring 13·9 c.c. of the alkali.[1]

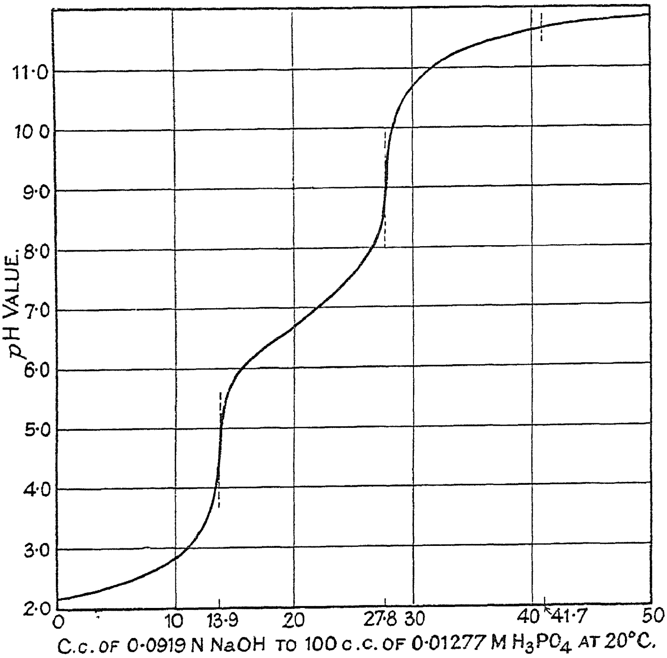

Fig. 5.—Neutralisation Curve of Orthophosphoric Acid.

THE TITRATION OF PHOSPHORIC ACID.

c.c. NaOH pH	0·0 2·14	2·55 2·28	5·0 2·40	7·5 2·57	10·0 2·81	11·0 2·94	12·0 3·10	13·0 3·48	13·5 4·10	14·5 5·60
c.c. NaOH pH	15·0 5·86	16·0 6·11	17·5 6·40	20·0 6·71	22·5 7·06	25·0 7·47	26·0 7·67	27·0 8·01	27·5 8·39	29·0 10·28
c.c. NaOH pH	30·0 10·72	31·0 10·92	32·0 11·05	34·0 11·26	36·0 11·40	38·0 11·49	40·0 11·57	42·5 11·66	45·0 11·72	47·5 11·81
c.c. NaOH pH	50·0 11·85	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..

The two points of inflection on the neutralisation curve have long been recognised by the effects upon indicators, which can be used for titrating the acid in two stages. The first, at NaH_2PO_4, $p\text{H} = 4{\cdot}5$, corresponds sufficiently well to the change-point of methyl orange (alkaline) or methyl red, while the second, at Na_2HPO_4 and $p\text{H} = 9$, corresponds to that of phenolphthalein.[2]

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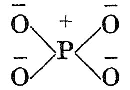
[1] Britton, *loc. cit.*

[2] See also Hahn and Klockmann, *Zeitsch. physikal. Chem.*, 1930, 151, 80.

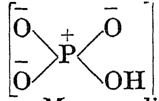
The basicity of the acid has also been determined by conductivity titrations.[1]

The *constitution* of phosphoric acid is deduced from the basicity, which shows three hydroxyl groups, and thus a saturated character, with no hydrogen directly attached to phosphorus; this explains the lack of oxidising properties, which indicates the absence of —O—O— chains, and the direct formation of the acid from $POCl_3$. The acid chloride and the resulting acid probably have the same structure, which is represented under the older theories as containing quinquevalent phosphorus, $O=P\equiv Cl_3$, or on the newer as being tercovalent with a " mixed bond," $O<\cdots\cdots P\equiv(OH)_3$ or $O\underset{-\quad +}{\overline{\cdots\cdots}}P\equiv(OH)_3$.[2]

Phosphoric acid is a co-ordinated compound with the co-ordination number 4, and may accordingly be written $H_3[PO_4]$ (see section on " Phosphorus in Combination "). Although the trivalent ion seldom is actually present, except perhaps in solid Na_3PO_4, etc., it is written according to Lowry as



Such a compound as Na_2HPO_4 is of course equally a co-ordination compound and may be written as



$2Na^+$ on this scheme.

Mono-, di- and tri-esters are known, *e.g.* ethyl phosphates, which have not been prepared in tautomeric forms. The trimethyl and triethyl phosphates have vapour densities corresponding to simple molecules $OP(OC_2H_5)_3$, etc.[3]

Chemical Properties.—The chemical reactions of phosphoric acid can be classified mainly under salt and ester formation, hydration, dehydration (see p. 170) and complex formation. Towards reducing and oxidising agents the aqueous solution is comparatively inert.

It has already been shown that even the first dissociation of phosphoric acid is much lower than the dissociation of the halogen acids and sulphuric acid. Consequently its catalytic action (due mainly to hydrion concentration) on various chemical reactions is much slighter; *e.g.* the relative strength of phosphoric acid in the inversion of cane sugar was 6·21 when that of HCl was 100.[4] It is largely expelled from its salts by the stronger mineral acids in ordinary aqueous solution, although in the presence of only small quantities of water, or at higher temperatures, these conditions are reversed owing to (*a*) the great affinity for water, (*b*) the low volatility, of phosphoric acid. Thus while on the one hand phosphoric acid is produced as described on p. 156 by the interaction of dilute sulphuric acid with calcium phosphate at temperatures below the boiling-point, on the other hand sulphuric acid is completely expelled by evaporation at 150° to 200° C. with concentrated phosphoric acid.

The direct action of phosphoric acid on ethyl alcohol at about 200° C. is one of dehydration, and the acid is therefore conveniently used in the preparation of ethylene, as it is not, like sulphuric acid, reduced under these conditions. Glycerophosphoric acid, which probably is mainly monoglycerylphosphoric acid, is made by heating glycerol with concentrated phosphoric acid at 100° C., neutralising with baryta and decomposing the barium salt with sulphuric acid.[1] Similar condensations have been reported with sugars, *e.g.* mannitol, etc.

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[1] Berthelot, D., *Ann. Chim. Phys.*, 1891, [6], 23, 5; 1893, [6], 28, 5.

[2] Prideaux, *J. Soc. Chem. Ind.*, 1923, 42, 672 (Chem. and Ind.).

[3] Vogelis, *Annalen*, 1849, 69, 190; Carré, *Ann. Chim. Phys.*, 1905, [7], 5, 345; Arbusov, *Ber.*, 1905, 38, 1171; Young, *Proc. Roy. Soc.*, 1909, 81, B, 528.

[4] Ostwald, *Zeitsch. physikal. Chem.*, 1888, 2, 127.

Phosphoric acid is not affected by the ordinary reducing agents in solution, including nascent hydrogen (*cp.* phosphorous acid, p. 148). The reduction of phosphorus pentoxide and phosphates by carbon at high temperatures has been discussed on p. 157.

Ordinary oxidising agents have no effect, but with the meta- or pyro-acid hydrogen peroxide gave perphosphoric acid (*q.v.* p. 184).

The formation of complexes with other acids is extremely characteristic of phosphoric acid and its anhydride. The phosphotungstates and phosphomolybdates are well-crystallised compounds which are used in analytical chemistry (see "Estimation," pp. 181–183). The yellow precipitate $(NH_4)_3PO_4.12MoO_3$ is the ammonium salt of a phosphomolybdic acid, $H_3PO_4.12MoO_3$, which is prepared by adding aqua regia in small quantities to the ammonium salt. Phosphotungstic acid, $H_3PO_4.12WO_3.xH_2O$, may be prepared as greenish crystals by evaporation of the mixed acids in the correct proportions and extraction with ether.[2] These acids, with the borotungstic, silicotungstic acids, etc., are usually formulated as co-ordination compounds. The phosphorus is represented as the central atom with a co-ordination number of 6, thus:[3]

$$H_7[P(W_2O_7)_6], \qquad H_7[P(Mo_2O_7)_6]$$

Phosphoiodic acids, such as $P_2O_5.18I_2O_5.4H_2O$, and their salts,[4] phosphotelluric acids and their salts, *e.g.* $(NH_4)_2P_2TeO_{10}$, have also been prepared.[5]

A complex acid is probably present when silica dissolves in phosphoric acid, as it does to the extent of about 5 per cent. at 260° C.[6] Concentrated phosphoric acid at 100° to 200° C. etches the surface of glass, and it has been found to attack quartz at 300° C.[7] Phosphoric acid at high temperatures also destroys the glaze on porcelain. Platinum is not affected unless a reducing agent is present, which may give phosphorus and a phosphide.

It is no doubt on account of this formation of complexes that concentrated phosphoric acid is capable of dissolving such inert metals as tungsten and zirconium, as well as silicon and carborundum.[8] The less noble metals are attacked by phosphoric acid, but iron tends to become passive.[9] The basic oxides, ferric oxide and alumina are dissolved by the concentrated acid.[6]

[1] Power and Tutin, *Trans. Chem. Soc.*, 1905, 87, 249.

[2] Wu, *J. Biol. Chem.*, 1920, 43, 189.

[3] Rosenheim and Pinsker, *Zeitsch. anorg. Chem.*, 1911, 70, 73.

[4] Chrétien, *Ann. Chim. Phys.*, 1898, [7], 15, 391.

[5] Prause, "*Ueber verbindung. der Tellursäure mit Iodaten, Phosphaten und Arsenaten,*" Leipzig, 1901.

[6] Hautefeuille and Margottet, *Compt. rend.*, 1884, 1886, 1887; 1888, 106, 135.

[7] Heraeus, *Zeitsch. angew. Chem.*, 1902, 15, 917.

[8] Wunder and Janneret, *Compt. rend.*, 1911, 152, 1770.

[9] Beyers and Darrin, *J. Amer. Chem. Soc.*, 1910, 32, 750; Clarkson and Hetherington, *Chem. Met. Eng.*, 1928, 32, 811.

Physiological Action.—The principal uses of combined phosphorus have already been dealt with (see p. 13). The ions of phosphoric acid, together with those of carbonic acid, play an important part as regulators of acidity, or natural "buffer" mixtures (see p. 164), in physiological fluids, especially in the blood. Salts which take part in this regulation are NaH_2PO_4 and Na_2HPO_4, $NaHCO_3$ and Na_2CO_3. The *p*H value of blood is 7·3 to 7·4 at blood temperature (37° to 38° C.) and about 7·5 at 18° C.; the ratio of monohydrogen phosphate, *i.e.* Na_2HPO_4, to dihydrogen phosphate, *i.e.* NaH_2PO_4, at this point is about 4 : 1 (see table of Neutralisation, p. 166). Even the small amount of phosphate present in the blood and cell protoplasm has a considerable effect in regulating the *p*H to its "resting" value—slightly on the alkaline side of neutrality. Any steady increase in the content of acid is countered by the formation of more NaH_2PO_4, which, being more readily diffusible than Na_2HPO_4, passes into the kidneys. Acidity of the urine is thereby increased and the cell protoplasm or blood loses some of its alkali reserve. The necessity of constant small amounts of phosphate for the body metabolism is evident.[1]

Phosphoric acid is poisonous only at a high concentration, when it shows the usual corrosive effects of acids.[2] The salts, and even the acid in low concentration, favour the growth of moulds and fungi, provided that the hydrogen-ion concentration also is favourable.

Phosphoric esters are also present in the blood, and their hydrolysis by means of an enzyme, phosphatase, which has been found in the bones, is probably one step in the process of ossification. The properties of these esters have been largely determined by Robison and his collaborators.[3]

Uses.—Many pharmaceutical preparations contain phosphoric acid or phosphates, or glycerophosphoric acid, which, as already stated, is made by heating glycerine with the ortho- or meta-acid. Lecithin is an ester of glycerophosphoric acid which contains choline, $(CH_3)_3 \equiv N(OH) - CH_2 - CH_2OH$, and two molecules of a fatty acid radical (stearyl or oleyl).

Acid phosphates are used in baking powders, "self-raising" flours and for "improving" flours. The acid is also an ingredient of some non-alcoholic beverages.

Sugar phosphates, mainly the hexose mono- and di-phosphates, play an important part in alcoholic fermentation. The calcium salts of these esters have been prepared.

The acid, or calcium superphosphate, is used in the sugar-refining industry as a defecator to coagulate gums and other organic impurities and cause them to form a scum.[4]

It has been employed instead of sulphuric acid in the hydrolysis of cellulose to give sugars. As a dehydrating agent in organic preparations, such as that of ethylene from ethyl alcohol, it is sometimes preferred to sulphuric acid.

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[1] Henderson, *Ann. J. Physiol.*, 1906, 15, 257; 1908, 21, 427; *J. Biol. Chem.*, 1909, 7, 29; Henderson, Bock, Field and Stoddard, *J. Biol. Chem.*, 1924, 59, 379; "*Lectures on Certain Aspects of Biochemistry,*" Dale, Drummond, Henderson and Hill, London, 1926.

[2] Poggiale, *J. Pharm. Chim.*, 1859, [3], 36, 241.

[3] Full references to this work may be obtained from the *Annual Reports of the Chemical Society*, especially vol. xxvi, 235, 1929; also "*The Significance of Phosphoric Esters in Metabolism,*" R. Robison, Oxford Univ. Press, 1933.

[4] Meekstroth, *Chem. Met. Eng.*, 1922, 26, 223.

Other miscellaneous uses are: In dental cements and filling pastes, with kaolin, other silicates, chalk and magnesia. Solutions containing the acid and ferrous phosphate will give a protective coating to iron and steel.* Carbon is activated by being dipped in a solution of metallic salts and phosphoric acid and then igniting. Solutions containing ammonium phosphate with the sulphate and a soluble zinc salt may be used for fireproofing materials. Phosphates are sometimes included in photographic toning and fixing baths.

Dehydration of Orthophosphoric Acid and Production of the Pyro- and Meta-acids.—When heated in open vessels of gold or platinum the acid loses water, being converted successively, and to some extent concurrently, into the pyro- and meta-acids, thus:—

$$2H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O$$
$$nH_3PO_4 \longrightarrow (HPO_3)_n + nH_2O$$

Salts of these acids are prepared by heating the orthophosphates (see p. 155).

According to Graham [1] the pyro-acid was formed largely even at 100° C., while Watson found that conversion was complete between 255° and 260° C.[2] Exposure to a current of moist air raised the temperature of dehydration, while dry air lowered it.[3] Thus air saturated with water vapour at 68° C. will leave 0·2 per cent. of water in the ortho-acid kept at 181° C., and will dehydrate it and produce 0·02 per cent. of $H_4P_2O_7$ at 191° C. When air which has been dried by passing through 96 per cent. sulphuric acid at 12° C. is drawn through phosphoric acid at 186° C. this acid is dehydrated to 86·8 per cent. of $H_4P_2O_7$. Other dehydrating agents have a similar effect. Phosphorus oxychloride reacts in the following manner:—

$$5H_3PO_4 + POCl_3 = 3H_4P_2O_7 + 3HCl$$ [4]

A mixture of the ortho- and meta-acids may be condensed together to form the pyro-acid by heating on the water-bath, thus:—

$$H_3PO_4 + HPO_3 = H_4P_2O_7$$ [5]

Metaphosphoric acid is the final product obtained when phosphoric acid is heated in the air and was produced in this way by Berzelius.[6] The minimum temperature required for dehydration is about that of molten lead, 327° C. The meta-acid begins to be formed at about 300° C. and dehydration can be completed at 316° C.[7] or by heating until fumes are continuously evolved.

Aqueous vapour pressures in equilibrium with the meta-acid are much lower than those over the pyro-acid. The pressure over the pyro-acid became appreciable at 100° C. and reached 100 mm. somewhat above 160° C., while that over the meta-acid became appreciable at 190° C. and reached 100 mm. a little over 240° C.[3]

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* Known as "Parkerising" or "Coslettising."

[1] *Loc. cit.*, p. 155.

[2] Watson, *Chem. News*, 1893, 68, 199.

[3] Balareff, *Zeitsch. anorg. Chem.*, 1910, 67, 234; 68, 266; 69, 215.

[4] Geuther, *J. prakt. Chem.*, 1873, [2], 8, 359.

[5] Geuther, *loc. cit.*; Joly, *Compt. rend.*, 1886, 102, 760.

[6] Berzelius, *Ann. Chim. Phys.*, 1819, [2], 10, 278.

[7] Gregory, *loc. cit.*, p. 155; Maddrell, *loc. cit.*, p. 155.

Other methods of preparing pyro- and meta-phosphoric acids are given later in this chapter.

Pyrophosphoric Acid, $H_4P_2O_7$.—The history and chief modes of preparation of this acid have already been given (p. 170). A purer product was made by the double decomposition of a soluble lead salt with sodium pyrophosphate, $Na_4P_2O_7$, whereby lead pyrophosphate, $Pb_2P_2O_7$, was precipitated; this was then decomposed by H_2S.[1] The silver salt, $Ag_4P_2O_7$, yielded anhydrous $H_4P_2O_7$ when warmed in a current of dry hydrogen chloride.[2]

Physical Properties.—The concentrated acid, prepared by dehydration of orthophosphoric acid, is a highly viscous liquid and probably is polymerised. By the depression of the freezing-point the molecules in aqueous solution showed a complexity corresponding to $(H_4P_2O_7)_4$ and $(H_4P_2O_7)_5$.[3] The molecular weight in glacial acetic acid corresponded to $(H_4P_2O_7)_3$, but diminished with time.[2] The acid prepared as above—from $Pb_2P_2O_7$—appeared to dissolve in water as simple molecules.[3] The freezing-point curve of $H_4P_2O_7$ showed two eutectics—one at 23° C. with a solution containing $H_4P_2O_7 + 1{\cdot}25H_2O$ and the other at $-75°$ C. with $H_4P_2O_7 + 6{\cdot}87H_2O$. The maximum freezing-points are (1) $+61°$ C. or higher, the melting-point of the anhydrous acid; (2) $+26°$ C., the melting-point of the crystalline hydrate $H_4P_2O_7 + \frac{1}{2}H_2O$.[2] The acid which crystallised from concentrated solution was, however, found to contain anhydrous H_3PO_4.[3]

The molar heat of fusion of the solid acid was about 2·3 Cals., therefore very similar to that of H_3PO_4. The heat of solution of $H_4P_2O_7$ (solid) was about 7·85 Cals., that of $H_4P_2O_7.1{\cdot}5H_2O$ (solid) 4·5 Cals. The heats of transformation by means of liquid water were :—

$$H_4P_2O_7 \text{ (solid)} + H_2O = 2H_3PO_4 \text{ (solid)} + 6{\cdot}97 \text{ Cals.}$$
$$H_4P_2O_7 \text{ (liquid)} + H_2O = 2H_3PO_4 \text{ (liquid)} + 9{\cdot}09 \text{ Cals.}$$
$$H_4P_2O_7 \text{ aq.} = 2H_3PO_4 \text{ aq.} + 4{\cdot}25 \text{ Cals.}$$

From these other thermal equations can be derived in the usual manner.

The heats of formation from the elements were close to those of $2H_3PO_4 - H_2O$.

$$2P + 3\tfrac{1}{2}O_2 + 2H_2 = H_4P_2O_7 + Q$$

$H_4P_2O_7$ solid	$H_4P_2O_7$ liquid	$H_4P_2O_7$ solution[2]
Q (Cals.) = 532·23, 535·69	529·94, 533·40	540·16, 543·62

The electrical conductivities of aqueous solutions of pyrophosphoric acid are as follows :—[4]

c, mols/litre . .	0·00125	0·0025	0·005	0·0125	0·025	0·05
μ, molar conductivity .	602·0	556·7	503·3	438·6	384·9	353·8

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[1] Braun, *Zeitsch. anal. Chem.*, 1865, 3, 468.

[2] Giran, *Compt. rend.*, 1902, 134, 1499; 135, 961, 1333; 1903, 136, 550; 1908, 146, 1270, 1394.

[3] Holt and Myers, *Trans. Chem. Soc.*, 1911, 99, 394.

[4] Abbott and Bray, *loc. cit.*

The degree of primary ionisation calculated from these values is high, being 96 per cent. at the lowest concentration. For dissociation constants, etc., see below.

All the evidence shows that pyrophosphoric acid is tetrabasic and that each hydrogen is that of a stronger acid, *i.e.* more dissociated at the same dilution, than orthophosphoric acid.

With regard to heats of neutralisation, 1 mol of the acid, to which *n* equivalents of strong alkali were added, gave the following successive amounts of heat, the sum of which is the total heat of neutralisation at each step :—

n	1	2	3	4	6
Q (Cals.) . .	14·4 15·3	14·2 15·65	3rd and 4th = 24·1 13·1	 7·8 [2]	1·8 [1]

The constants of the successive dissociations were deduced from the conductivities of the salts: [3]

$NaH_3P_2O_7$	$Na_2H_2P_2O_7$	$Na_3HP_2O_7$	$Na_4P_2O_7$
K_1	K_2	K_3	K_4
0·14	0·011	$0{\cdot}0_629$	$0{\cdot}0_836$

or $K_3 = 7{\cdot}6 \times 10^{-7}$, $K_4 = 4 \times 10^{-9}$,[4] or $K_4 = 4{\cdot}9 \times 10^{-9}$.[5]

These constants determine the titration exponents *p*H and the best indicators for the successive hydrions. The acid can be titrated as dibasic, using methyl yellow, methyl orange or bromophenol blue, and as tetrabasic using phenolphthalein, thymolphthalein or thymol blue in the presence of a moderate excess of soluble barium salt. The values of *p*H in the partly neutralised acid were corrected for the salt error, and the constants K_3 and K_4 which prevail in solutions of low concentration were thus deduced :—[6]

$$K_3 = 2{\cdot}1 \times 10^{-7},\ pK_3 = 6{\cdot}68\ ; \qquad K_4 = 4{\cdot}06 \times 10^{-10},\ pK_4 = 9{\cdot}4$$

The true constant K_4 found by introducing the correction for ionic strength was $0{\cdot}45 \times 10^{-10}$ at a concentration of 0·02 mol/litre, and increased with decreasing concentration to $4{\cdot}6 \times 10^{-10}$ at $c = 0{\cdot}00128$. The uncorrected constant decreased from $4{\cdot}9 \times 10^{-9}$ at $c = 0{\cdot}02$ to $1{\cdot}5 \times 10^{-9}$ at $c = 0{\cdot}00125$.[5]

Hydration to Orthophosphoric Acid.—The process of depolymerisation of concentrated solutions of pyrophosphoric acid which has already been noted very likely consists in the hydration of the molecules of condensed or poly-acid. The further hydration, with formation of orthophosphoric acid, proceeds only slowly at low temperatures and in dilute solutions. A dilute aqueous solution was kept for six months without change.[7] The velocity of the reaction has been followed by taking the difference in the relative titres to methyl orange and phenolphthalein.

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[1] Thomsen, *loc. cit.*

[2] Giran, *loc. cit.*

[3] Abbott and Bray, *loc. cit.*

[4] Kolthoff, *Rec. Trav. chim.*, 1927, 46, 350.

[5] Morton, *Trans. Chem. Soc.*, 1928, p. 1401.

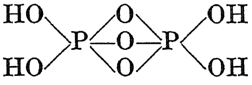
[6] Kolthoff, *Rec. Trav. chim.* 1928, 47, 826.

[7] Graham, *loc. cit.*

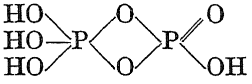
$$H_4P_2O_7 + H_2O = 2H_3PO_4$$

A solution containing 15·6 grams of P_2O_5 per litre was about half-transformed in 121 days ($H_4P_2O_7/H_3PO_4$ initially $=87/4$; finally $43{\cdot}1/47{\cdot}9$).[1] The reaction was greatly accelerated by hydrogen ions, which in practice are usually supplied by nitric acid (see " Analysis," p. 181). It was found to be unimolecular.[2]

Constitution.—The formulæ must, on account of the properties of pyrophosphoric acid and its relation to orthophosphoric acid, show the phosphorus atoms as saturated. This can be done either by the electronic formulæ or by those containing quinquevalent phosphorus, since as already shown the two kinds of formulæ are interchangeable. The molecule may be (1) symmetrical or (2) unsymmetrical :—



(1)



(2)

The corresponding acid chloride is pyrophosphoryl chloride (*q.v.*). When this is treated with water it gives orthophosphoric acid, but when water vapour acts on a solution of the chloride in carbon disulphide some pyrophosphoric acid is produced.

Pyrophosphates may split up in an unsymmetrical manner. Thus by heating with PCl_5 in a sealed tube :—

$$Na_4P_2O_7 + 3PCl_5 = NaPO_3 + 4POCl_3 + 3NaCl$$

and by fusion :—

$$NaAg_3P_2O_7 = Ag_3PO_4 + NaPO_3$$

The ethyl and methyl esters have been prepared by the usual methods. Thus $(C_2H_5)_4P_2O_7$ by the action of C_2H_5I on $Ag_4P_2O_7$ at 100° C. The product was a liquid soluble both in water and in alcohol.[3] The elevation of the boiling-point of benzene by this ester corresponded to simple molecules.[4] The decomposition of the ester on heating supports the asymmetrical constitution :—

$$(C_2H_5O)_3 \equiv P = O_2 = PO(OC_2H_5) \longrightarrow (C_2H_5O)_3PO + O_2P(OC_2H_5)$$
$$O_2P(OC_2H_5) \longrightarrow O_2POH + C_2H_4$$

the products being triethyl phosphate, metaphosphoric acid and ethylene.

In most reactions pyrophosphoric acid is transformed into orthophosphoric acid. It was dehydrated by PCl_5, thus

$$H_4P_2O_7 + PCl_5 = 2HPO_3 + POCl_3 + 2HCl$$ [5]

Thionyl chloride, $SOCl_2$, and phosphorus trichloride also gave HPO_3.

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[1] Berthelot and André, *Compt. rend.*, 1896, 123, 776.

[2] Montemartini and Egidi, *Gazzetta*, 1902, 32, 381; 1903, 33, 52; Pessel, *Monatsh.*, 1923, 43, 601.

[3] de Clermont, *Compt. rend.*, 1854, 39, 338.

[4] Cavalier, *Compt. rend.*, 1906, 142, 885; Rosenheim and Pritze, *Ber.*, 1908, 41, 2708.

[5] Geuther, *J. prakt. Chem.*, 1873, [2], 8, 359.

The acid gave compounds with albumin which, unlike those of HPO_3, were soluble.[1]

The pyrophosphates are more stable than the free acid and show some reactions which are described on p. 180. Among these may be mentioned the white precipitate of $Ag_2H_2P_2O_7$ which is insoluble in acetic acid (see "History").[2]

Polyphosphoric Acids.—The complex metaphosphates, $(MPO_3)_x$, probably contain a complex anion. The di-, tri-, etc. phosphoric acids however (pyrophosphoric acid and its series) are not polymers but condensation products, belonging to the series $mH_3PO_4-(m-1)H_2O$, and give tetra-, penta- and hexa-valent ions from $H_4P_2O_7$, $H_5P_3O_{10}$ and $H_6P_4O_{13}$.[3] The salts were made by melting together $(NaPO_3)_6$ and $Na_4P_2O_7$ in various proportions. They were transformed into orthophosphates in warm water.[4]

Metaphosphoric Acid.—The production of this lowest hydrate of phosphoric anhydride by heating phosphoric acid (p. 170), or the production of metaphosphates by heating dihydrogen phosphates (p. 163), has already been outlined. In those methods of preparation, NH_4 may take the place of H; thus HPO_3 has been prepared by heating $(NH_4)_2HPO_4$ [5] and $NaPO_3$ by heating $Na(NH_4)_2PO_4$ or microcosmic salt, $NaNH_4HPO_4$.[6] The free acid can also be produced by the combined oxidation and dehydration of H_3PO_3, as for example by bromine, thus

$$2H_3PO_3+2Br_2=4HBr+2HPO_3$$ [7]

The acid appears as a transparent, vitreous, tough mass, which usually is deliquescent and dissolves in water with much heat. At a red heat it volatilises without decomposition [8] giving a vapour with a density corresponding to a molecular weight of 76·8 to 78·2, the theoretical value for $(HPO_3)_2$ being 80.[9]

The properties of the vitreous acid varied considerably according to the mode of preparation. The degree of hydration never corresponded exactly to HPO_3, which requires 88·7 per cent. of P_2O_5, but reached a constant value at about 78 per cent., and the acid then volatilised unchanged. After a short heating the acid contained 83·89 per cent. of HPO_3 and 16·13 per cent. of water, and was readily soluble in water. After heating at dull redness for periods of several hours the acid dissolved at first readily and then with difficulty and with a characteristic crackling sound. This sound was due to the splitting of small particles with a glassy fracture. The product was not yet pure HPO_3, but contained water in the ratios $HPO_3/H_2O=89{\cdot}29/10{\cdot}71$ and $89{\cdot}9/10{\cdot}1$. After heating for 24 hours at a dull red heat the acid dissolved very slowly (several days) without crackling.[10]

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[1] Worms, *J. Russ. Phys. Chem. Soc.*, 1899, 31, 556; Panormoff, *ibid.*, 1900, 32, 249.

[2] Balareff, *Zeitsch. anal. Chem.*, 1921, 60, 385.

[3] Fleitmann and Henneberg, *Annalen*, 1845, 65, 30, 387; Stange, *Zeitsch. anorg. Chem.*, 1896, 12, 444.

[4] Glühmann, "*Beitrag zur Kenntnis der Triphosphorsäure und ihrer Salze,*" Berlin, 1899; Kroll, "*Über Ultraphosphate,*" Leipzig, 1712; Schwarz, *Zeitsch. anorg. Chem.*, 1895, 9, 257.

[5] Besson, *Compt. rend.*, 1896, 122, 814.

[6] Graham, *loc. cit.*

[7] Gustavson, *J. prakt. Chem.*, 1867, [1], 101, 123.

[8] Rose, *Annalen*, 1850, 76, 2; 1851, 77, 319.

[9] Tilden and Barnett, *Trans. Chem. Soc.*, 1896, 69, 154.

[10] Holt and Myers, *Trans. Chem. Soc.*, 1911, 99, 394; 1913, 103, 534.

The lowering of the freezing-point of aqueous solutions shows that metaphosphoric acid is polymerised.[1] In a fresh solution containing initially 0·852 mol of HPO_3 the molecular weight lay between $(HPO_3)_2$ and $(HPO_3)_3$.[2] Pure metaphosphoric acid is best prepared from $Pb(PO_3)_2$ (from $Pb(NO_3)_2$ and $NaPO_3$ aq.). The precipitate is suspended in water and decomposed by a current of H_2S. The lowering of the freezing-point of the acid freshly prepared in this manner indicated a molecular weight of 102, which, as the acid was ionised, indicated the presence of some complex molecules. Evaporation of this solution gave one in which the acid had a molar weight of 172.[2]

The heat of formation of the solid acid from its elements is given as 224·9 to 226·6 Cals., and that of the acid in solution as 236·4 Cals.[3] On adding the heat of formation of 1 mol of water the sum of the heats (for H_2O and HPO_3) is found to be almost the same as that evolved in the formation of orthophosphoric acid.

Esters of metaphosphoric acid are known. Ethyl metaphosphate, $C_2H_5PO_3$, was prepared by heating dry ethyl acetate with phosphoric oxide and extracting the product with ether and warm alcohol, from which the ester was precipitated by ether.[4]

Aqueous Solutions of Metaphosphoric Acid.—The physical properties of the solutions are not well defined, as the acid is in process of depolymerisation and hydration (see below). The refractive index was investigated by Gladstone.[5] Heats of neutralisation were those of a monobasic acid; when one equivalent of alkali was added the heat evolved was 14·4 Cals.,[6] 14·84 Cals.[7] The electrical conductivity of the simple acid HPO_3, calculated from that of the changing acid which contained both $(HPO_3)_n$ and H_3PO_4, was found to be of the same order as that of a strong monobasic acid (*e.g.* HIO_3).[8]

The Hydration of Metaphosphoric Acid.—The change of metaphosphoric into orthophosphoric acid was observed by Graham.[9] In solutions of ordinary metaphosphoric acid two changes are proceeding, the depolymerisation of $(HPO_3)_n$ and hydration with formation of H_3PO_4. The change of osmotic pressure on standing was shown by the freezing-point method. The lowering in a normal solution of the acid changed from 0·697° to 1·452° in 12 days, that in a double-normal solution from 1·425° to 3·150° in the same time.[2] The conductivity at 18° C. did not alter much for the first 20 hours; it then fell steadily. The first period lasted longer at 18° C. than at 25° C., and presumably at lower temperatures would be greatly extended. During this period depolymerisation may be the main reaction. The subsequent decrease in conductivity is due to the conversion of the highly dissociated HPO_3 into the less dissociated H_3PO_4.[8] The velocity of the change was such that a half-normal solution kept at 0° C. was completely converted in 150 days, at 31° C. in 5 days and at 95° C. in less than an hour.[1] The change was accelerated by strong mineral acids.

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[1] Raoult, *Compt. rend.*, 1884, 98, 509, 1047; 1884, 99, 914; Cornec, *Ann. Chim. Phys.*, 1913, [8], 29, 490; [8], 30, 63.

[2] Holt and Myers, *loc. cit.*

[3] Giran, *loc. cit.*

[4] Langheld, *Ber.*, 1910, 43, 1857; *ibid.*, 1911, 44, 2076.

[5] Gladstone, *J. Chem. Soc.*, 1870, 23, 101.

[6] Thomsen, "*Thermochemische Untersuchungen*," Stuttgart, 1906.

[7] Giran, *loc. cit.*, and "*Récherches sur le phosphore et les acides phosphoriques*," Paris, 1903.

[8] Prideaux, *Trans. Faraday Soc.*, 1909, 5, 37.

[9] Graham, *loc. cit.*

There is general agreement that during the change the titre to methyl orange remains constant. This will be the case whether pyrophosphoric acid is formed as an intermediate product or not (see p. 181). The titre to phenolphthalein increases, and this also agrees equally well with both suppositions. The velocity constant was found to correspond to a unimolecular reaction.[1] The change, however, consists of at least two, if not three parts, and several observers have found that there is no simple constant—thus, the velocity did not agree with either a unimolecular or a bimolecular reaction;[2] the constant increased with time;[3] the velocity was not proportional at each moment to the amount of unchanged substance.[4]

It cannot be assumed that, because pyrophosphoric acid is produced as an intermediate product in the dehydration of H_3PO_4 that it will also be produced during the hydration of HPO_3. The amounts observed may be present in the original HPO_3 or be produced by the heat developed when this is placed in water. The pyro-acid has been detected in the last fractional precipitates of silver phosphates, etc. (see "Estimation").[2] Since there is some evidence that metaphosphoric acid is hydrated more rapidly than pyrophosphoric acid[5] the latter may accumulate up to a certain maximum concentration.

The foregoing results have been elucidated by the observation that hydration of the simple molecules HPO_3 leads to a preponderance of orthophosphoric acid, while hydration of the hexapolymer, $(HPO_3)_6$, leads to a considerable proportion of each acid, ortho- and pyro- (see p. 177).

Metaphosphates become hydrated in neutral and alkaline as well as in acid solution, according to the equations

$$NaPO_3 + H_2O = NaH_2PO_4$$
$$NaPO_3 + NaOH = Na_2HPO_4$$

At a temperature of 73° C. the velocity constant whether referred to a unimolecular or a bimolecular reaction diminished with time; after an hour rather less than three-quarters of the original metaphosphate remains.[6] The product is mainly orthophosphate, as was proved by titration with methyl orange and phenolphthalein, although small quantities of pyrophosphate were formed by a side reaction. The pyro-acid was determined by titration to bromophenol blue in the presence of zinc sulphate, which leads to a complete precipitation of pyrophosphate, the ortho-acid being unaffected, thus

$$Na_2H_2P_2O_7 + 2ZnSO_4 = Zn_2P_2O_7 + Na_2SO_4 + H_2SO_4$$

The hydration of hexametaphosphate, $(NaPO_3)_6$, also proceeded as a unimolecular reaction. In neutral or alkaline solution orthophosphate is formed; in acid solution ortho- and pyro-acids in about equal amounts.

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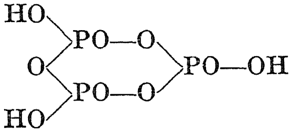
[1] Sabatier, *Compt. rend.*, 1888, 106, 63; 1889, 108, 738, 804.
[2] Holt and Myers, *loc. cit.*
[3] Pessel, *Monatsh.*, 1923, 43, 601.
[4] Blake, *Amer. Chem. J.*, 1902, 27, 68; Giran, *Compt. rend.*, 1908, 146, 1393.
[5] Vogel, *Neues Jahrb. Pharm.*, 1857, 8, 94.
[6] Dragunov and Rossnovskaya, *Zeitsch. anorg. Chem.*, 1931, 200, 321.

The *chemical properties* of metaphosphoric acid, apart from those which are due to the fact that dehydration has proceeded to a maximum, do not differ essentially from those of the other hydrates of phosphorus pentoxide. The acid dissolves freely in certain oxygenated organic compounds—aldehydes, ketones and anhydrides, *e.g.* benzaldehyde, benzophenone and acetic anhydride.[1] It was chlorinated but not dehydrated by phosphorus pentachloride :—

$$HPO_3 + 2PCl_5 = 3POCl_3 + HCl$$ [2]

Complex Metaphosphoric Acids and their Salts.—The polymers of metaphosphates are considerably more stable than those of the acid itself and consequently a great variety of these salts has been reported, having the general formula $(MPO_3)_n$, in which n varies from 1 to 6 or possibly up to 10. The heating of $Na_2H_2P_2O_7$ yielded a soluble salt, " Graham's salt," [3] and an insoluble salt, " Maddrell's salt." [4] A sodium salt having the formula $Na_3P_3O_9.6H_2O$ may be crystallised from the melt obtained by fusing $Na_2HPO_4.12H_2O$ either alone or with ammonium nitrate.[5] From the sodium salt there may be prepared by double decomposition salts of many of the heavy metals, *e.g.* $Pb_3P_3O_9.3H_2O$. These may be decomposed by H_2S, etc. giving the free acids, which slowly decompose, yielding the ortho-acid. One structure which has been assigned to the complex acid $H_3P_3O_9$ is



Trimetaphosphates are often moderately soluble, *e.g.* $Ag_3(PO_3)_3.H_2O$ and $Ba_3(PO_3)_6.6H_2O$. They often crystallise with 9 molecules of water, *e.g.* $Zn_3(PO_3)_6.9H_2O$, and also up to 15, *e.g.* $Mg_3(PO_3)_6.15H_2O$. The electrical conductivities of their solutions agree well with those which should be shown by the salts of a tribasic acid.[6]

Monometaphosphates.—The insoluble salt obtained by heating microcosmic salt, $NaNH_4HPO_4$, was apparently polymerised metaphosphate,[7] while soluble salts obtained by neutralising metaphosphoric acid with sodium carbonate belonged to two series and quickly changed into orthophosphate when moist.[8]

A salt which proved to have the simple molecular weight by the freezing-point method was prepared by the action of ethyl hexametaphosphate dissolved in alcohol on sodium ethoxide :—

$$(C_2H_5PO_3)_6 + 6C_2H_5ONa = 6(C_2H_5)_2NaPO_4$$
$$(C_2H_5)_2NaPO_4 = NaPO_3 + (C_2H_5)_2O$$

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[1] Heimann, "*Beiträge z. Kenntnis der Ortho- und Metaphosphorsäure,*" Heidelberg, 1902.

[2] Geuther, *J. prakt. Chem.*, 1873, [2], 8, 359; Heimann, *loc. cit.*

[3] Graham, *Phil. Trans.*, 1833, 123, 253.

[4] Maddrell, *Phil. Mag.*, 1847, [3], 30, 322.

[5] Fleitmann and Henneberg, *Annalen*, 1848, 65, 304; v. Knorre, *Zeitsch. anorg. Chem.*, 1900, 24, 369.

[6] v. Knorre, *loc. cit.*; Warschauer, "*Beiträge zur Kenntnis der Metaphosphate,*" Leipzig, 1903. See also Wiesler, "*Beiträge, etc.,*" Berlin, 1901; Muller, "*Beiträge, etc.,*" Berlin, 1906; Tammann, *Zeitsch. physikal. Chem.*, 1890, 6, 122; Lindboom, *Ber.*, 1875, 8, 122.

[7] Fleitmann, *Annalen*, 1849, 72, 228.

[8] Tammann, *loc. cit.*

The sodium salt was crystallised as a granular substance. It precipitated salts of barium, silver and lead (see " Trimetaphosphates ").[1]

Dimetaphosphates of copper, manganese, cobalt and zinc are said to be formed when an oxide or nitrate of these metals is heated with an excess of phosphoric acid between 316° and 400° C.[2] The zinc salt had the formula $ZnP_2O_6.4H_2O$, and when treated with alkali sulphides gave the alkali salts $K_2P_2O_6.2H_2O$, etc.[3] Other authorities, however, have adduced reason for supposing that these salts are tri- or tetrametaphosphates.[4]

Tetrametaphosphates.—These salts are said to be formed when orthophosphates of metals of high atomic weight—silver, barium, lead—are heated with an excess of phosphoric acid at about 300° C.[5] The free acid, $H_4P_4O_{12}$, prepared by decomposing the silver salt with H_2S, was rapidly hydrated to $H_4P_2O_7$.[6]

Pentametaphosphates.—Alkali and ammonium salts of $H_5P_5O_{15}$ have been prepared—the latter by heating $(NH_4)_2P_2O_6$ to 200° or 250° C. The melt was dissolved in water and the salt precipitated by alcohol as an amorphous white mass.[7] $K_4NH_4P_5O_{15}.6H_2O$ was obtained in the crystalline state. Calcium, strontium and barium salts, when added to solutions of pentametaphosphates, gave gummy or flocculent precipitates.

Hexametaphosphates were made by heating to a red heat NaH_2PO_4 or $NaNH_4HPO_4$, *i.e.* in a platinum crucible at about 700° C., with rapid cooling.[8] When the solution from this melt was added to silver nitrate, one of the products was a crystalline salt, probably $Ag_6P_6O_{18}$.[9]

The conductivities of these salts and of the pentametaphosphates showed that only some of the kations were dissociated, and that there were probably complex anions, *e.g.* $Na_4[Na_2(PO_3)_6]$.[7] Complex ferro- and ferri-metaphosphates are also known, $M_4[Fe(PO_3)_6]$, $M_3[Fe(PO_3)_6]$.

The ethyl ester has been prepared by boiling ethyl alcohol with P_2O_5 for some hours. A viscous liquid insoluble in ether but soluble in chloroform was obtained, the molar weight of which in naphthalene corresponded to $(C_2H_5)_6P_6O_{18}$.[10]

The polymetaphosphates are distinguished by giving gelatinous precipitates with salts of most metals, and by decolorising red solutions containing $Fe(CNS)_3$.[9]

Still more complex metaphosphates have been reported as resulting from the fusion of salts of bivalent metals with $NaNH_4HPO_4$.[11]

Sodium tetraphosphate, $Na_6P_4O_{13}$, and decaphosphate, $Na_{12}P_{10}O_{31}$, were also said to be among the products obtained by fusing complex metaphosphates with pyrophosphates.[12] The acid $H_6P_4O_{13}$ was crystallised from a syrupy liquid obtained by adding more phosphorus pentoxide to a solution obtained by adding the pentoxide to water (*q.v.*, p. 133).[1]

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[1] Pascal, *Compt. rend.*, 1923, 177, 1298; 1924, 178, 211; 1924, 179, 966; 1924, 180, 664.

[2] Fleitmann and Henneberg, *loc. cit.*; Maddrell, *loc. cit.*; v. Knorre, *loc. cit.*

[3] Glatzel, "*Über Dimetaphosphorsäure und Tetrametaphosphorsäure Salze,*" Würzburg, 1880.

[4] Pascal, *loc. cit.*; Tammann, *loc. cit.*

[5] Fleitmann, *Annalen*, 1849, 72, 228. See also Glatzel, v. Knorre, Tammann, Warschauer, *loc. cit.*

[6] Glatzel, *loc. cit.*

[7] Tammann, *loc. cit.*

[8] Lüdert, *Zeitsch. anorg. Chem.*, 1894, 5, 15.

[9] Rose, *Sitzungsber. K. Akad. Wiss. Berlin*, 1867, 129, 450.

[10] Pascal, *loc. cit.*

[11] Tammann, *loc. cit.*; v. Knorre, *loc. cit.*

[12] Fleitmann and Henneberg, *loc. cit.*

The complex basic phosphates such as $5CaO.3P_2O_5$, which was made by passing the vapour of phosphorus pentoxide over anhydrous calcium oxide, are supposed to be derived from more hydrated condensed acids such as $H_{10}P_6O_{20}$.[2]

Properties and Reactions of Ortho-, Meta- and Pyro-phosphates.

Orthophosphates.—*Solubility.*—The tribasic phosphates of the alkali metals and ammonia are soluble, while those of the alkaline earth metals and the common metals are insoluble. They are usually prepared by double decomposition between disodium hydrogen phosphate and a salt of the required metal, thus

$$2Na_2HPO_4 + 3Pb(O_2C.CH_3)_2 = Pb_3(PO_4)_2 + 4CH_3CO_2Na + 2CH_3CO_2H$$
$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$$

Formation of the yellow precipitate of Ag_3PO_4 is a common test for orthophosphates. On account of the acid which is liberated precipitation is not complete (see p. 181). Acid phosphates of the alkaline earth metals, *e.g.* $CaHPO_4$, are precipitated from solutions which are nearly neutral. Monoammonium phosphates, MNH_4PO_4, which are so much used in quantitative analysis, are precipitated from neutral or slightly acid solution then made ammoniacal ($MgNH_4PO_4$),[3] or neutral or slightly acid solution ($ZnNH_4PO_4$ in presence of sodium acetate and acetic acid, pH = 6·1–6·9).[4]

The effect of igniting orthophosphates is stated on p. 174. The nature of the original salts may be deduced from the nature of the residue. $CaHPO_4$ may be distinguished from $Ca_3(PO_4)_2$ by washing with ammonia; in the former case the washings will contain soluble phosphate. $Mg_3(PO_4)_2$ may be detected in ignited $Mg_2P_2O_7$ by wetting with $AgNO_3$ solution, which, if the former is present, imparts a yellow colour due to Ag_3PO_4.

Precipitated phosphates of the zinc group and of the alkaline earth metals and magnesium dissolve in acetic acid, whereas those of iron, aluminium and chromium remain undissolved, a fact which is much used in qualitative analysis. The hydrion concentrations, expressed as pH, at which the various precipitates appear have been determined.[5] All phosphates dissolve in excess of dilute strong acids, in many cases only that amount of acid being required which will convert the precipitate into a primary or dihydrogen phosphate (*cf.* $CaH_4(PO_4)_2$, p. 222).

The precipitates obtained with magnesia mixture (magnesium chloride in ammoniacal solution), or ferric chloride in an acid solution to which sodium acetate has been added, are often used as tests for phosphate (see p. 180), and in the latter case the phosphate is removed from solution as ferric phosphate. Another common test is the formation of yellow ammonium phosphomolybdate when a nitric acid solution of ammonium molybdate is added to phosphate solution (see pp. 180, 181).

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[1] Rakusin and Arseneeff, *Chem. Zeit.*, 1923, 47, 195.
[2] Kroll, *Zeitsch. anorg. Chem.*, 1912, 76, 387; 77, 1; 78, 5.
[3] Epperson, *J. Amer. Chem. Soc.*, 1928, 50, 321.
[4] Ball and Agruss, *J. Amer. Chem. Soc.*, 1930, 52, 120.
[5] Britton, *Trans. Chem. Soc.*, 1927, p. 614.

It is also possible to eliminate phosphate as insoluble phosphometastannic acid by adding tin to a nitric acid solution of phosphoric acid.

Pyro- and Meta-phosphates.—The behaviour of the pyro- and meta-phosphates towards the foregoing reagents and others which may be used in distinguishing these salts are tabulated below:—

COMMON AND DISTINCTIVE REACTIONS OF ORTHO-, PYRO- AND META-PHOSPHATES.

Reagent.	*Ortho-.*	*Pyro-.*	*Meta-.**
Silver nitrate, neutral or slightly alkaline solution.	Yellow precipitate, dissolving in acetic acid.	White crystalline precipitate, not dissolving in acetic acid.	White gelatinous precipitate, not dissolving in acetic acid.
Barium chloride, neutral or alkaline. Do. acid.	White precipitate. No precipitate.	White precipitate. No precipitate.	White precipitate. White precipitate.
Albumin, acid solution.	No reaction.	No reaction.	Coagulated.
Ammonium molybdate with nitric acid.	Yellow crystalline precipitate on warming.	No precipitate in cold or on gentle warming.	No precipitate in cold or on gentle warming.
Zinc acetate to acid solution.	No precipitate.	White precipitate, soluble in excess of pyrophosphate.	No precipitate.
Salts of chromium.	Precipitate, soluble in cold acetic acid.	Precipitate, insoluble in acetic acid.	Precipitate, insoluble in acetic acid.
Special tests.	Lead acetate gives white $Pb_3(PO_4)_2$, almost insoluble in acetic acid.	Magnesium chloride gives white precipitate, soluble in excess of $MgCl_2$ or pyrophosphate. Luteo cobaltic chloride, $Co(NH_3)_6Cl_3$, gives a reddish-yellow crystalline precipitate, $Co(NH_3)_6NaP_2O_7 . 11\frac{1}{2}H_2O$.	Magnesium salts give no precipitate. Bismuth salts in alkaline solution give a white precipitate.

Estimation of the Phosphoric Acids.

The titrations are based upon the degrees of dissociation of the first, second, etc. hydrogen ion. The dissociation constants and appropriate indicators are mentioned on pp. 165, 172, 176.

Orthophosphoric Acid may be titrated with sodium or potassium hydroxide free from carbonate. The equivalent point indicating NaH_2PO_4 occurs at $pH = ca.\ 4{\cdot}2$, which is within the transition range of methyl yellow, methyl orange and bromophenol blue. The end-point tint should be matched against that of a comparison solution containing about the same concentration of NaH_2PO_4.

The acid may also be titrated as dibasic, using phenolphthalein, thymolphthalein or thymol blue, the end-point tint being matched against a solution of Na_2HPO_4.

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* *Note.*—The results depend somewhat on the complexity of the metaphosphates (see pp. 177 *et seq.*).

The results are closer to the theoretical if the solutions are saturated with sodium chloride. See also " Neutralisation Curve," p. 166.

Pyrophosphoric Acid (p. 171) may be titrated as a dibasic acid to $pH = 4{\cdot}0$ using methyl yellow, etc. as before; also as a tetrabasic acid using phenolphthalein, thymolphthalein or thymol blue in the presence of barium salt. Electrometric titrations have also been performed.[1]

Metaphosphoric Acid may be titrated with methyl orange, etc. irrespective of its progressive hydration (p. 175). The phenolphthalein titre, however, varies with time (see p. 176).

Special methods of analysing the pyro- and meta-acids have been indicated on pp. 172, 176, 180. These acids may easily be converted into the ortho- form by boiling alone or in the presence of some nitric acid, and then determined by one of the methods described in the following.

Determination of Orthophosphates.—(1) *With Silver Nitrate.*—This depends upon the precipitation of silver orthophosphate in solutions of low and controlled acidity. In the assay of commercial 85 per cent. phosphoric acid of density 1·710 the syrup is diluted to a convenient volume and an aliquot part is taken which contains about 0·1 gram of H_3PO_4. It is neutralised to phenolphthalein with approximately decinormal alkali (free from chloride). 50 c.c. of decinormal silver nitrate are then added while the solution is kept neutral to litmus by stirring in zinc oxide or a suspension of the hydroxide. The whole or a measured part of the filtered solution is acidified with nitric acid and, after the addition of ferric alum, the unused silver nitrate is titrated with standard decinormal ammonium thiocyanate in the usual manner. Alkali phosphates may also be determined in this way.

Silver phosphate is also quantitatively precipitated in the presence of sodium acetate and acetic acid, the phosphoric acid then being titrated as a tribasic acid according to the equation

$$H_3PO_4 + 3AgNO_3 + 3CH_3COONa = Ag_3PO_4 + 3NaNO_3 + 3CH_3COOH$$

This reaction is also used in the method of Holleman [2] as modified by Wilkie.[3] A phosphate solution containing phenolphthalein is reddened by the addition of alkali, then just decolorised with nitric acid. An excess of standard silver nitrate is then added and decinormal sodium acetate and alkali to slight pink colour, followed by 2 c.c. of decinormal H_2SO_4. The solution is diluted and filtered and the excess of silver determined by titration with decinormal ammonium thiocyanate.

(2) *With Molybdate.*—Precipitation of phosphate in nitric acid solution by means of ammonium molybdate serves not only as a qualitative test, but also for the quantitative separation of phosphate in a preliminary or even final manner. Insoluble phosphates are previously dissolved in nitric acid, while the phosphoric acids are nearly neutralised with ammonia and then acidified with nitric acid. The nitric acid solution of ammonium molybdate (3 per cent.) is added hot, the mixture boiled and the precipitate collected on a filter. The precipitate may now be treated in various ways :—

(*a*) The precipitate is redissolved in ammonia, reprecipitated with nitric acid and ammonium molybdate, washed with a solution of ammonium nitrate and nitric acid, and dried for a long time at 160° to 180° C. preferably in a current of air. The precipitate is then $(NH_4)_3PO_4.12MoO_3$ containing theoretically 3·782 per cent. P_2O_5 and 1·65 per cent. phosphorus. Under the conditions given the practical factor for conversion to per cent. P_2O_5 is 3·753.[1] If the precipitate is greenish it should be heated again with a small crystal of NH_4NO_3 and a little ammonium carbonate which gives the correct yellow.

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[1] Morton, *Quart. J. Pharm.*, 1930, 3, 438.

[2] Holleman, *J. Soc. Chem. Ind.*, 1894, 13, 763, 843.

[3] Wilkie, *J. Soc. Chem. Ind.*, 1910, 29, 794; Rosin, *J. Amer. Chem. Soc.*, 1911, 33, 1099.

(*b*) On gentle ignition the precipitate is converted into a blue-black substance $24MoO_3.P_2O_5$ which contains 3·947 per cent. P_2O_5.

(*c*) The precipitate is dissolved in 2·5 per cent. ammonia, the solution nearly neutralised with hydrochloric acid and precipitated with a solution of magnesium salts (see p. 183).

(*d*) The well-washed precipitate is dissolved in a known quantity in excess of standard alkali, the excess alkali being titrated with standard nitric acid using phenolphthalein:—

$$2[(NH_4)_3PO_4+12MoO_3]+46NaOH+H_2O=2(NH_4)_2HPO_4 \\ +(NH_4)_2MoO_4+23Na_2MoO_4+23H_2O$$

1 c.c. decinormal NaOH corresponds to 0·000309 gram P_2O_5.

(*e*) The molybdate method has been adapted to the determination of small quantities of phosphorus colorimetrically. The solution in nitric acid is evaporated to dryness to render the silica insoluble, and the residue taken up with nitric acid. After the addition of an excess of ammonium molybdate the colour is matched against a standard of nearly the same concentration in phosphate. The maximum colour is developed after a few minutes, while that in the presence of silicic acid requires some hours. Darker solutions precipitate in time while lighter ones fade.[2]

A colorimetric method has also been devised which is not interfered with by silicic acid. Iron, however, should be removed by means of cupferron. The solution should contain 0·002 to 0·025 milligram of P_2O_5 and 2 c.c. of nitric acid (density 1·12). To this is added 2 c.c. of a quinine solution made by dissolving 1 gram of the sulphate in a slight excess of nitric acid and adding enough baryta to precipitate all the sulphate. The colour developed after the addition of the molybdate is compared with that of a standard.[3]

A nephelometric method using a strychnine molybdate reagent has also been devised.[4]

A similar method is used for the determination of inorganic phosphates in urine.[5] 1 to 5 c.c. of the urine, containing about 0·5 milligram of phosphorus, are diluted and treated with a solution of ammonium molybdate in 15 per cent. sulphuric acid (5 c.c.), 1 c.c. of 1 per cent. hydroquinone solution and 1 c.c. of 20 per cent. sodium sulphite solution. The blue colour is compared in Nessler glasses with that developed by the same solutions when mixed with a standard phosphate solution of which 5 c.c. contain 0·5 milligram of phosphorus.

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[1] Treadwell-Hall, "*Analytical Chemistry, Vol. II, Quantitative,*" Chapman and Hall, 1930.

[2] Schreiner, *J. Amer. Chem. Soc.*, 1903, 25, 1056; Schreiner and Brown, *ibid.*, 1904, 26, 975.

[3] Gregoire, *Bull. Soc. chim. Belg.*, 1920, 29, 253.

[4] Juliusberger, *Biochem. Zeitsch.*, 1926, 177, 140.

[5] Briggs, *J. Biol. Chem.*, 1922, 53, 13.

The standard phosphate is made by dissolving 4·388 grams of KH_2PO_4 in 1 litre and diluting this stock 10 times before use.

(*f*) The amount of molybdenum in the precipitate may also be determined by several methods. A quick volumetric method consists in reduction to molybdenum sesquioxide and titration with permanganate. The precipitate, after washing with acid ammonium sulphate solution, is dissolved in 10 per cent. ammonia, then treated with an excess of dilute sulphuric acid and filtered through zinc. The reduced solution and its washings are run directly into 50 c.c. of 20 per cent. ferric alum. The MoO_3 is reduced by the zinc to Mo_2O_3 (or $Mo_{24}O_{37}$) and this is again oxidised by the ferric sulphate, giving its equivalent of ferrous sulphate, which is titrated with $KMnO_4$. Since the precipitate contains 1P to $12MoO_3$ and 3 atoms of oxygen oxidise Mo_2O_3, it follows that $36Fe \equiv 1P$. Therefore the iron value of the $KMnO_4$ multiplied by P/36Fe (*i.e.* 0·01540) gives the value of the $KMnO_4$ in terms of phosphorus. The factor is 0·0158 if the reduction product is $Mo_{24}O_{37}$.

(3) *Volumetrically, by Uranyl Solutions.*—Phosphates which are soluble in water or acetic acid may be determined quickly with a solution of uranyl acetate or nitrate which has been standardised against pure sodium or potassium phosphate. The uranium solution is run into that of the phosphate, containing ammonium acetate and acetic acid. A greenish-yellow precipitate of uranyl ammonium phosphate is deposited. The excess of uranium which appears at the end-point is recognised by spotting on a white tile and mixing with drops of a solution of potassium ferrocyanide. The uranyl salt gives a dark brown colour of uranyl ferrocyanide.

$$KH_2PO_4 + UO_2(CH_3CO_2)_2 + CH_3CO_2NH_4 = UO_2NH_4PO_4 + CH_3CO_2K + 2CH_3CO_2H$$

It is possible also to use cochineal as an inside indicator, the end-point being shown by a change of colour from pink to green.

(4) *Magnesium Phosphate Method.*—This is the most important and most accurate final method for the determination of phosphorus in all its compounds. If the phosphate is present as a salt soluble in water the solution is slightly acidified and magnesia mixture (containing magnesium chloride and ammonium chloride) is added. The solution is heated to boiling and a hot 2·5 per cent. solution of ammonia is added drop by drop until phenolphthalein is reddened and a crystalline precipitate obtained, which is ready for filtration after standing about 10 minutes. The precipitate is washed with 2·5 per cent. ammonia, filtered off on a Gooch crucible or on paper and ignited wet or dry to $Mg_2P_2O_7$, which contains 27·86 per cent. of phosphorus, 63·79 per cent. of P_2O_5 and 85·342 per cent. of PO_4.

An ammonium phosphomolybdate precipitate is treated as described under (2*c*) (p. 182) for conversion into $MgNH_4PO_4$. The washed precipitate of $MgNH_4PO_4$ may be determined volumetrically by solution in a known quantity in excess of standard hydrochloric acid and back-titration with decinormal alkali using methyl orange, thus

$$MgNH_4PO_4 + 2HCl = NH_4H_2PO_4 + MgCl_2$$

The most important materials or products in which it is necessary to determine phosphorus are phosphatic rocks of all sorts, soils, fertilisers (including basic slag), iron, steel and non-ferrous phosphor alloys. The former classes are dealt with in the appropriate sections of this Volume, so that it remains only to mention some special methods which are used in the case of phosphorus alloys.

Phosphorus in Alloys.—Many commercial varieties of iron contain phosphorus, probably in the form of a phosphide (*q.v.*, p. 66). The metal is dissolved in HNO_3 (1 : 1), the solution evaporated to dryness, the residue taken up with hydrochloric acid and evaporated again until the silica has all been rendered insoluble. The residue is then taken up in hydrochloric acid, evaporated to dryness again, taken up in nitric acid and treated with ammonium nitrate and ammonium molybdate reagent. The precipitate is washed with dilute nitric acid until free from iron salts, then with water if it is to be weighed as under (2*a*) (p. 181) or with a solution of potassium nitrate if it is to be titrated as under (2*d*) (p. 182). This method also applies to other metals which contain phosphides. If tin is present, as in the phosphor bronzes, all the phosphoric oxide is found with the insoluble metastannic acid after solution of the alloy in nitric acid. This precipitate, after washing, drying and weighing, may be fused with three times its weight of potassium cyanide. The residue is extracted with water, the metallic tin filtered off, and the excess of cyanide destroyed with HCl, any copper and tin remaining in solution being precipitated with H_2S. In the filtrate, after boiling, the phosphate is determined by any of the methods already described.

Perphosphoric Acids.—The methods which have been used successfully in the preparation of persulphuric acids and persulphates have also been applied to perphosphoric acid and the perphosphates, *i.e.*—

(*a*) The addition of H_2O_2 at low temperatures.
(*b*) Anodic oxidation.

(*a*) Hydrogen peroxide does not combine with orthophosphoric acid. But when metaphosphoric acid or phosphorus pentoxide were treated with 30 per cent. hydrogen peroxide at 0° C., solutions were obtained which had oxidising properties and which by analysis proved to contain *permonophosphoric acid*, H_3PO_5. With pyrophosphoric acid in excess, *perdiphosphoric acid*, $H_4P_2O_8$, was obtained.[1]

Slightly acid or alkaline phosphate solutions of the alkali metals, etc., combine with varying proportions of H_2O_2 in a loose manner. Such solutions give the reactions of H_2O_2.[2]

(*b*) Electrolytic oxidation. The perphosphates of the alkali metals and of ammonium have been prepared in this way. As in the electrolytic production of persulphates[3] low temperatures are advantageous and the presence of fluorides and chromates increases the yield, probably by maintaining a high anodic over-voltage. A low anodic current-density (*e.g.* about 0·015 amp./cm.^{2}) is favourable. The electrolyte may consist of a solution of KH_2PO_4 with fluoride and chromate. On evaporation at 100° C. after the electrolysis potassium perphosphate, $K_4P_2O_8$, can be crystallised.[4]

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[1] Schmidlin and Massini, *Ber.*, 1910, 43, 1162; d'Ans and Friedrich, *Ber.*, 1910, 43, 1880; d'Ans, *Zeitsch. Elektrochem.*, 1911, 17, 850.

[2] Husain and Partington, *Trans. Faraday Soc.*, 1928, 24, 235.

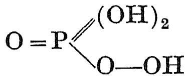
[3] This Series, Volume VII, Part II.

[4] Fichter and Muller, *Helv. Chim. Acta*, 1918, 1, 297; Miro, *ibid.*, 1919, 2, 3.

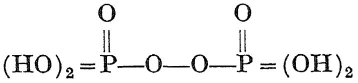
Perphosphates of ammonium may be prepared in good yields by electrolysis, but auto-oxidation and -reduction may occur with the production of ammonium phosphate and ammonium nitrate.[1]

Perphosphates of rubidium and cæsium are more easily prepared, even in the absence of fluorides or chromates. The permonophosphates of these metals however require in their preparation rather higher current-densities.[2]

If the perphosphoric acids are regarded as derivatives of hydrogen peroxide their constitution with quinquevalent phosphorus will be



Permonophosphoric Acid.



$$(HO)_2=\overset{\overset{\displaystyle O}{\|}}{P}-O-O-\overset{\overset{\displaystyle O}{\|}}{P}=(OH)_2$$

Perdiphosphoric Acid.

Reactions and Detection.—Permonophosphoric acid is a strong oxidising agent. It liberates iodine at once from acidified potassium iodide (*cf.* Caro's acid) and oxidises manganous salts in the cold to permanganates. Hydrolysis in dilute solutions is represented by the equation

$$H_3PO_5+H_2O=H_3PO_4+H_2O_2$$

Perdiphosphoric acid liberates iodine only slowly from acidified potassium iodide, and can be kept for long periods in dilute solution.

Oxidation of manganous salts in acid solution to red manganic salts is characteristic of true perphosphates. They should not give the characteristic tests of hydrogen peroxide with chromic acid or titanic acid. They oxidise acid aniline solutions to nitrosobenzene and gradually to nitrobenzene.

Potassium perphosphate gives with silver nitrate a dark precipitate which changes to white Ag_3PO_5, then to yellow Ag_3PO_4 with evolution of ozone and oxygen.

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[1] Gutzwiller, *Helv. Chim. Acta*, 1928, 11, 323; Husain and Partington, *loc. cit.* See also Fichter, *J. Soc. Chem. Ind.*, 1929, 48, 347T.

[2] Husain and Partington, *loc. cit.*

CHAPTER XIII.

PHOSPHORUS AND SULPHUR OR SELENIUM.

PHOSPHORUS combines directly with sulphur in various proportions to give sulphides, the formulæ of some of which resemble those of the oxides. It also gives oxysulphides, thiophosphites, thiophosphates and the corresponding acids. The latter salts may be made by the action of alkalies or alkali sulphides on phosphorus sulphides.

Historical.—It was recognised early that phosphorus combines violently with sulphur when the two are heated together to a sufficiently high temperature (see p. 187),[1] and various products were examined, some of which afterwards proved to be compounds and others mixtures.[2] Among the earliest products to be prepared and analysed were P_4S [3] and P_4S_3.[4] The substance P_4S was shown later to be merely a solid solution of the two elements, while the latter, P_4S_3, is one of the best-known compounds and is prepared in large quantities for use in the match industry (*q.v.* and see p. 10).

Physical Mixtures.—When sulphur and phosphorus are melted together at temperatures below 100° C. each lowers the melting-point of the other but there is no sign of combination. The eutectic mixture solidified at +9·8° C. and contained 22·8 per cent. of sulphur.[5] The mixed crystals deposited on the sulphur side of the eutectic were isomorphous with the octahedral form of sulphur up to a maximum of about 20 per cent. of phosphorus, while the crystals on the phosphorus side were isomorphous with phosphorus up to a maximum of about 5 per cent. of sulphur. On distillation at low temperatures (under reduced pressures) the products behaved as mixtures; all the phosphorus distilled away and the sulphur was left.[6]

The System Phosphorus-Sulphur and Compounds.—The two elements mixed in various proportions were fused in sealed tubes at about 200° C. The solids so formed were heated and the temperatures determined at which complete liquefaction took place. These temperatures are the initial freezing-points of liquid at that temperature in equilibrium with the solid phases.

By this method points on the temperature-composition curves were obtained corresponding to the compounds P_4S_3, P_2S_3, P_2S_5 and perhaps P_3S_6, P_4S_7, PS_6.[1]

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[1] Marggraf, *Miscellan. Berolin.*, 1740, 6, 54.

[2] Berzelius, *Annalen*, 1843, 47, 129, 255; Faraday, *Quart. J. Sci.*, 1818, 4, 361; Pelletier, *Ann. Chim. Phys.*, 1790, [1], 4, 1.

[3] Berzelius, *loc. cit.*

[4] Lemoine, *Compt. rend.*, 1864, 58, 890; 1881, 93, 489; 1883, 96, 1630; 1884, 98, 45.

[5] Boulouch, *Compt. rend.*, 1902, 135, 165; 1904, 138, 364; 1906, 142, 1045.

[6] Isambert, *Compt. rend.*, 1883, 96, 1499, 1628, 1771; 1885, 100, 355; 1886, 102, 1386.

FREEZING-POINTS AND COMPOSITIONS OF THE SYSTEM PHOSPHORUS-SULPHUR.[2]

[The melting-points of compounds and eutectics are printed in heavy type, the corresponding compositions of the liquid phases in italics. Solid phases of uncertain composition are enclosed in brackets.]

Per cent. Sulphur.	Solid Phase.	Freezing-point, ° C.	Per cent. Sulphur.	Solid Phase.	Freezing-point, ° C.
0·0	P	+44	*43·6*	P_4S_3	**167**
6·0	,,	27	45·0	,,	154
10·0	,,	20	*50·0*	$P_4S_3+P_2S_3$	**46**
12·0	,,	13	55·0	P_2S_3	230
16·0	,,	+ 3	*60·8*	P_2S_3	**296**
20·0	$P+(P_2S)$	**− 7**	*67·5*	$P_2S_3+P_2S_5$	**230**
24·0	(P_2S)	+ 5	*72·1*	P_2S_5	**272**
26·0	,,	11	*75·0*	$P_2S_5+(PS_6)$	**243**
30·0	,,	24	80·0	(PS_6)	300
34·0	,,	38	*86·1*	(PS_6)	**314**
36·0	$(P_2S)+P_4S_3$	**44**	90·0	,,	308
38·0	P_4S_3	86	95·0	,,	260
40·0	,,	122	100·0	S	115·2
41·0	,,	146			

Other compounds not included in this set of experiments have been described, *e.g.* P_4S_7 (m.pt. **303°** C.), P_3S_6 (m.pt. **298°** C.),[3] and P_4S_8 (m.pt. **311°** C.).

A metastable series between phosphorus and P_4S_3 has also been reported, with a eutectic at − 40° C. and 33·5 per cent. sulphur, but the latter point may be due to supercooling.[4]

Tetraphosphorus Trisulphide or *Phosphorus Tetritatrisulphide*, P_4S_3, may be prepared by heating together the theoretical proportions of red phosphorus and sulphur in a sealed tube or in an atmosphere of carbon dioxide.[5] It is recommended [6] to use an excess of red phosphorus, mix intimately with powdered sulphur and heat to 100° C. in a wide tube in a current of carbon dioxide. The reaction is started by stronger heating in one spot. After the reaction has ceased, the contents of the tube are heated until distillation begins, in order to dissociate the higher sulphides of phosphorus. The product, after cooling in an atmosphere of carbon dioxide, may be extracted with carbon disulphide, which dissolves the P_4S_3, or distilled, when P_4S_3 passes over.

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[1] Giran, *Compt. rend.*, 1906, 142, 398; Boulouch, *loc. cit.*; Helff, *Zeitsch. physikal. Chem.*, 1893, 12, 196; Mai and Scheffer, *Ber.*, 1903, 36, 780; Stock and Hofmann, *ibid.*, 1903, 36, 315; Rudolph, "*Zur Kenntnis der Phosphorsulfide, insbesondere des Tetraphosphortrisulfides,*" Berlin, 1910; Schenck and Scharff, *Ber.*, 1906, 39, 1522; Stock and Rudolph, *ibid.*, 1909, 42, 2062; 1910, 43, 150; Stock and Herscovici, *ibid.*, 1910, 43, 415, 1223; Herscovici, "*Zur Kenntnis der Phosphorsulfide,*" Berlin, 1910; Stock and v. Bezold, *Ber.*, 1908, 41, 657.

[2] Giran, *loc. cit.*

[3] Stock and v. Bezold, *loc. cit.*

[4] Boulouch, *loc. cit.*

[5] Lemoine, *loc. cit.*; Isambert, *loc. cit.*; Ramme, *Ber.*, 1879, 12, 941; Helff, *loc. cit.*; Mai and Scheffer, *loc. cit.*; Stock and v. Bezold, *loc. cit.*; Rudolph, *loc. cit.*; Stock and Rudolph, *loc. cit.*

[6] Stock and Rudolph, *loc. cit.*

Details of the preparation according to Stock[1] are as follows :—The sulphur, phosphorus, carbon disulphide and benzene should be both pure and dry. The red phosphorus (155 grams) is mixed with the sulphur (95 grams). This mixture, in portions of 40 to 50 grams is carefully warmed to 100° C. in a beaker standing on a sand-bath, while a current of CO_2 is passed on to the surface. The part of the beaker which is on a level with the upper edge of the mixture is then heated with a small flame until the reaction starts and spreads rapidly through the mass. The melted substance is then heated to the point of distillation in a current of CO_2, which is maintained until the product is cold. It is then crushed and extracted with about twice its weight of warm CS_2. On evaporation of this, the sulphide, having a melting-point of 130° to 150° C., remains. It is powdered, boiled with water and steamed. The powder is again extracted with CS_2, which is shaken with P_2O_5, filtered and evaporated until crystals form. These are dried over P_2O_5 in a water-pump vacuum. The product now melts at 160° to 171° C. but still contains CS_2, which may be removed by extraction in a Soxhlet apparatus with benzene. As this proceeds, fine crystals are deposited from the benzene. These are sucked dry on a filter and finally freed from solvent in a current of dry hydrogen. Another crop of crystals may be obtained by evaporation of the mother-liquors. The yellowish needles, of melting-point about 173° C., are soluble in benzene and carbon disulphide. Solutions are turbid on exposure to air, but remain unaltered in an atmosphere of hydrogen. They can be heated to 700° C. without alteration in the absence of oxygen and moisture.

In the commercial process phosphorus and sulphur are heated together in a current of carbon dioxide to 330° or 340° C., and the compound sublimed. The commercial product may contain 83 to 98 per cent. of P_4S_3 with free sulphur, water, volatile matter, phosphoric acid and other impurities.[2] If it is to be used in the match industry it should not contain free phosphorus.

The purified compound is a yellow crystalline substance which has a constant composition and which does not alter on fractional distillation or crystallisation.[3] The vapour density was found to agree with the formula P_4S_3.[4] It has been confirmed that the molecular weight of the vapour agrees with the theoretical (220) at about 700° C., but above this temperature dissociation takes place, a molecular weight of 179 being found at 1000° C.[5] Molecular weights slightly above the theoretical (228 to 264) were found for this compound when dissolved in benzene at its boiling-point.[6]

The density of the solid was 2·0.[7] The melting-point was found to be 165° to 167° C. by Isambert, Helff, Mai and Scheffer,[1] also by Rebs and Giran,[2] but Stock and his collaborators give 171° to 172·5° C. The boiling-point is above 400° C.; it is given as 410° to 420° C.,[3] 408° to 418°,[4] 407° to 408°.[5] In a water-pump vacuum the sulphide may be distilled at about 230° C.

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[1] Stock, *loc. cit.*

[2] Clayton, *Proc. Chem. Soc.*, 1902, 18, 129; 1903, 19, 231.

[3] Lemoine, *loc. cit.*

[4] Lemoine, *loc. cit.*; Ramme, *loc. cit.*; Helff, *loc. cit.*

[5] Stock and v. Bezold, *loc. cit.*

[6] Stock and Rudolph, Stock and v. Bezold, Helff, *loc. cit.*

[7] Lemoine, *loc. cit.*; Isambert, *loc. cit.*; Stock and v. Bezold, *loc. cit.*

The heat of formation was low, namely, 16·4 Cals. per mol P_4S_3 and of the same order as the heat of transformation of yellow into red phosphorus. As already mentioned, the vapour is dissociated at higher temperatures, and in an atmosphere of carbon dioxide this dissociation appears to begin at about 380° C.

The compound ignites in air at about 100° C.[3] and shows a greenish glow of slow combustion at about 80° C.[6] The conditions of this glow resemble, but are not identical with, those required in the cases of white phosphorus and phosphorous oxide.[4] It did not appear in pure oxygen until, at 65° C., the pressure was reduced below 300 mm., and was steady at 242 mm. in dry and 250·3 mm. in moist oxygen. At higher temperatures the glow appeared and disappeared at higher pressures. Inflammation occurred between 80° and 90° C.[6] The products of combustion are phosphoric oxide and sulphur dioxide. Chlorine converts the sulphide into phosphoric and sulphuric acids, while aqua regia also dissolves it.[7]

Cold water has no effect, but boiling water slowly decomposes the sulphide into phosphoric acid and hydrogen sulphide.[3] With potassium hydroxide solution the sulphide behaves like a mixture of sulphur and phosphorus, giving phosphine, hydrogen, etc., and potassium sulphide.[8]

Like its constituent elements, this sulphide of phosphorus dissolves very freely in CS_2 (solubility 60 to 100 at ordinary temperatures). It is also moderately soluble in solvents such as benzene and toluene.

Diphosphorus Trisulphide or *Phosphorus Tetritahexasulphide*, P_2S_3 or P_4S_6.—The preparation of a compound of this composition by heating the constituent elements in the correct proportions was reported by the earlier workers.[7] It was described as a yellowish-white substance which could be obtained as a sublimate[9] and purified by sublimation.[10] It gave a vapour the density of which corresponded to P_4S_6.[11] When hydrogen sulphide is caused to react with phosphorus trihalides the solid remaining has the composition P_2S_3.[12]

The substance melted at 290° C.,[3] 296° C.[13] It sublimed between 490° and 550° C. It did not fume or glow in the air, but in other respects its chemical properties resembled those of P_4S_3.

Tetraphosphorus Heptasulphide or *Phosphorus Tetritaheptasulphide*, P_4S_7.—This compound was first obtained during the distillation of P_4S_6 in a vacuum,[14] and was separated by heating under pressure with carbon disulphide in which, as distinguished from P_4S_3, it was only sparingly soluble. In the methods of preparation which have been described [1] the phosphorus should be in slight excess over that required for P_4S_7. The ingredients may be heated together in a sealed tube and the product recrystallised from carbon disulphide in pale yellow crystals.

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[1] *Loc. cit.*

[2] Rebs, *Annalen*, 1888, 246, 365; Giran, *loc. cit.*

[3] Lemoine, *loc. cit.*

[4] Mai and Scheffer, *loc. cit.*

[5] Stock and Rudolph, *loc. cit.*

[6] Scharff, "*Ueber das Leuchten des Phosphors und einiger seiner Verbindungen*," Marburg, 1907.

[7] Lemoine, Isambert, *loc. cit.*

[8] Lemoine, *loc. cit.*; Stock and Rudolph, *loc. cit.*

[9] Berzelius, *Annalen*, 1843, 47, 129, 255.

[10] Krafft and Neumann, *Ber.*, 1901, 34, 567.

[11] Isambert, *loc. cit.*

[12] Sérullas, *Ann. Chim. Phys.*, 1829, [2], 42, 33; Gladstone, *Phil. Mag.*, 1849, [3], 35, 345; Ouvrard, *Ann. Chim. Phys.*, 1894, [7], 2, 221. For other methods, see also Springer, *Pharm. Zeitung*, 1900, 43, 164; Besson, *Compt. rend.*, 1896, 122, 467; 1896, 123, 884; 1897, 124, 151.

[13] Giran, *loc. cit.*, p. 187.

[14] Mai, *loc. cit.*

The melting-point was 310° C. and the boiling-point 523° C.[2] A maximum melting-point corresponding to P_4S_7 was found on the thermal diagram of P_4S_6 and P_4S_{10}.[3] The solubility in carbon disulphide was 0·0286 gram per 100 grams solvent at 17° C.

A compound having the empirical formula PS_2 was said to be formed by heating together the elements in the proportions theoretically required,[4] or by distillation [5] or heating with carbon disulphide in a sealed tube at 210° C.[6] Other methods include the exposure to sunlight of P_4S_3 (1 part) with sulphur (2 parts) dissolved in carbon disulphide,[7] or a solution of phosphorus and sulphur with a little iodine in carbon disulphide.[8] Pale yellow transparent needles of the compound are deposited.

The molecular weight deduced from the vapour density was P_4S_8 [5] or P_3S_6.[9] The melting-point was 248° to 249° C.[10] or 290° to 298° C.[11] The boiling-point is given as 516° to 519° C.[12]

The chemical properties are similar to those of the other sulphides of phosphorus, but the compound is less stable, and easily decomposes, giving P_4S_3 with separation of sulphur.

Phosphorus Pentasulphide or *Diphosphorus Pentasulphide* or *Phosphorus Tetritadecasulphide*, P_2S_5 or P_4S_{10}.—The methods which have been already described in connection with the other sulphides have been successfully used in the preparation of this compound from the theoretical proportions of the elements :—

(*a*) By fusion. This method is used in the preparation of the commercial product, which is not pure.[13] A slight excess of sulphur should be used and the heating should take place in an atmosphere of CO_2. The compound may be purified by heating in a vacuous sealed tube for several hours at 700° C., and then by crystallisation from carbon disulphide.[14]

(*b*) By heating phosphorus (20 grams) and sulphur (60 grams) in a sealed tube with iodine (0·5 gram) and carbon disulphide (150 c.c.) at 211° C., followed by recrystallisation.[15]

(*c*) By the action of H_2S on $POCl_3$.[16]

(*d*) By passing the vapour of $PSCl_3$ through a red-hot tube.[17]

Details of the preparation have been given by Stock.[18] Pure, dry, red phosphorus (100 grams) is intimately mixed with sulphur (260 grams). Portions of 30 to 40 grams are heated until they combine, in the manner described under P_4S_3. The product is ground up and heated in an evacuated and sealed glass tube to about 700° C. The contents are powdered and extracted with CS_2. They are recrystallised twice from the same solvent and dried at 100° C. in a current of hydrogen. The yield should be about 60 per cent. of the theoretical.

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[1] Stock and v. Bezold, *loc. cit.*; Stock and Herscovici, *loc. cit.*

[2] Stock and Herscovici, *loc. cit.*

[3] Stock, *Ber.*, 1906, 39, 1967; 1909, 42, 2062.

[4] Ramme, *loc. cit.*; Helff, *loc. cit.*

[5] Mai, *Annalen*, 1891, 265, 192.

[6] Seidel, "*Ueber Schwefelphosphorverbindungen, etc.*," Göttingen, 1875.

[7] Dervin, *Compt. rend.*, 1904, 138, 366.

[8] Boulouch, *loc. cit.*

[9] Ramme, Helff, *loc. cit.*

[10] Seidel, *loc. cit.*

[11] Ramme, Helff, Dervin, *loc. cit.*

[12] Recklinghausen, *Ber.*, 1893, 26, 1517.

[13] Kekulé, *Annalen*, 1854, 90, 399; Goldschmidt, *Ber.*, 1882, 15, 303; V. and C. Meyer, *Ber.*, 1879, 12, 609; Helff, *loc. cit.*; Rebs, *loc. cit.*

[14] Ramme, *loc. cit.*

[15] Ramme, *loc. cit.*; Stock and Thiel, *Ber.*, 1905, 38, 2720.

[16] Besson, *loc. cit.*

[17] Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 5.

[18] Stock, *Ber.*, 1910, 43, 1223.

Properties.—The compound has been prepared in two forms :—

(*a*) Pale yellow crystals obtained by repeated recrystallisation from carbon disulphide, in which they are only sparingly soluble (1 in 195). Density 2·03.

(*b*) A nearly white substance obtained by rapid condensation of the vapour, followed by extraction with carbon disulphide. This form was more soluble in this solvent (1 in 30), had a higher density (2·08) and a lower indefinite melting-point (247° to 276° C.).[1]

The melting-point of the commercial sulphide was 255° C.[2] and that of the recrystallised product 275° to 276° C.[3] The melting-point was raised to 284° to 291° C. by repeated recrystallisation from carbon disulphide.[4] Boiling occurs with partial decomposition at 513° to 515° C.[4] Other values which have been found are 520° C.,[5] 523·6° C.[6] The sulphide distils in a water-pump vacuum at 332° to 340° C., probably with considerable dissociation (see " Vapour Density ").[7]

The vapour density at temperatures slightly above the boiling-point corresponded to simple molecules P_2S_5.[8] Later investigators, however, found that it was slightly below the theoretical, being 208 at 300° C., and decreased at higher temperatures, down to 133 at 1000° C.[9] The molecular weight in boiling carbon disulphide was 482 to 491, corresponding approximately to double molecules (P_4S_{10} requires 444).[10]

The compound does not glow in air, but is highly inflammable, giving a mixture of the oxides. It was attacked only slowly by cold water, but rapidly by hot water, giving phosphoric acid and hydrogen sulphide.[11] It did not form addition compounds with bromine or iodine.[12] It was converted into $PSCl_3$ by phosphorus pentachloride and by several other acid chlorides :—[13]

$$\begin{gathered} P_2S_5 + 3PCl_5 = 5PSCl_3 \\ P_2S_5 + 5POCl_3 = 5PSCl_3 + P_2O_5 \\ 2P_2S_5 + 6SOCl_2 = 4PSCl_3 + 3SO_2 + 9S \\ P_2S_5 + SbCl_3 = PSCl_3 + SbPS_4 \end{gathered}$$

Ammonia, in the gaseous or liquid form, was readily absorbed by the pentasulphide giving a phosphorus hexammonio-pentasulphide,

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[1] Stock and Thiel, *loc. cit.*; Thiel, "*Zur Kenntnis des Phosphorpentasulfides,*" Berlin, 1905.

[2] Stock and Scharfenberg, *Ber.*, 1908, **41**, 558.

[3] Stock, *loc. cit.*; V. and C. Meyer, *loc. cit.*; Helff, *loc. cit.*

[4] Stock and Herscovici, *loc. cit.*

[5] Isambert, *loc. cit.*

[6] Recklinghausen, *loc. cit.* See also Goldschmidt, *Ber.*, 1882, **15**, 303.

[7] Mai, *loc. cit.*

[8] Isambert, *loc. cit.*; Meyer, *loc. cit.*; Helff, *loc. cit.*

[9] Stock and v. Bezold, *loc. cit.*

[10] Stock and Thiel, *loc. cit.*

[11] Kekulé, *loc. cit.*; Stock and Herscovici, *loc. cit.*

[12] Hunter, *Chem. News*, 1925, **131**, 38, 174.

[13] Carius, *Annalen*, 1858, **106**, 331; 1859, **112**, 80; Weber, *J. prakt. Chem.*, 1859, [1], **77**, 65; Glatzel, *Zeitsch. anorg. Chem.*, 1893, **4**, 186; 1905, **44**, 65.

$P_2S_5.6NH_3$, as well as lower ammoniates. This compound may be ammonium diimidopentathiopyrophosphate, $S\{P(SNH_4)_2(NH)\}_2$.[1]

The pentasulphide dissolved slowly in cold alkalies, quickly in hot, and gave salts of thiophosphoric acid.[2] Sodium sulphide also gave a thiophosphate.[3]

Uses of the Sulphides of Phosphorus.—The pentasulphide of phosphorus is used to replace the oxygen of organic compounds by sulphur; thus ethyl alcohol gives ethyl mercaptan, and acetic acid thioacetic acid.[4] The reactions, however, are somewhat complex; thus with ethyl alcohol the first product has been shown to be diethyldithiophosphate, $SP(SH)(OEt)_2$, the mercaptan being produced by a secondary reaction.[5] Phosphorus pentasulphide, boiling under atmospheric or other definite pressure, has been recommended for use in constant temperature baths in place of sulphur. The compound P_4S_3, which is one of the most stable sulphides in dry air, but resembles phosphorus in some respects, is used as a substitute for this element in the manufacture of matches.[6]

Phosphorus Oxysulphides.—The compound $P_4O_6S_4$ was prepared by heating together P_4O_6 and sulphur in an atmosphere of nitrogen or carbon dioxide :—

$$P_4O_6 + 4S = P_4O_6S_4$$

It appears as colourless rectangular prisms which melt at about 102° C. and boil at 295° C. The vapour density is 11·8 to 12·5 (air = 1), which corresponds to the formula given. It is very easily soluble in CS_2. In moist air it decomposes as follows :—

$$P_4O_6S_4 + 6H_2O = 4HPO_3 + 4H_2S$$ [7]

Another oxysulphide, also a derivative of P_2O_5, was produced when H_2S dissolved in $POCl_3$ containing carbon disulphide was allowed to react for some weeks at 0° C. Small needle-shaped crystals having the composition $P_2O_2S_3$ then separated. They melted at about 300° C. and sublimed in a vacuum with decomposition. The compound was decomposed by moist air with production of H_2S.

$$2POCl_3 + 3H_2S = P_2O_2S_3 + 6HCl$$ [8]

Thiophosphites, Thiohypophosphates and Thiophosphates.

Since the sulphides, oxysulphides and halosulphides of phosphorus are completely hydrolysed by water with evolution of H_2S, it is evident that the thioxyacids of phosphorus are unstable. Various salts of these acids may however be prepared by using alkalies or ammonia instead of water and by other reactions, of which a general outline only is given here.

Thiophosphites.—These salts may be regarded as derived from mono-, H_3PSO_2, di-, H_3PS_2O, and tri-thiophosphorous acids, H_3PS_3. They were prepared, with other products, by heating metals with a mixture of sulphur and phosphorus, *e.g.* Ag_3PS_3, or metallic sulphides with phosphorus sulphides, *e.g.* Cu_3PS_3 from Cu_2S and P_2S_5.[1] When P_4S_3 was dissolved in alkalies phosphine, hydrogen and phosphorus were produced. By evaporation *in vacuo* crystals of $Na_2H(PSO_2).2H_2O$ were obtained. With an excess of sodium hydroxide, after long standing, the normal salt Na_3PSO_2 was deposited. When the alkali was replaced by Na_2S the evaporation *in vacuo* gave $Na_2H(PS_2O).2\frac{1}{2}H_2O$.[2] An ammonium salt, $(NH_4)_2H(PSO_2).H_2O$, has been prepared similarly from P_4S_3 and solution of ammonia after long standing at 0° C. Solutions of these salts gave a characteristic yellow to red precipitate when mixed with a solution of lead acetate. When the salts were heated or their solutions were boiled, H_2S was evolved and phosphites produced.

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[1] Stock, *loc. cit.*

[2] Berzelius, *loc. cit.*; Stock and Herscovici, *loc. cit.*

[3] Glatzel, *loc. cit.*

[4] Kekulé, *loc. cit.*

[5] Pischtschiminko, *J. Russ. Phys. Chem. Soc.*, 1925, 57, 11.

[6] Sévène and Cohen, *British Patent*, 16314, 1898.

[7] Thorpe and Tutton, *Trans. Chem. Soc.*, 1891, 59, 1019.

[8] Besson, *Compt. rend.*, 1897, 124, 151.

Thiohypophosphates, for example those of copper, silver and nickel, $Cu_2P_2S_6$, $Ag_4P_2S_6$, and $Ni_2P_2S_6$, respectively, have been prepared by heating the metals with phosphorus and sulphur. The ease with which they are decomposed by water depends on the electroaffinity of the metal. Thus the zinc salt is decomposed by boiling water, while the nickel salt, which forms grey hexagonal crystals, is scarcely affected by water.[3]

Thiophosphates.—The general methods of preparation recall those used in the preparation of phosphates, sulphides being used in place of oxides, with protection of the product from oxidation or hydrolysis:—

(*a*) The heating of metallic sulphides with phosphorus pentasulphide gives the most highly thionised thiophosphates. The polysulphides which are formed at the same time may be removed by alcohol. From the solutions dithiophosphates may be isolated.

$$3M_2S + P_2S_5 = 2M_3PS_4$$

(*b*) The heating of metallic chlorides with phosphorus pentasulphides gives thiophosphates together with $PSCl_3$.

(*c*) By the action of alkalies on thiohalides. $PSCl_3$ is the chloride of monothiophosphoric acid, and with alkalies it gives monothiophosphates.

By fusing crystalline sodium sulphide with phosphorus pentasulphide and dissolving the product in a little water, crystals of *trisodium tetrathio-orthophosphate* were obtained.

$$3(Na_2S.9H_2O) + P_2S_5 = 2(Na_3PS_4.8H_2O) + 11H_2O \text{ [4]}$$

The crystals were needle-shaped or tabular, in the monoclinic system. The corresponding *potassium salt*, K_3PS_4, was obtained as a yellow crystalline mass by fusing KCl with P_2S_5.

These thiophosphates are hydrolysed in dilute solution with evolution of H_2S. They can be dissolved unchanged in alkalies. With salts of the heavy metals they give precipitates which are decomposed on warming, giving H_2S. They are easily oxidised by nitric acid, potassium dichromate, etc. with deposition of sulphur. When treated with solutions of sulphides, *e.g.* BaS, the trithiophosphates were produced, as represented by the equation

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[1] Ferrand, *Ann. Chim. Phys.*, 1899, [7], 17, 388.
[2] Lemoine, *Compt. rend.*, 1881, 93, 489.
[3] Ferrand, *loc. cit.*, and *Compt. rend.*, 1896, 122, 621; Friedel, *ibid.*, 1894, 119, 260.
[4] Glatzel, *Zeitsch. anorg. Chem.*, 1893, 4, 186; 1905, 44, 65.

$$2Na_3PS_4 + 3BaS + 2H_2O = Ba_3(PS_3O)_2 + 3Na_2S + 2H_2S$$

Dithiophosphates, $M_3(PS_2O_2)$, were also produced by this reaction.[1]

Other *tetrathiophosphates* which have been prepared by the foregoing methods are Cu_3PS_4 (CuCl and P_2S_5),[2] Ag_3PS_4 (AgCl and P_2S_5),[2] $Hg_3(PS_4)_2$ (HgS and P_2S_5), $Pb_3(PS_4)_2$ ($PbCl_2$ and P_2S_5), $Fe_3(PS_4)_2$ (FeS and P_2S_5), $Ni_3(PS_4)_2$ ($NiCl_2$ and P_2S_5). (For thiophosphates of As, Sb, Bi see this Volume, Part IV.[3])

The preparation of *barium trithiophosphate* has been described above. The *magnesium salt*, $Mg_3(PS_3O)_2.20H_2O$, was prepared by the action of the tetrathiosodium salt on magnesium hydrosulphide.[1] The *ammonium salt*, $(NH_4)_3(PS_3O).H_2O$, was prepared by the action of water on ammonium imidothiophosphate (see "Ammoniates of P_2S_5"). From a solution of this compound by interaction with salts of various metals, *e.g.* $CuSO_4$, their trithiophosphates have been prepared.[4]

Trisodium dithiophosphate, $Na_3(PS_2O_2).11H_2O$, has been prepared from P_2S_5 and a rather concentrated solution of sodium hydroxide. The solution was heated to 50° to 55° C. until the trithio-salt was decomposed. The salt was precipitated by alcohol, and when recrystallised from water appeared as colourless six-sided prisms.[5] The *ammonium salt*, $(NH_4)_3(PS_2O_2).2H_2O$, was prepared similarly from aqueous ammonia and P_2S_5. From these soluble thiophosphates those of the heavy metals may be obtained by double decomposition.[5]

Trisodium monothiophosphate was obtained from the solution of mixed thiophosphates by heating to 90° C. in order to decompose dithiophosphate. On cooling, the crystalline salt $Na_3(PSO_3).12H_2O$ separated in six-sided tables, melting at 60° C.[5] This salt was also prepared from $PSCl_3$ as follows:—

$$PSCl_3 + 6NaOH = Na_3(PSO_3) + 3NaCl + 3H_2O$$ [6]

Ammonium dihydromonothiophosphate was prepared by the hydrolysis of imidotrithiophosphoric acid, thus

$$H_3[P(NH)S_3] + 3H_2O = (NH_4)H_2(PSO_3) + 2H_2S$$ [4]

The salt was repeatedly precipitated by alcohol and dissolved in water. A similar or identical salt having the constitution $SP(OH)_2(ONH_4)$ was prepared by the action of phosphorus pentasulphide on acetoxime in carbon disulphide solution. The part insoluble in CS_2 was extracted with alcohol, boiled and crystallised from cold water in monoclinic prisms.[7]

From the alkali monothiophosphates those of other bases have been obtained by precipitation.

A series of *pyrothiophosphates*, $M_2P_2S_7$ (in which M is a divalent metal), has been prepared by the methods already described.[8] The free acids decompose immediately on liberation, but a mixture of them has been prepared as a yellow oil having the composition $H_4P_2O_2S_5$ by the action of liquid hydrogen chloride on ammonium trithiophosphate at low temperatures.[1]

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[1] Ephraim and Majler, *Ber.*, 1910, 43, 285.

[2] Glatzel, *loc. cit.*

[3] See also Wallsom, *Chem. News*, 1928, 136, 113.

[4] Stock, *Ber.*, 1906, 39, 1967.

[5] Kubierschky, *J. prakt. Chem.*, 1885, [2], 31, 93.

[6] Wurtz, *Compt. rend.*, 1847, 24, 288.

[7] Dodge, *Annalen*, 1891, 264, 185.

[8] Ferrand, *loc. cit.*

Esters of the thiophosphoric acids have been prepared, *e.g.* ethyl tetrathiophosphate, $(C_2H_5)_3PS_4$.[2]

The compounds containing nitrogen as well as sulphur are described in Chapter XIV., pp. 202–204.

Thiophosphates, Detection.—Many of the reactions already described, such as the production of H_2S and phosphoric acid when these salts are treated with acids, will serve to detect the thiophosphates. The alkali and ammonium salts are soluble, the others mostly insoluble. Calcium, barium and strontium monothiophosphates, barium and strontium dithiophosphates and barium trithiophosphate are insoluble, the other alkaline earth salts soluble. Thiophosphate solutions mixed with alkali sulphides give a green colour with ferric chloride. Monothiophosphates give a blue precipitate with cobalt sulphate soluble in excess of the cobalt salt, dithiophosphates a green precipitate soluble in excess of dithiophosphate, and trithiophosphates a brown solution. Several other tests have been described.[3]

PHOSPHORUS AND SELENIUM.

When red phosphorus is melted with selenium in a current of carbon dioxide a reaction is said to occur without notable loss of weight. The products are sensitive to moist air, phosphine and seleniuretted hydrogen being evolved. The action of concentrated alkalies or alkali selenides gives selenophosphates (*q.v.*).[4]

The solution of selenium in yellow phosphorus is also extremely sensitive to moisture, and quantities of phosphine and hydrogen selenide are evolved during the preparation, unless the selenium is dried at a temperature which is high enough to convert the red partly into the black modification. The melting-point of the phosphorus is greatly lowered; the solution containing phosphorus 4·4 parts and selenium 3·0 parts melts at $-7°$ C. On distillation of such solutions, approximating to P_4Se and P_2Se, phosphorus passes over with only traces of selenium. The residue, or other mixtures containing more selenium, when distilled in a current of carbon dioxide at a higher temperature gave a distillate of oily drops which solidified to a red mass which had a composition closely approximating to P_4Se_3. The second residue, a black vitreous mass, distilled at a red heat and had approximately the composition P_2Se_5.[5]

A compound P_4Se_3 has also been prepared by warming 5·6 grams of powdered selenium with 2·8 grams of yellow phosphorus in 30 c.c. of tetralin (tetrahydronaphthalene). After the reaction has begun the mixture is boiled for a long time in an atmosphere of carbon dioxide. The liquid is decanted and immediately deposits an orange substance, sometimes in crystalline form (needles). Further quantities extracted with boiling tetralin and washed with alcohol increase the yield to

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[1] Stock, *loc. cit.*

[2] Michaelis, *Annalen*, 1872, 164, 39.

[3] Kubierschky, *loc. cit.*

[4] Hahn, *Chem. Zentr.*, 1865, p. 376; *J. prakt. Chem.*, 1864, [1], 93, 430; Muthmann and Clever, *Zeitsch. anorg. Chem.*, 1896, 13, 171.

[5] Meyer, *Zeitsch. anorg. Chem.*, 1902, 30, 258.

3·5 grams. The substance may be purified by extraction with a 1 : 1 mixture of carbon disulphide and petroleum ether. A crystalline deposit forms in the extraction flask. The substance melts at 242° C. to a dark red liquid with the formation of a slight sublimate. It is inflammable, and slightly decomposed by boiling water with evolution of the hydrides of selenium and phosphorus. It is oxidised powerfully by cold nitric acid. The resulting solution was used for analysis, which gave results agreeing fairly well with the formula P_4Se_3 and also with the analysis of Meyer,[1] being about 1 per cent. high in phosphorus and 1 per cent. low in selenium.[2]

Selenophosphates.—By treating melts of the composition P_2Se_5 and P_2Se_3 with concentrated KOH greenish to colourless crystals of an octahedral habit are obtained having a composition corresponding to $K_2HPSe_3O + 2\frac{1}{2}H_2O$. When a solution of K_2S is substituted for KOH a thioselenophosphite is crystallised, $2K_2S.P_2Se_3 + 5H_2O$. When NaOH is used instead of KOH long greenish prisms of $Na_3PSe_3O + 10H_2O$ are obtained.

Sulphoselenides.—When the selenides of phosphorus are melted with sulphur, products are obtained which have the composition P_4SSe_2 (m.pt. 225° to 230° C.) and P_4S_2Se (m.pt. 190° to 200° C.).[3] *

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[1] *Loc. cit.*

[2] Mai, *Ber.*, 1926, 59, [B], 1888.

[3] Meyer, *loc. cit.*

* *Note.*—Compounds of phosphorus and tellurium are described in this Series, Vol. VII., Part II.

CHAPTER XIV.

PHOSPHORUS AND NITROGEN.

AMIDO-PHOSPHOROUS and -phosphoric acids are prepared by the action of dry ammonia on the anhydrous oxides or oxyhalides such as phosphoryl chlorides. The imido-derivatives, in which $=NH$ replaces $=O$, can often be obtained from the amido-derivatives by heating. Other methods are the hydrolysis of amido-esters and of phosphorus chloronitrides (*q.v.*).

Amido-derivatives of Phosphorous and Orthophosphoric Acids.

Diamidophosphorous Acid, $(NH_2)_2POH$, was made, together with diammonium phosphite, by the action of ammonia on phosphorous oxide dissolved in ether or benzene :—

$$P_4O_6 + 8NH_3 = 3(NH_2)_2POH + (NH_4O)_2POH$$ [1]

It is a white solid, which can be melted and sublimed with some decomposition, and combines with water, evolving much heat. It was hydrolysed by hydrochloric acid giving phosphorous acid, which was decomposed into phosphine and phosphoric acid.

Phosphorus Triamide, $P(NH_2)_3$, is said to be formed by the action of dry ammonia on phosphorus tribromide at −70° C. It was a yellow solid which decomposed at 0° C. giving a brown substance, diphosphorus triimide, $P_2(NH)_3$, and was further decomposed on further heating into phosphorus, nitrogen and ammonia.[2]

Monamidophosphoric Acid, $NH_2PO(OH)_2$, has been obtained by several reactions, among which are the hydrolysis of diphenyl amidophosphate by means of alkali, thus

$$NH_2PO(OC_6H_5)_2 + 2NaOH = NH_2PO(OH)_2 + 2C_6H_5ONa$$

and the action of nitrous acid on diamidophosphoric acid. The sodium salt (which results in the former method) may be converted into the lead salt, which may then be decomposed by hydrogen sulphide at 0° C. The acid is precipitated from the filtrate by alcohol in the form of tabular or cubic crystals. It is very soluble in water, has a sweetish taste, and is hydrolysed after long standing at room temperature or rapidly in hot solution, into ammonium dihydrogen phosphate, thus

$$NH_2PO(OH)_2 + H_2O = NH_4OPO(OH)_2$$ [3]

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[1] Thorpe and Tutton, *Trans. Chem. Soc.*, 1891, 59, 1027.

[2] Hugot, *Compt. rend.*, 1905, 141, 1235.

[3] Stokes, *Amer. Chem. J.*, 1893, 15, 198; 1894, 16, 123, 140; 1898, 20, 740.

Ammonium and hydroxylamine salts of this acid furnish interesting examples of isomerism. Thus, ammonium hydrogen amidophosphate, $NH_2PO(OH)ONH_4$ (prepared by double decomposition between the silver salt and ammonium sulphide, with subsequent precipitation with alcohol as needle-shaped crystals), is isomeric with hydrazine phosphite, $N_2H_4.H_3PO_3$, while hydroxylamine amidophosphate, $NH_2PO(OH)(ONH_3OH)$, is isomeric with hydrazine phosphate, $N_2H_4.H_3PO_4$.[1]

The mono- and di-sodium salts and the corresponding potassium salts have also been prepared. The salt $NH_2PO(OH)(OK)$ was obtained by hydrolysing diphenylamidophosphate with a boiling solution of KOH, acidifying the cold solution with acetic acid and washing the precipitate with alcohol. It forms rhombohedral crystals which are very soluble in water. The solution is neutral and is gradually hydrolysed on standing. Lithium, silver and lead amidophosphates were precipitated by adding salts of these metals to alkali amidophosphates.

Diamidophosphoric Acid, $(NH_2)_2PO(OH)$, is capable of giving salts of a tribasic acid, such as $(NH_2)_2P(OK)_2(OAg)$. Silver salts have been prepared in which hydrogen of the amido-group is replaced by silver, yielding ultimately the dark brown explosive $(NHAg)_2\ P(OAg)_3$.[2]

The free acid was prepared by hydrolysing the compound $(NH_2)_2PO(OC_6H_5)$ obtained from $Cl_2PO(OC_6H_5)$ and aqueous ammonia, thus

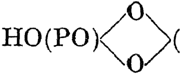
$$Cl_2PO(OC_6H_5) \xrightarrow[2NH_3]{} (NH_2)_2PO(OC_6H_5) \xrightarrow[H_2O]{} (NH_2)_2PO(OH) + C_6H_5OH$$

Triamidophosphoric Acid or *Phosphoryl Triamide*, $PO(NH_2)_3$, was prepared by passing dry ammonia into dry phosphoryl chloride. After washing out the ammonium chloride, an insoluble white powder was left, which was scarcely affected by dilute acids or alkalies, but was decomposed by fusion with potash.[3]

The preparation of this compound has not been confirmed by other investigators.[4]

The products of further heating of the amides are described on p. 202.

Amido- and Imido-derivatives of Metaphosphoric Acid.

In metaphosphoric acid, $O(PO)OH$, or its polymers such as dimetaphosphoric acid,  $HO(PO)\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle(PO)OH$, the hydroxyl may be replaced by $-NH_2$, and the $=O$ by $=NH$, giving amidometaphosphoric acids and imidometaphosphoric or *metaphosphimic acids.*

The action of ammonia on phosphorus pentoxide at low temperatures yielded a substance, or mixture, which was easily soluble in water and in alcohol.

The composition of the product corresponded to the formula $NH(PO)OH$, which may be regarded as derived from $(NH_2)_2PO(OH)$ by loss of ammonia. It may also be represented as phosphoryl hydroxylamine, (PO)NHOH.[1] The soluble salts gave precipitates with salts of the heavy metals.[2]

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[1] Stokes, *loc. cit.*; Sabaneeff, *Zeitsch. anorg. Chem.*, 1898, 17, 486.

[2] Stokes, *loc. cit.*

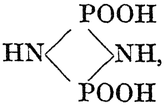
[3] Schiff, *Annalen*, 1857, 101, 299; 103, 168.

[4] Stokes, *loc. cit.*; Gladstone, *J. Chem. Soc.*, 1850, 2, 121; *ibid.*, 1851, 3, 135, 353; Mente, *Annalen*, 1888, 248, 232.

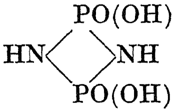
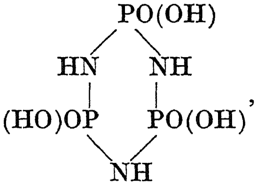
When the products of the action of ammonia on phosphorus pentachloride (*q.v.*) were well washed, the residue was found to have the empirical composition of a phosphoryl imidoamide, $NH(PO)NH_2$, of which it is probably a polymer.[3] On heating this compound, or other amides of phosphoric acid, ammonia is lost and *phosphonitril*, PNO, is left, thus

$$NH(PO)NH_2 = PNO + NH_3 \,^4$$

This is a white powder which fuses at a red heat giving a black glass. It is not affected by aqueous acids and alkalies, nor even by hot nitric acid, but may be hydrolysed by fusion with caustic alkalies. On account of these properties it is represented as a polymer $(PNO)_n$ of high molecular weight and probably cyclic structure (see below).[5]

Dimetaphosphimic Acid, $[HO(NH)\equiv P=O]_2$ or  was considered to be identical with the diamide of pyrophosphoric acid, $O=[(PO)OH.NH_2]_2$, and both formulæ have been assigned to the product of the action of ammonium carbamate on $POCl_3$.[6]

Trimetaphosphimic Acid, $[NH(POOH)]_3$, was obtained by the action of water on a sodium acetate ethereal solution of $P_3N_3Cl_6$ (*q.v.*, p. 205). The acid was soluble in water, and was obtained as a colloidal substance on evaporation. It gave a series of salts. The trisodium salt, $Na_3H_3P_3N_3O_6.4H_2O$, crystallised in rhombic prisms below 80° C., whilst above 80° C. a monohydrate was formed. The trisilver salt was precipitated in plates when silver nitrate was added to a nitric acid solution of the sodium salt. A hexasilver salt, $Ag_6P_3N_3O_6$, was thrown down as a white precipitate when an excess of ammoniacal silver nitrate was added to a solution of the trisodium trimetaphosphimate. On heating or long standing in solution, especially in the presence of strong acids, the metaphosphimates are hydrolysed into ammonium salts and phosphoric acid. Several cyclic structures are possible for the acids; the metaphosphimic ring contains the radicals —NH—PO(OH)—, the nitrilophosphoric ring the radicals —N=P—$(OH)_2$—. On the former hypothesis, di- and tri-metaphosphimic acids are:—

 and , respectively.

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[1] Gladstone and Holmes, *Trans. Chem. Soc.*, 1864, 17, 225; 1866, 19, 1; 1868, 21, 64; Mente, *Annalen*, 1888, 248, 232.

[2] Schiff, *loc. cit.*

[3] Gerhardt, *Ann. Chim. Phys.*, 1846, [3], 18, 188, 204; 1847, [3], 20, 255.

[4] Gerhardt, *loc. cit.*; Gladstone, *Trans. Chem. Soc.*, 1850, 3, 121; Schiff, *loc. cit.*

[5] Gladstone, *Trans. Chem. Soc.*, 1850, 3, 121; 1869, 22, 15; Gladstone and Holmes, *loc. cit.*; Stokes, *loc. cit.*; Salzmann, *Ber.*, 1874, 7, 294.

[6] Mente, *loc. cit.*; Gladstone, *loc. cit.*

Tetrametaphosphimic Acid, which was prepared by the hydrolysis of $P_4N_4Cl_8$, may be regarded as constituted in a similar manner, forming an eight-membered ring. It crystallised in needles containing two molecules of water, $P_4N_4H_8O_8.2H_2O$, and was only slightly soluble in water, still less so in acids. The solubility in 10 per cent. acetic acid was about 0·5 gram in 100 grams solvent.

This acid is more stable towards hydrolysing agents than the other metaphosphimic acids, and even resists the action of hot nitric acid and aqua regia. There are two series of salts derived from a di- and a tetra-basic acid respectively. Thus the dipotassium salt, $K_2H_6P_4N_4O_8$, which forms prismatic crystals, on treatment with excess of potassium hydroxide gives the tetrapotassium salt, $K_4H_4P_4N_4O_8$, which forms sparingly soluble tabular crystals. Ammonium and sodium salts have also been prepared. The tetra-argentic salt, $Ag_4H_4P_4N_4O_8$, was formed as a white precipitate on mixing silver nitrate with the acid, and the octo-salt, $Ag_8P_4N_4O_8$, as a yellow precipitate from ammoniacal silver nitrate and ammonium tetraphosphimate.

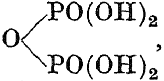
Pentametaphosphimic Acid and **Hexametaphosphimic Acid** were similarly obtained by hydrolysis in ethereal solution of the corresponding nitrilo-chlorides. Like the lower polymers they gave crystalline sodium salts containing water of crystallisation, and anhydrous penta- and hexa-silver salts by the use of ammoniacal silver nitrate. The free acids can be regenerated by the action of H_2S on the silver salts. The acids are more stable towards hydrolysing agents than is trimetaphosphimic acid.

These acids may be regarded as the lactams of amidopolyimidophosphoric acids, and the first stage in the hydrolysis probably consists in the formation of these open-chain acids, thus

$$[HN(PO)OH]_n + H_2O = H_2N\{HN(PO)OH\}_{n-1}(PO)(OH)_2$$

The hydrolysis of heptaphosphorus chloronitride appears to yield at once the hydrated open-chain compound of the type shown on the right-hand side of the above equation, in which n is 7. Heptasodium and heptasilver salts of this acid have been prepared.[1]

Amides and Imides of Condensed Phosphoric Acids.

These may be regarded as derivatives of diphosphoric acid (pyrophosphoric), tri- and tetra-phosphoric acids, etc., *i.e.*  $O\!<\!\begin{matrix}PO(OH)_2\\PO(OH)_2\end{matrix}$, etc., by the substitution of $=NH$ for $=O$ or of $-NH_2$ for hydroxyl in these open-chain compounds. The possibilities of isomerism are evidently very numerous, since either the amido- or the imido- replacement gives the same empirical formula. The general method of preparation consists (*a*) in the hydrolysis of the metaphosphimic acids already described, or (*b*) in heating, or fractionally precipitating with alcohol, the products of the reactions between $POCl_3$ and NH_3.

Monamidodiphosphoric Acid, $(NH_2)P_2O_3(OH)_3$, was made by several reactions, amongst which were the hydrolysis of a solution of diamidodiphosphoric acid (*q.v.*), or as barium salt by saturating a solution of pyrophosphoric acid with ammonia and adding $Ba(OH)_2$. The trisilver salt was obtained as a white precipitate.

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[1] Stokes, *Amer. Chem. J.*, 1893, 15, 198; 1894, 16, 123, 140; 1895, 17, 275; 1896, 18, 629; 1898, 20, 740; idem, *Zeitsch. anorg. Chem.*, 1899, 19, 42.

Diamidodiphosphoric Acid was prepared by the action of phosphoryl chloride at low temperatures on ammonia in the presence of some water, thus

$$2NH_3 + 2POCl_3 + 3H_2O = 6HCl + (NH_2)_2P_2O_3(OH)_2$$

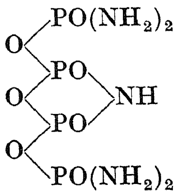
It may also be obtained by several other reactions. The diammonium salt has been prepared in the crystalline state and various other salts as precipitates.[1]

Triamidodiphosphoric Acid, $(NH_2)_3P_2O_3(OH)$, was prepared by similar reactions. It formed a series of salts in which it was monobasic. But in addition to the white monosilver salt, $(NH_2)_3P_2O_3(OAg)$, an orange-coloured trisilver salt was prepared from ammoniacal silver nitrate, to which the constitution $NH_2(NHAg)_2P_2O_3(OAg)$ was assigned.[1]

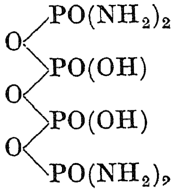
Amido- and imido- derivatives of condensed phosphoric acid of still higher molecular weight have been prepared in great variety by Gladstone, and by Stokes. For example, **monoimidotetramidotetraphosphoric acid**, $NH = P_4O_7(NH_2)_4$, has been obtained by heating the product of general reaction (*b*) (p. 200) to about 200° C.,[2] while **tetramidotetraphosphoric acid**, $(HO)_2P_4O_7(NH_2)_4$, was obtained by hydrolysing ammonium diamidotetraphosphate either with acids or with alkalies, thus

$$(NH_2)_2P_4O_7(OH)(ONH_4)_3 + HCl = (NH_2)_4P_4O_7(OH)_2 + NH_4Cl + 2H_2O\ ^2$$

The structures assigned were



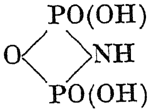
and



Many other derivatives have been obtained.[3] Their general properties have already been indicated.

The **imidodiphosphoric acids** are isomeric with amidodiphosphoric acids. **Monimidodiphosphoric acid,**

$HN = \{PO(OH)_2\}_2$, or



was prepared by heating trimetaphosphimic acid,[3] dissolving in aqueous ammonia, and adding a salt of magnesium, which precipitated magnesium ortho- and pyro-phosphates, leaving a soluble magnesium salt which on treatment with ammoniacal silver nitrate gave a crystalline precipitate of $NH = P_2O_2(OAg)_3OH$. This, when treated with sodium chloride, gave a soluble non-crystallisable trisodium salt. A tetrasilver salt has also been prepared in two modifications—as a voluminous white precipitate which on boiling passes into a yellow form. These may have the imido- and the amido-structures (see p. 200) respectively.[1]

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[1] Gladstone and Holmes, *loc. cit.*

[2] Gladstone, *loc. cit.*

[3] Stokes, *loc. cit.*

A **dibasic imidodiphosphoric acid,** which can be regarded as derived from the last-mentioned compound by the loss of the elements of water, was prepared by warming to about 50° C. a solution of 4 grams ammonium carbamate in 10 grams of phosphoryl chloride.[2] Thus

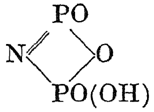
$$3NH_2COONH_4 + 4POCl_3 = 2NH(POCl_2)_2 + 3CO_2 + 4NH_4Cl$$
$$NH(POCl_2)_2 + 3H_2O = NH(POOH)_2O + 4HCl$$

The barium or ferric salt may be precipitated, and from the former the free acid may be regenerated. Other derivatives were prepared by similar reactions.[2]

Nitrilophosphoric Acids.

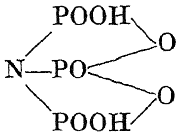
These compounds, in which trivalent nitrogen bridges phosphoryl radicals, are obtained by heating amido-compounds, with loss of ammonia. The polymerised $[NPO]_n$, phosphonitril, has been referred to already (p. 199).

The potassium salt of **nitrilodiphosphoric acid,**



was obtained by heating potassium triamidodiphosphate, the ammonium salt by heating triamidodiphosphoric acid, and the silver salt by interaction between silver nitrate and a suspension of the sparingly soluble potassium salt in water.[3]

Nitrilotrimetaphosphoric acid is said to be formed by heating crude imidodiphosphoric acid to 290°–300° C., washing out ammonium chloride, dissolving the residue in ammonia, acidifying and filtering off the white precipitate. The solution contained this acid,



which yielded a crystalline sodium salt.[2]

Amido-, Imido- and Nitrilo-thiophosphoric Acids.

These compounds are made by the application of a few general methods :—

(1) By the action of ammonia on thiophosphoryl halides.
(2) By the action of ammonia on sulphides of phosphorus.
(3) By heating ammonium chloride with sulphides of phosphorus.

Monothioamidophosphoric Acids.—These are derivatives of $SP(OH)_3$ in which the hydroxyl groups are successively replaced by $-NH_2$.

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[1] Stokes, *loc. cit.*
[2] Mente, *loc. cit.*
[3] Gladstone and Holmes, *loc. cit.*

The **monamide**, $SP(NH_2)(OH)_2$, was prepared from aqueous ammonia and $PSCl_3$. The solution, which contained NH_4Cl, gave precipitates with salts of cadmium and lead. The salts of the alkaline earth metals were soluble.[1]

The **diamide**, $SP(NH_2)_2OH$, was obtained by the action of gaseous ammonia on $PSCl_3$.[1] It was also prepared by the action of ammonia on PSF_3.[2] In both cases the product was digested with water. Hydrolysis proceeded according to the equation

$$SP(NH_2)_2F + H_2O = SP(NH_2)_2OH + HF$$

The solution contained a new acid radical, which gave precipitates with salts of mercury, copper, silver and lead. The product derived from $PSCl_3$, but not that derived from PSF_3, gave precipitates also with salts of zinc and cadmium. No precipitates were obtained with salts of barium and calcium.

The **triamide**, $SP(NH_2)_3$, was prepared by saturating $PSCl_3$ with ammonia. It was a white solid of density 1·7. When heated it dissociated into ammonium sulphide and sulphur, leaving phosphorus in the residue, probably as " phospham," and was decomposed by warm water giving H_2S and ammonium thiophosphate.[3] It was only slightly soluble in alcohol or carbon disulphide.

Thiophosphoryl Nitride or **Nitrilomonothiophosphoric Acid**, SPN, was obtained by gradually heating together, from 180° to 328° C., P_2S_5 and NH_4Cl in the quantities required by the equation

$$P_2S_5 + 2NH_4Cl = 2SPN + 2HCl + 3H_2S$$

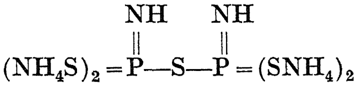
It resulted also on heating amido- and imido-thiophosphates in a vacuum. It was a white powder, fairly stable to aqueous reagents, but hydrolysed by water at 140° C., thus

$$SPN + 4H_2O = H_3PO_4 + H_2S + NH_3$$

On strong heating it gave P_3N_5 (*q.v.*).[4]

Di- and Tri-imido- and -amido-thiophosphates.—A great variety of these compounds, chiefly in the form of their ammonium salts, was obtained by the action of ammonia, usually in the liquid form, on phosphorus pentasulphide.[5] Some of the ammonia could be driven off by heating under reduced pressure, leaving the acid salts.

Gaseous ammonia at ordinary temperatures reacted with phosphorus pentasulphide giving a hexammoniate, $P_2S_5.6NH_3$, and perhaps a heptammoniate, $P_2S_5.7NH_3$. The former may rearrange itself so as to give tetrammonium diimidopentathiodiphosphate :—



$$(NH_4S)_2{=}\overset{\overset{NH}{\|}}{P}{-}S{-}\overset{\overset{NH}{\|}}{P}{=}(SNH_4)_2$$

The addition of another molecule of ammonia, either by means of liquid ammonia or by saturating with the gas, yields a substance having the empirical composition of the heptammoniate, which, however, may consist of equal mols of (*a*) **diammonium nitrilodithiophosphate**, $N \equiv P(SNH_4)_2$, and (*b*) **triammonium imidotrithiophosphate**, $HN = P(SNH_4)_3$. On treatment with liquid ammonia the nitrilo-compound dissolved and could be obtained by evaporating the solvent, while the imido-compound, being sparingly soluble, crystallised. The nitrilo-compound lost one or more molecules of ammonia when heated in a vacuum. When treated with KOH or NaOH it gave hydrated dipotassium or disodium compounds as oils, the latter of which could be made to crystallise. Characteristic insoluble salts were those of lead (yellow) and of barium (white). The imido-compound, $HN = P(SNH_4)_3$, was a white crystalline substance which deliquesced in moist air and gradually lost ammonia. It was insoluble in all ordinary solvents. It was hydrolysed slowly by water and smelt of H_2S. It lost one molecule of NH_3 when warmed to 50° C. in a vacuum. By heating at gradually increasing temperatures from 90° to 180° C. in an atmosphere of H_2S it was transformed into the free acid.

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[1] Gladstone and Holmes, *loc. cit.*

[2] Thorpe and Rodger, *Trans. Chem. Soc.*, 1889, 55, 320.

[3] Schiff, *Annalen*, 1857, 101, 303; Chevrier, *Compt. rend.*, 1868, 66, 748.

[4] Stock and Hofmann, *Ber.*, 1903, 36, 314, 898; Stock, Hofmann, Müller, v. Schönthan and Küchler, *Ber.*, 1906, 39, 1967. See also Glatzel, *loc. cit.*

[5] Stock and co-workers, *loc. cit.*

Imidotrithiophosphoric Acid, $HN = P(SH)_3$, prepared as above, was a yellow liquid having a density of 1·78, and like its ammonium salt, was insoluble in all the solvents which were tried. It was dissociated only at a high temperature, but was partly hydrolysed by water, thus

$$HN = P(SH)_3 + 3H_2O = OP(OH)_2(SNH_4) + 2H_2S$$

With liquid hydrogen chloride this acid formed the addition product $HN = P(SH)_3.HCl$.

Phosphorus Halonitrides or Amidohalides.

The action of ammonia on phosphorus halides gives either ammoniates or, by elimination of all hydrogen as ammonium chloride, halonitrides. The amides, which should be formed as intermediate products, seem to be difficult to isolate from the true halides, although the oxyhalides (p. 109) and thiohalides (p. 113) readily yield such compounds. Exceptionally, **phosphorus diamidotrifluoride**, $PF_3(NH_2)_2$, was prepared as a white mass by the following reaction :—

$$PF_3Cl_2 + 4NH_3 = PF_3(NH_2)_2 + 2NH_4Cl \text{ [1]}$$

Chloronitrides.—It was shown by Liebig in 1832 that when PCl_5 was treated with dry ammonia and the product heated, a white stable sublimate was obtained. The empirical formula $PNCl_2$ was assigned to this substance by Laurent, while Gladstone and Holmes on account of its high vapour density represented it as $(PNCl_2)_3$.[2]

Preparation.—Equal mols of PCl_5 and NH_4Cl may be heated to 150° C. in a sealed tube which is opened occasionally to permit the escape of hydrogen chloride formed according to the equation

$$nPCl_5 + nNH_4Cl = nPNCl_2 + 4nHCl$$

The product was extracted with petroleum ether and the insoluble part distilled up to nearly a red heat. The distillate, after washing with hot water, was redistilled under reduced pressure, and yielded the fractions described below.[1] Alternatively, 120 to 130 grams of ammonium chloride may be added to 400 grams of phosphorus pentachloride dissolved in a litre of *sym*-tetrachloroethane, and the mixture boiled under a reflux condenser guarded by a calcium chloride drying tube until hydrogen chloride is no longer evolved. This requires about 20 hours. The ammonium chloride is filtered off and the solvent distilled away in a water-pump vacuum. The residue, about 220 grams of a pasty material, is freed from oil by suction and by washing with benzene at 0° C. This leaves about 100 grams of a crystalline powder which is recrystallised from benzene and fractionated at a low pressure. The fractions may be recrystallised from benzene.

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[1] Poulenc, *Compt. rend.*, 1891, 113, 75.

[2] Liebig, *Annalen*, 1834, 11, 139; Laurent, *Compt. rend.*, 1850, 31, 356; Gladstone and Holmes, *Trans. Chem. Soc.*, 1864, 17, 225.

When the powder is heated above 255° C. it changes to a colourless transparent solid, while at 350° C. there is produced a colourless elastic mass which resembles rubber in appearance and in its property of swelling when placed in benzene.[2]

MELTING- AND BOILING-POINTS OF THE PHOSPHORUS CHLORONITRIDES OR PHOSPHONITRILIC CHLORIDES.

Formula.	$(PNCl_2)_3$	$(PNCl_2)_4$	$(PNCl_2)_5$	$(PNCl_2)_6$
Melting-point, ° C. . .	114	123·5	41	91
Boiling-point (13 mm.), ° C. .	127	188	224	262
Boiling-point (760 mm.), ° C. .	256·5	328·5	Polymerises	Polymerises

Triphosphonitrilic Chloride, $P_3N_3Cl_6$, forms large rhombic crystals of density 1·98. Its properties are typical of those found in the series. It is easily soluble in the usual organic solvents, also in glacial acetic acid and sulphuric acid, undergoing reaction with the latter. It also reacts with many organic compounds containing hydroxyl groups—alcohols, phenols, etc. Aniline when added to the benzene solution gave a *dianilide*, $N \equiv P(NH.C_6H_5)_2$. Ammonia when passed into a solution of $P_3N_3Cl_6$ in carbon tetrachloride gave needles of a chloroamide, possibly $P_3N_3Cl_4(NH_2)_2$, which was insoluble in organic solvents. Liquid ammonia gave a white solid hexamide, $P_3N_3(NH_2)_6$.[3] Hydrolysis proceeds when an ether solution is shaken with water, with production first of $P_3N_3Cl_4(OH)_2$, then of trimetaphosphimic acid, $[NH(POOH)]_3$ and HCl, and finally ammonium phosphate.

Tetraphosphonitrilic Chloride, $P_4N_4Cl_8$, forms colourless prisms, density 2·18. The molar weight was determined by vapour density and depression of the freezing-point of benzene. Solubility relations are similar to those of the tripolymer. An *octoanilide*, $\{NP(NHC_6H_5)_2\}_4$, has been prepared.[4] Like the trinitrilic chloride it was scarcely affected by water alone, but an ether solution gave first an hydroxychloride and then tetrametaphosphimic acid, $[NH(POOH)]_4.2H_2O$.

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[1] Stokes, *Amer. Chem. J.*, 1895, 17, 275; 1897, 19, 782.
[2] Schenck and Römer, *Ber.*, 1924, 57, B, 1343.
[3] Besson and Rosset, *Compt. rend.*, 1906, 143, 37.
[4] Schenck, *Ber.*, 1927, 60, B, 160.

Pentaphosphonitrilic Chloride, $P_5N_5Cl_{10}$, was also crystalline. The formula was established by analysis, and by molar weight in boiling benzene. The chloride was hydrolysed in ether solution giving pentametaphosphimic acid.

Hexaphosphonitrilic Chloride, $P_6N_6Cl_{12}$, forms long prismatic crystals. The formula was established by the methods used in the case of $P_5N_5Cl_{10}$. Hydrolysis takes place rather more readily, since hydrochloric acid is evolved when the chloride is kept in moist air. Hydrolysis in ether solution gave hexametaphosphimic acid.

Heptaphosphonitrilic Chloride, $P_7N_7Cl_{14}$, was a liquid which, after solidifying, melted at $-18°$ C.; otherwise its properties were similar to those of the other chloronitrides.

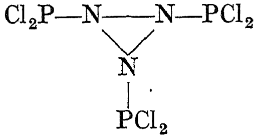
When strongly heated these compounds leave an inert residue of NPO (*q.v.*, p. 199).

Bromonitrides or **Nitrilic Bromides.**—These compounds have formulæ similar to those of the chloronitrides, *i.e.* $(PNBr_2)_n$, and were prepared by analogous reactions, *i.e.* by the action of ammonia on phosphorus pentabromide.

Triphosphonitrilic Bromide, $(PNBr_2)_3$, formed rhombohedral crystals which melted at 188° to 190° C., were insoluble in water but soluble in organic solvents.[1]

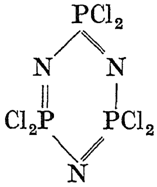
Structure of Halonitrides.—On account of their stability towards heat and hydrolysing agents, as well as the requirements of valency, cyclic formulæ have been assigned to the halonitrides in which the rings are composed either of $>N—PCl_2$ or of $\geqslant N$ and $\geqslant PCl_2$ alternately.[2] Thus the tri-compounds may be represented by

(*a*)



or

(*b*)



It has been supposed that the angle of least strain of the rings or polyhedra is 135°, which is most closely realised in the tetra-compound, which is also the most stable of the series. The structure assigned will determine that of the corresponding metaphosphimic acid which is produced by hydrolysis. Dimetaphosphimic acid, if its existence is admitted, could not be cyclic according to formula (*a*). Formula (*b*) is adopted in describing these compounds.

Phosphorus Nitride or **Triphosphorus Pentanitride,** P_3N_5.—A compound which appears to have this composition has been obtained by several methods :—

(*a*) By passing the vapour of phosphorus pentachloride in a current of nitrogen over heated magnesium nitride.[3]

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[1] Besson, *Compt. rend.*, 1892, 114, 1264, 1480.

[2] Wichelhaus, *Ber.*, 1870, 3, 163; Stokes, *loc. cit.*

[3] Brieglieb and Geuther, *Annalen*, 1862, 123, 236.

(*b*) The black substance produced by the reaction between liquid ammonia and phosphorus in a sealed tube gave an analysis which agreed fairly well with the foregoing composition.[1]

(*c*) By saturating the pentasulphide, P_2S_5, with pure dry ammonia at ordinary temperatures, and heating the product in a current of ammonia at 850° C.[2]

The product is described as a powder, white to dark red in colour according to the time of heating at 250° C. The density was 2·5. The nitride was tasteless, odourless, and chemically inactive at ordinary temperatures. The heat of formation (from white phosphorus) is given as +81·5 Cals. per mol.[3] The molar heat of combustion was 474·7 Cals. (at constant pressure). The nitride dissociated into its elements in a vacuum at about 760° C.[4] It was reduced to phosphorus and ammonia by hydrogen at a red heat, and burned when heated in oxygen or chlorine. It was hydrolysed by boiling water, thus

$$P_3N_5 + 12H_2O = 3H_3PO_4 + 5NH_3$$

It acted as a reducing agent on metallic oxides and was decomposed by many metals from 80° C. upwards, giving phosphides of the metals.

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[1] Stock and Johansen, *Ber.*, 1908, 41, 1593.

[2] Stock and Hofmann, *Ber.*, 1903, 36, 314; Stock and Grüneberg, *ibid.*, 1907, 40, 2573.

[3] Stock and Wrede, *Ber.*, 1907, 40, 2925.

[4] Stock and Gruneberg, *loc. cit.*

CHAPTER XV.

PHOSPHATIC FERTILISERS.

Occurrence and Circulation of Phosphorus.

Mineral Phosphates.—Practically all the phosphorus in the ten-mile crust of the earth is present in the lithosphere, of which it forms 0·157 per cent.,[1] and is combined as phosphates of many bases. Compared with other acidic and basic oxides phosphoric anhydride is eleventh in order of abundance, falling immediately below titania (1·050 per cent.) and above carbonic anhydride (0·101 per cent.). On the average igneous rocks contain 0·299 per cent. of phosphoric anhydride, which is greater than the percentage in sedimentary rocks generally, and about three times the proportion found in average limestones. The mineral *apatite*, which is widely diffused in the deep-seated igneous rocks, is only slowly attacked by atmospheric weathering, but in the course of ages it and other phosphatic igneous rocks gradually dissolve as phosphates of calcium, iron and aluminium,[2,3] and become changed into the carbonated or hydrated secondary phosphate rocks.

Phosphates occur in rocks of all the geological epochs. Apatite is associated with granites and gneisses.

Palæozoic phosphorites (coprolites) have been found in England and Germany. In the Mesozoic epoch phosphorites occur in the Triassic, Jurassic and Cretaceous formations. The tertiary phosphate deposits in the United States of America and N. Africa are the most extensive and valuable in the world. Quaternary deposits include fossil bones, the guanos and phosphoguanos. The high-grade secondary deposits which are used as sources of fertilisers and of phosphorus generally have no doubt been segregated by processes in which animal life has played a large part. Thus the skeletons of marine animals and organisms collecting on the floor of the ocean are dissolved in areas containing a high concentration of carbon dioxide; their component phosphates are reprecipitated on shells, or by ammonia derived from the decay of nitrogenous matter, and form concretions of tribasic calcium phosphate.[4, 5, 6] The small quantities of phosphates which are widely present in limestones [7] and dolomites may under certain conditions be concentrated by the leaching out of the calcium carbonate in the form of bicarbonate. All sedimentary deposits which consist of the remains of animals or plants must contain phosphate. The breaking down of these deposits disseminates the phosphatic material in the soil. These deposits are largely derived also from the gradual solution and subsequent deposition of widely diffused particles of apatite which are a constant constituent of igneous rocks. Granite contains 0·6 per cent., basalt 1 per cent. and gneiss 0·25 per cent. of phosphoric oxide on the average. Fertile soils contain 0·2 to 0·5 per cent. of phosphoric oxide, poor soils about 0·1 per cent. Some phosphate must be present in a soil which supports any flora. The plants use these supplies mainly in their seeds, which are eaten by animals, and the phosphorus subsequently segregated mainly in the nerves, brain and bone. It is then partly returned to the soil as animal remains. Phosphorus is not of course lost in the same way as combined nitrogen, by decomposition, since phosphorus compounds which are likely to be formed in nature are non-volatile. But considerable quantities of dissolved phosphates find their way to the sea, and this occurs especially under a system of water-borne sewage. The loss thus incurred is an additional argument in favour of the treatment of sewage with recovery of all fertiliser values.

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[1] Clarke and Washington, *Proc. Nat. Acad. Sci., U.S.A.*, 1922, 8, 108. See also Clarke, "*Data of Geochemistry*," Washington, 1920.

[2] Lindgren, *Econ. Geol.*, 1923, 18, 419.

[3] Blackwelder, *Amer. J. Sci.*, 1916, [4], 42, 285.

[4] Clarke, *loc. cit.*

[5] Murray and Renard, "*Deep-Sea Deposits*" (London, 1891), p. 397.

[6] Steel, *J. Ind. Eng. Chem.*, 1921, 40, 59T.

[7] Davidson, *Trans. Amer. Inst. Min. Eng.*, 1893, 21, 139.

Ordinary sea-water may contain from 0·06 to 0·07 milligram of P_2O_5 per litre,[1] the amount varying with the season. This supply is drawn upon by diatoms and algæ, and returned when they decay. The supply is also continually supplemented from rivers, etc.[2, 3] The algæ are devoured by molluscs and crustaceans, which in their turn supply food to animals higher in the scale,[4] until finally, as the bodies of fishes, the phosphorus is assimilated by sea-birds, who return some of it to the land in their excrement. This ultimately becomes guano, and the phosphate may then be converted into phosphatic limestone. The remainder of the phosphate from these and other sources accumulates on the bottom of the sea as a mud which contains $3Ca_3(PO_4)_2.CaF_2$, as well as $Ca_4P_2O_9.4H_2O$ and $Ca_3P_2O_8.H_2O$, derived from minerals and animal remains.[5]

Assimilation by Plants.—It is probable that plants obtain all their phosphorus from phosphates. Organic compounds containing phosphorus, like the phosphoproteins, are rapidly decomposed by soil bacteria, and the phosphoric acid combines with the bases in the soil. The assimilation of phosphorus from phosphates which are insoluble in water is probably aided by acid secretions from the root-hairs, and also perhaps by the carbon dioxide exhaled during the respiratory process. Soluble phosphates are quickly assimilated. The absorption of $H_2PO_4^-$ ion by a growing plant may be demonstrated by a fall of acidity. If the plant absorbs the base as well (*i.e.* lime), the acidity or hydrogen-ion concentration of the soil is maintained, and phosphate thus remains in solution. This is, of course, only one of the numerous reactions by which the acidity is regulated. A difference in the lime requirements may thus account for the difference in the availability of phosphatic fertilisers for different plants.[6] This theory will also account for the greater availability of insoluble basic phosphates when applied to soils which lack lime, and thus confer on the phosphate a potential acidity which is due to the demands of vegetation for this base. The demands are greatest in the case of leguminosæ (beans, etc.), brassicæ (cabbages, etc.) and roots, and especially potatoes and beetroot.

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[1] Matthews, *J. Marine Biol. Assoc.*, 1917, 11, 122, 251.

[2] Gill, *ibid.*, 1927, 14, 1057. [3] Atkins, *ibid.*, 1926, 14, 447. [4] Lindgren, *loc. cit.*

[5] Basset, *Zeitsch. anorg. Chem.*, 1908, 59, 51.

[6] *Annual Reports of the Chemical Society*, 1926, 23, 217, and 1927, 24, 237.

The general effect of phosphates is to favour the formation and ripening of seeds, and in this respect it acts in the opposite direction to combined nitrogen, which favours the growth of stalks or straw at the expense of seed or fruit.

The concentration of phosphorus in vegetable matter is not high, being rather less than 0·1 per cent. in dry fodder, but much higher—about ½ per cent.—in grains. The phosphates assimilated by plants supply the loss of phosphorus eliminated in animal metabolism, and which, in the case of human adults, amounts to 3 or 4 grams of phosphoric anhydride a day. The reserve of calcium phosphate present in the bones weighs about 2 kilograms.[1]

From the earliest ages the natural circulation of phosphorus has been altered and controlled by farmers. The systematic return of all kinds of excreta to the soil is still the basis of the intensive cultivation practised in densely populated areas of India and China, where the soil bacteria are so active at the favourable temperature prevailing that the nitrogen and phosphorus become available almost at once for another crop. The return of bones to the soil is a less obvious form of economy, partly because when in the massive form these disintegrate very slowly.

After the demonstration of the chemical basis of agriculture by Liebig in 1840, and others, bones were recognised as essential on account of their high phosphorus content. Great quantities of bones were imported into England for this purpose in the first quarter of the nineteenth century. Later, they were largely superseded by the highly concentrated Peruvian guano or by superphosphate, which are more readily available to the plants. Bones, however, when finely ground, and after the extraction of fat and of gelatin by steaming, still retain their place as a slow fertiliser in schemes of manuring. A typical analysis of raw bones shows—

Moisture	12 per cent.
Organic matter	28 ,,
Fat	10 ,,
Calcium and magnesium phosphates . .	44 ,,
Calcium carbonate, sand, etc. . . .	5 ,,

If a good deal of the organic protein (ossein) has been left in the bone, as is the case when the fat has been extracted by solvents, and not by steaming, the resulting bone-meal quickly decomposes in the soil, the phosphoric acid being made partly soluble by the decomposition products of the proteins. Such a bone-meal will contain (approximately) 45 per cent. of calcium phosphate, 1·5 per cent. of magnesium phosphate and over 30 per cent. of organic matter.

The question of availability is largely one of solubility. It was suggested by Liebig that bone-dust should be rendered soluble by treatment with sulphuric acid. But the action of the acid on the protein matter makes the product viscous and difficult to dry. Bone superphosphate is more easily made from a degelatinised bone-dust or from bone-ash. This latter product was formerly imported in large quantities from South America, and contained from 65 to over 80 per cent. of calcium phosphate. The ash may be completely dissolved in an excess of hydrochloric acid, and the calcium monohydrogen phosphate then precipitated by careful addition of lime. This process is also used to recover phosphate of lime from the acid liquid which is obtained as a by-product in the manufacture of glue from bones. The phosphate of lime so prepared is fairly free from impurities, and may of course be made soluble again by the addition of more acid :—

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[1] See further, p. 4.

$$Ca_3(PO_4)_2 + 4HCl = CaH_4(PO_4)_2 + 2CaCl_2$$
$$CaH_4(PO_4)_2 + Ca(OH)_2 = 2CaHPO_4 + 2H_2O$$

The chemical exploitation of bones thus led by a gradual transition to the artificial fertiliser or mineral phosphate industry which will now be described.

Sources of Phosphates.—The most available and most exploited sources of phosphorus and its compounds at the present day are the phosphatic rocks, or phosphorites, which consist of tribasic calcium phosphate associated with calcium carbonate, alumina, magnesia, etc.[1] Phosphates of alumina are also useful. The production of these secondary rocks from the older rocks has already been mentioned (p. 208). Although the apatites themselves, as pure minerals, contain a high proportion of phosphoric anhydride, they are difficult to decompose, and are admixed with other minerals of a still more refractory nature.

There are many other possible sources of phosphates in which the acid is combined with the common bases. Thus there are nearly 150 minerals which contain 1 per cent. or more of phosphoric oxide.[2] In the following table is given a small selection of those which are of special interest :—

MINERALS CONTAINING PHOSPHORUS.

Table I.

Name, Occurrence, etc.	Chemical Composition.	Crystal System.	Density.
Apatite . . . . Igneous rocks and metamorphic limestones.	$3Ca_3(PO_4)_2.Ca(Cl \text{ or } F)_2$	Hexagonal	3·16–3·23
Pyromorphite . . Upper levels of lead mines.	$3Pb_3(PO_4)_2.PbCl_2$	Hexagonal	6·5–7·1
Wavellite . . . Fissures in slate.	$2Al_3(OH)_3(PO_4)_2.9H_2O$	Rhombic	2·33–2·49
Vivianite . . . . Some iron (copper and tin) ores and as earthy mineral.	$Fe_3(PO_4)_2.8H_2O$	Monoclinic	2·6–2·7
Struvite . . . Guanos.	$MgNH_4PO_4.6H_2O$	Orthorhombic	1·68
Turquoise . . . Trachyte or breccia.	$Al_2(OH)_3.PO_4.H_2O$ or $2Al(OH)_3.4AlPO_4.9H_2O$	Amorphous with crystal granules	2·72

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[1] See analyses, p. 213.

[2] Phillips, *Trans. Amer. Inst. Min. Eng.*, 1893, **21**, 188.

The next table illustrates the great variation of basicity and hydration shown by phosphoric acid in nature, and also of the bases with which it may combine. Minor constituents are omitted for the sake of brevity. When the crystalline system is not stated the mineral is amorphous or massive.

MINERALS CONTAINING PHOSPHORUS.

TABLE II.

Stercorite	$NaNH_4HPO_4.4H_2O$	Monoclinic
Bobierrite	$Mg_3(PO_4)_2.8H_2O$	,,
Launayite	$Mg_3(NH_4)_2H_4(PO_4)_4.8H_2O$	Triclinic
Monetite	$CaHPO_4$	Monoclinic
Brushite	$CaHPO_4.2H_2O$	,,
Collophane	$Ca_3(PO_4)_2.H_2O$	..
Isoclase	$Ca_2(OH)PO_4.2H_2O$	Monoclinic
Dihydrite	$Cu(CuOH)_4(PO_4)_2$	Triclinic
Libethinite	$CuPO_4(CuOH)$	Rhombic
Tagelite	$CuPO_4(CuOH).H_2O$	Monoclinic
Hopeite	$Zn_3(PO_4)_2.4H_2O$	Rhombic
Variscite	$AlPO_4.2H_2O$	,,
Zepharovichite	$AlPO_4.3H_2O$	..
Callainite	$AlPO_4.2\frac{1}{2}H_2O$	..
Callaite	$Al_2(OH)_3PO_4.6H_2O$	Rhombic
Augelite	$Al_2(OH)_3PO_4$	Monoclinic
Sphærite	$Al_5(OH)_9(PO_4)_2.12H_2O$	..
Evansite	$Al_2(OH)_6.AlPO_4.6H_2O$	..
Kraurite	$Fe_2(OH)_3PO_4$	Rhombic
Ludlamite	$Fe_7(OH)_2(PO_4)_4.8H_2O$	Monoclinic
Monazite	$CePO_4$	Triclinic
Xenotime	YPO_4	Tetragonal
Autunite	$(UO_2)_2Ca(PO_4)_2.8H_2O$	Rhombic
Borickite	$CaFe_4(OH)_6(PO_4)_2.3H_2O$	..
Cirrolite	$Ca_3Al_2(OH)_3(PO_4)_3$	..
Triphyllite	$(Mn, Li, Fe)PO_4$	Rhombic
Amblygonite	$Al(Li)PO_4(F, OH)$	Triclinic
Chalcosiderite	$(Al, Fe)_2(FeO)_4.Cu(PO_4)_4.8H_2O$	,,

Iron ores often contain phosphates which are reduced during the smelting process, the phosphorus passing into the iron as phosphide and being again eliminated as basic calcium phosphate in basic slag (*q.v.*, p. 216).[1]

The phosphates of lime are the most valuable natural fertilisers and raw material of the fertiliser and phosphorus industry, which uses also to a less extent phosphates of aluminium and the apatites. Over 80 per cent. of the easily decomposible phosphorites mined are used in the preparation of superphosphate or other fertilisers (1930).

The Composition of Phosphorites.—Phosphoric anhydride, in the form of tribasic calcium phosphate, forms about 65 to 79 per cent. of a rock suitable for use in the fertiliser industry. There is present, in addition, an excess of calcium carbonate, also ferric oxide and alumina, silica (2 to 8 per cent.), organic matter and moisture (2 to 3 per cent.). The following analyses furnish a comparison between the principal constituents of the raw materials. Complete analyses are given in three typical cases of the most important classes.

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[1] See also this Series, Volume IX., Part II.

ANALYSES OF PHOSPHATIC MATERIALS.

	P_2O_5.	CaO.	MgO.	Al_2O_3.	Fe_2O_3.	CO_2.	SiO_2.	Other Constituents.
Bone-ash . .	39·55	52·46	..	..	..	..	..	..
Precipitated phosphate .	39·45	44·88	..	..	..	..	..	..
Canadian Rock.	33·51	46·14	..	..	..	..	..	..
Spanish Rock .	33·38	47·16	..	..	..	..	..	..
Floridan Rock .	33·61	48·08	5·54	1·20	1·38	2·29	7·15	0·75 volatile on ignition.
Algerian Rock .	30·38	49·53	1·01	0·32	0·47	7·5	1·85	2·01 SO_3.
Nauru Rock .	39·34	48·43	..	..	..	..	..	..

ANALYSIS OF AMERICAN ROCK.

	P_2O_5.	CaO.	MgO.	Al_2O_3.	Fe_2O_3.	Loss on Ignition.	SiO_2.	Other Constituents.
Anaconda Manuf. Co.[1] . .	32·0	44·2	0·47	1·20	0·53	7·20	5·60	Na_2O, 0·42; K_2O, 0·14; S, 0·71; Cr, 0·05; V, 0·09; F, 1·10; H_2O, 1·0.

The Distribution of Phosphatic Rocks.—*Great Britain.*—The deposits are of historic interest only, in view of the abundant high-grade rock which is imported. The nodular deposits of the Eastern counties, known as coprolites, contain the remains of the teeth and bones of fish and reptiles. The richer beds contain a satisfactory percentage of phosphate, as is evident from the following analysis :—

	Lyme Regis.	Cambridge.	Suffolk.	
Calcium phosphate, per cent.	60·77	77·7	56·0	70·9
Calcium carbonate, per cent.	23·67	2·3	10·0	10·3

The fossil bone bed at Sutton (Suffolk) once contained 50 to 60 per cent. of calcium phosphate, but the remaining deposits are of much poorer quality.

The working of the English beds has long been discontinued, except that during the Great War some thousands of tons of coprolites were mined at Trumpington, Cambridge, and in Suffolk.

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[1] Larison, *Ind. Eng. Chem.*, 1929, 21, 1172.

Europe.—Useful deposits are found in France, Germany, Czecho-Slovakia, Poland, Belgium and Spain, the deposits of Estremadura in the last-named country being inspected by Dr Daubeny as early as 1843.

France.—Phosphatic limestones are found in the Pas de Calais, Meuse and Somme regions, and the last-named deposits were among the earliest to be worked. Specimens have been found which contain up to 78 per cent. of calcium phosphate. Those from the Meuse and the Ardennes contain about 40 per cent. A limestone with less than 30 per cent. of calcium phosphate is hardly considered worth using for the manufacture of superphosphate. France also controls the output of North Africa.

North Africa.—The deposits of Algiers were discovered in 1873 and were fully reported upon in 1886. They are of Eocene age and contain 58 to 68 per cent. of calcium phosphate in a soft rock, together with marl, considerable amounts of silica, calcium fluoride and chloride, nodules of gypsum and almost pure limestone. The beds usually are several feet thick and run continuously from Morocco to Egypt at a distance of over 100 miles from the sea. Those at Constantine (Algiers) are 120 miles from the port of Bona, and those at Gafsa (Tunis) 150 miles from the port of Sfax.

The potential resources in this region have not yet been fully explored but are probably the greatest which have been discovered up to the present. It has been estimated that there are 1000 million tons available in Morocco.[1] This estimate has recently been increased to 3000 million metric tons.[2]

United States.—The principal deposits are in South Carolina, Florida, Tennessee, Arkansas, Utah and Wyoming. The South Carolina deposits are of Miocene age and occur both as " land " and " river " rock. They contain 25 to 28 per cent. of phosphoric oxide and 35 to 42 per cent. of lime. They were the earliest to be exploited, namely, from 1868 onwards, and in 1893 they furnished about one-fifth of the world's supply. Since this date the production has declined, while that of Florida has greatly increased. In 1913 Florida and Tennessee together produced some 96 per cent. of the total output from the United States of America. The hard-rock deposits of Florida are of Tertiary age, and they run parallel to the coast for 144 miles. After concentration by mechanical means they contain usually from 77 to 79 per cent. of calcium phosphate (more rarely up to 82 per cent.) with 3 per cent. of oxides of iron and alumina, some calcium fluoride and other constituents, and 3 per cent. of moisture. The best grades of Tennessee rock were guaranteed to contain 72 per cent. of calcium phosphate, and 65 per cent. is common. The soft rock is a phosphatic clay. The river pebbles are dark grey to black and are very cheaply obtained by dredging.

Deposits are found also in *Canada,* the *West Indies, Mexico* and *South America.*

Oceanic Deposits and Guanos.—*Guano.*—This valuable natural manure is produced from the excrement of sea-birds, and occasionally of other animals, which has been chemically altered by exposure. Peruvian guano has been mined for many centuries. That from the Chincha Islands was used by the ancient Peruvians according to von Humboldt, 1804.

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[1] Pietvkowsky, *Naturwiss.*, 1922, 10, 350.

[2] *Chemical Age*, 1931, p. 281.

Guano contains from 11 to 17 per cent. of phosphoric oxide, 11 to 19 per cent. of lime, up to 1 per cent. of magnesia, 3 to 15 per cent. of nitrogen, about 2·5 per cent. of potash and 13 to 30 per cent. of water. Hence it is almost a complete plant food.

Phospho-guanos.—These deposits occur chiefly in oceanic islands, situated in tropical latitudes, and have probably the same origin as guano, but the changes have been more far-reaching, so that their composition is transitional between the guanos and the phosphatic rocks. By intense bacterial action the nitrogenous compounds have been converted quickly into ammonia and nitric acid, and the soluble nitrates and ammonium salts have been washed out by heavy rain, or the breaking of high seas over low-lying atolls. The resulting deposit contains usually less than 1 per cent. of nitrogen. The phosphate of lime ranges from 60 to 77 per cent. When it is 50 per cent. or less the deficit is usually composed of organic matter (loss on ignition) or calcium carbonate, or both.

The Pacific Island deposits belong to this class and are found chiefly on those islands which lie between Australia and Japan. The Barker Island deposit, now exhausted, contained about 78 per cent. of calcium phosphate and 6 per cent. of magnesium phosphate. Rich deposits were also found on the Fanning Island and Makatea Islands in the Paumotu Group, Angaur Island in the Pelew Group, etc.

The Australasian Dominions, Australia and New Zealand, largely obtain their supplies from Nauru and Ocean Islands, the produce of which was, after 1920, divided in definite ratios between the United Kingdom, Australia and New Zealand. Nauru is a coral island over 200 feet high and covering an area of about 5,000 acres, a considerable part of which consists of a deep deposit containing 80 to 87 (usually 86 to 87) per cent. of calcium phosphate, which probably has been formed by the leaching of guano deposits into the coral limestone. The phosphate is quarried out, leaving pinnacles of the harder limestone. The reserves on the island are estimated at 80 to 100 million tons. From 1913 onwards the island has yielded nearly 100,000 tons per annum. The Ocean Island deposits are of about the same quality, and about 50 feet thick on the central table-land. The reserves are estimated at 50 million tons, and the output for several years was between 100,000 and 200,000 tons per annum.

Other well-known deposits are those of Christmas Island, also Redonda and Sombrero (West Indies).

The phosphates of the British Empire are described in an official pamphlet.[1] Analyses of all the different types of phosphate minerals have been collected by Fritsch.[2]

The World's Production of Phosphate Rock.—The amounts of phosphate rock mined annually increased only slowly from the beginnings of the industry in 1847 to 250,000 tons in 1869, then to about one million tons in 1887 and about seven million tons in 1913.

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[1] "*Phosphates, 1913–1919,*" *Imperial Mineral Resources Bureau,* H.M. Stationery Office, 1921.

[2] Fritsch, "*The Manufacture of Chemical Manures,*" Scott, Greenwood, 1920.

After the great fluctuations during the Great War and post-War years, the production had again reached four million tons in 1919 and seven million tons in 1920, made up as follows (round numbers) :—

	Tons.
United States of America	3,000,000
North Africa	3,000,000
Oceanic Islands	500,000
Other Countries	500,000
Total . .	7,000,000[1]

The amounts, in round numbers, for the succeeding years (millions of tons) are :—

1924	1925, 1926	1927, 1928	1929, 1930
Less than 8	Average 9	Average 10	Average 11

The greater part of the increase is due to the North African deposits.[2] The yearly production from these sources is now greater than that which is obtained from the North American deposits.

It has been estimated that the available phosphate deposits would last for a century,[3] but this estimate does not fully take into account the North African deposits (p. 214) or the proportion which will be conserved and returned to the soil by future generations. The present annual requirements of a great agricultural country like France or Germany appear to be of the order of a million tons.[4]

Basic Slag.

This is a by-product produced in the manufacture of steel from pig iron which contains phosphorus (phosphide) (see p. 66).[5] The possibility of removing the phosphide dissolved in pig iron by carrying out oxidation in a Bessemer converter lined with a basic instead of a siliceous material was demonstrated by Snelus in 1872, by Thomas and Gilchrist at Blaenavon in 1878 and at the Eston works in 1879. The utility of the slag as a fertiliser was tested in the South and North of England from 1884 by Wrightson, Somerville, Middleton and Gilchrist.

The converters, and afterwards the open hearths, in or on which the pig iron containing phosphide[6] was oxidised, are lined with lime or magnesia. The ferrous phosphate produced by oxidation, instead of being immediately reduced again by the excess of iron, is decomposed by the lime according to the equation

$$Fe_3(PO_4)_2 + 4CaO = Ca_4P_2O_9 + 3FeO$$

and the phosphate combines further with any calcium silicate or fluoride which is present. The hard slag is crushed, separated from inclusions of iron, and then ground in a ball mill.

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[1] Parrish and Ogilvie, "*Artificial Fertilisers*," Benn, London, 1927.

[2] A. N. Gray, *Chemical Age*, 1931, pp. 90, 584; 1932, p. 97.

[3] Goldschmidt, "*Der Stoffwechsel der Erde*," Leipzig, 1922.

[4] Dyes, *J. Soc. Chem. Ind.*, 1932, 51, 387.

[5] See this Series, Volume IX., Part II.

[6] Phosphate rock is sometimes added to increase the phosphorus of the slag.

In the open-hearth process the slag may be removed by ladling or tilting, when the phosphorus content of the iron has been reduced from 1 per cent. or over to about 0·2 per cent. This furnishes a high-grade slag. A " new " slag by means of which the phosphorus content is reduced to about 0·02 per cent. is of much poorer quality (see Table I.).

OPEN-HEARTH SLAG: HIGH-GRADE AND "NEW."

TABLE I.

	Silica.	Lime.	Iron.	Total P_2O_5.	Soluble P_2O_5.*	Citrate-Soluble P_2O_5.*
High-grade .	18·80	37·30	7·80	18·54	14·33	77·39
New . . .	9·40	51·30	14·60	7·40	11·10	14·90

In the ordinary process the slag is allowed to flow off continuously. It then shows a diminution in phosphoric and silicic anhydrides and an increase in lime and total iron as the carbon and phosphorus in the metal diminish say from 1·77 and 1·30 per cent. respectively to 0·09 and 0·023 per cent. (see Table II.).

OPEN-HEARTH SLAG: CONTINUOUS FLOW.

TABLE II.

	Silica.	Lime.	Iron.	Total P_2O_5.	Soluble P_2O_5.*	Citrate-Soluble P_2O_5.*
At first . .	20·30	33·20	8·60	17·08	15·36	89·92
After 6½ hours .	10·20	47·80	14·70	10·85	1·66	15·30

The solubility of basic slag has been found to increase with increasing calcium silicate. Some of the constituents other than phosphate have value on certain soils which happen to be deficient in these constituents.

Basic slag is a slow fertiliser; the phosphate is not immediately available as is that of calcium superphosphate. It is particularly valuable for fruit trees, and for heavy grass-land, on which it develops the growth of white clover and hence increases the amount of combined nitrogen. It neutralises acid soils, and its beneficial effects extend over many years.[1]

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* *Note.*—Percentage of the total P_2O_5.

[1] "Basic Slags: their Production and Utilisation in Agriculture," *Trans. Faraday Soc.*, 1921, 16 (ii), 263.

SUMMARY OF PHOSPHATIC FERTILISERS.

The chief varieties of naturally occurring or manufactured phosphatic fertilisers may be classified briefly as follows :—

(1) Natural nitrogenous phosphates such as guano, bone-dust.
(2) Finely ground phosphatic rock.
(3) Superphosphate of various grades—with 16 to 20 per cent. total phosphoric acid or with 8 to 10 per cent. of water-soluble phosphoric acid.
(4) Double superphosphate—with about 40 per cent. of soluble phosphoric acid.
(5) Precipitated dicalcium phosphate.
(6) Basic slag or " Thomas phosphate."
(7) " Wolter phosphate," obtained by decomposing phosphate rocks with calcium carbonate, sand, carbon and sodium sulphate in a furnace. " Rhenania phosphate," obtained by decomposing the rock with leucite or phenolite, potash or soda.
(8) Ammonium phosphates and superphosphates, which may contain also ammonium sulphates.

A scientific study of the various systems should determine the best conditions for the various reactions between salts and acids. The phosphates of calcium are the most important.

THE SYSTEM LIME AND PHOSPHORIC ACID.

Since the phosphorus compounds which are used in the arts, as well as phosphatic fertilisers, are derived from the decomposition of phosphates of lime, and the interactions of these are also of importance in biochemistry, a short account of the best investigated of these compounds will be given here.*

The phosphates of lime which occur in nature or are produced during the course of manufacture of phosphorus compounds are salts of orthophosphoric acid. The hydrogen is replaced by calcium in stages giving successively mono-, di- and tri-calcium phosphate. Of these the mono-calcium salt alone is freely soluble. The solids deposited on evaporation, or obtained by double decomposition, are generally mixtures of the di-, tri- or more basic compounds, but pure crystalline forms have been prepared, especially of the more acid phosphates. The more basic phosphates are very sparingly soluble, and the solubilities are not definite. The solids are not in equilibrium with solutions of their own composition, but are in process of transformation which is so slow that equilibrium is not attained in most operations.

Tribasic calcium phosphate, $Ca_3P_2O_8$, may be made by washing precipitated calcium phosphate with ammonia, which dissolves any excess of phosphoric acid above that required to form this compound. It is a white earthy powder which retains water tenaciously, and also adsorbs halides, bicarbonates and hydroxides.[1] It has also been prepared from $CaH_4(PO_4)_2$ by dissolving this in a large excess of water and adding ammonia free from carbonate with constant stirring and at such a rate that the solution is only faintly alkaline until the end of the operation. The amorphous gelatinous precipitate is washed with water by decantation until the dissolved phosphate is reduced to a minimum. Analysis of a dried sample gave a ratio $P_2O_5/CaO = 0{\cdot}835$, the theoretical ratio being 0·845.[1] $Ca_3(PO_4)_2$ contains 54·2 per cent. of CaO and 45·8 per cent. of P_2O_5. According to the analyses given on p. 213, phosphate rock evidently is more basic than this, and often contains much carbonate. It is considered probable that these rocks contain oxy-apatite, $CaO.3Ca_3P_2O_8$, hydroxy-apatite, $Ca(OH)_2.3Ca_3P_2O_8$, or carbonato-apatite, $CaCO_3.3Ca_3P_2O_8$, with usually a further excess of lime or calcium carbonate. The composition of the solid phases formed by long shaking of $CaHPO_4$ with $Ca(OH)_2$ passes the point corresponding to $Ca_3P_2O_8$, and becomes fixed only at a ratio which corresponds nearly to $Ca(OH)_2.Ca_3P_2O_8$.[2]

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* *Note.*—In accordance with the general plan of this Series, full accounts of the various phosphates will be found under the heading of the metal in the appropriate Volume of this Series.

[1] Bassett, *Trans. Chem. Soc.*, 1917, **III**, 620.

Repeated extraction of $Ca_3P_2O_8$ with boiling water yields finally $Ca(OH)_2.Ca_3P_2O_8$.[3] The preparation is more certain in the presence of alkali.[1] The tribasic phosphate is suspended in a large excess of water contained in a pyrex flask and boiled for long periods with alkali free from carbonate, removing the supernatant liquid each day. After several weeks the precipitate reaches a constant composition which undergoes no further change, the ratio of P_2O_5/CaO (in grams) being then 0·76. The hydrolysis is expressed by the equation

$$10Ca_3(PO_4)_2 + 6H_2O = 3[3Ca_3(PO_4)_2.Ca(OH)_2] + 2H_3PO_4$$

Both the basic phosphate and $Ca_3(PO_4)_2$ adsorb definite quantities of $Ca(OH)_2$. These quantities when plotted as functions of the concentrations of $Ca(OH)_2$ have the usual form of adsorption isotherms and therefore give no evidence of the formation of definite compounds, 1 gram of the basic calcium phosphate when in equilibrium with a solution containing 1·099 grams of $Ca(OH)_2$ per litre adsorbs 0·0201 gram of the hydroxide. After 6 months of contact this amount is increased to 0·0243 gram.[1]

A hydrate $Ca_3P_2O_8.H_2O$ has been described as a hygroscopic powder, but this also is not in equilibrium with a definite solution but gives solutions containing greater proportions of phosphoric acid and dissolves with hydrolysis, depositing lime.[4]

Dicalcium phosphate, $Ca_2H_2P_2O_8$ or $CaHPO_4$, is the first substance to be precipitated when calcium hydroxide is added to phosphoric acid. It is formed by the interaction of mono- and tri-calcium phosphates, and is then called " reverted phosphate." Thus

$$Ca_3P_2O_8 + CaH_4P_2O_8 = 2Ca_2H_2P_2O_8$$

It is also deposited when any aqueous solution of calcium phosphate is evaporated to dryness with hydrochloric acid. It occurs as an anhydrous more soluble form and as a hydrated less soluble crystalline form (monoclinic needles). The solubility product $[Ca^{++}][HPO_4^{=}]$ is variously given[1, 2] as 4×10^{-7} or $3{\cdot}5$ to 12×10^{-6}. This compound, like the tribasic and indeed all the phosphates of lime, decomposes in contact with water giving a more acid solution and a more basic solid. The original solid compound is in equilibrium only with a solution containing a higher ratio of PO_4/CaO. This is clearly shown in the accompanying table.

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[1] Lorah, Tartar and Wood, *J. Amer. Chem. Soc.*, 1929, 51, 1097.

[2] Bassett, *Trans. Chem. Soc.*, 1917, 111, 620.

[3] Warington, *Trans. Chem. Soc.*, 1873, 26, 983.

[4] Cameron, Seidell and Bell, *J. Amer. Chem. Soc.*, 1905, 27, 1503.

THE COMPOSITION OF SOLUTIONS SATURATED WITH CALCIUM HYDROGEN PHOSPHATES.[3]

Solid Phases.	25° C.		40° C.		50·7° C.	
	Concentration—Grams per 100 Grams Saturated Solution.					
	CaO	P_2O_5	CaO	P_2O_5	CaO	P_2O_5
$CaH_4P_2O_8.H_2O$ . .	3·09 to 4·91	36·1 to 28·3	1·77 to 3·58	42·4 to 36·8	0·636 to 4·88	58·08 to 33·2
$CaH_4P_2O_8.H_2O + CaHPO_4$.	5·81	24·20	5·76	27·25	$5{\cdot}72_5$	29·61
$CaHPO_4$	5·52 to 0 83	22·9 to 2·39	4·81 to 0·059	21·7 to 0·158	3·51 to 0·69	15·5 to 2·28
$CaHPO_4 + CaHPO_4.2H_2O$.	0 165	0·417	..	..	..	..
$CaHPO_4.2H_2O$ . . .	0 070 to 0·040	0·166 to 0·093	$0{\cdot}059_6$	0·153	..	..

Three quintuple points in this system have been determined by Bassett[4] as follows :—[5]

EQUILIBRIA BETWEEN SOLID PHASES AND SOLUTIONS AT THREE TEMPERATURES.

° C.	Solid phases as specified; solutions in square brackets.
21	$CaHPO_4.2H_2O + 0{\cdot}138CaH_4(PO_4)_2.H_2O \rightleftharpoons 1{\cdot}0747CaHPO_4 + [2{\cdot}374H_2O + 0{\cdot}10007P_2O_5 + 0{\cdot}0627CaO]$
36	$CaHPO_4.2H_2O \rightleftharpoons 0{\cdot}9985CaHPO_4 + 0{\cdot}000384Ca_3(PO_4)_2.H_2O + [2{\cdot}00036H_2O + 0{\cdot}00033CaO + 0{\cdot}00036P_2O_5]$
152	$CaH_4(PO_4)_2.H_2O \rightleftharpoons 0{\cdot}495CaH_4(PO_4)_2 + 0{\cdot}427CaHPO_4 + [1{\cdot}80H_2O + 0{\cdot}292P_2O_5 + 0{\cdot}078CaO]$

Changes during Neutralisation.—In the neutralisation of phosphoric acid with lime there is only a gradual increase in the *p*H value until more than one equivalent of lime has been added ; that is until

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[1] Farnell, *J. Soc. Chem. Ind.*, 1926, 45, 343T.
[2] Bassett, *loc. cit.*; also Britton, *Trans. Chem. Soc.*, 1927, p. 614.
[3] Cameron, Seidell and Bell, *J. Amer. Chem. Soc.*, 1905, 27, 1503.
[4] Bassett, *Zeitsch. anorg. Chem.*, 1908, 59, 1.
[5] See this Series, Volume III., Part I.

some 33 per cent. of the acid has been neutralised, corresponding to the formation of $CaH_4P_2O_8$. The *p*H value then begins to increase more rapidly with further addition of lime and a precipitation of dicalcium phosphate, $Ca_2H_2P_2O_8$, may occur if sufficient time is allowed.[1] When 39 to 45 per cent. of the acid has been neutralised there is a sharp drop in the *p*H value, which is due probably to the precipitation of dicalcium phosphate from supersaturated solution. This not only leaves the solution relatively poorer in hydroxyl ions through the removal of $HPO_4^{=}$, since by hydrolysis

$$HPO_4^{=} + H^+ + OH^- \longrightarrow H_2PO_4^- + OH^-$$

but also diminishes the ratio CaO/P_2O_5 in the solution, since a solid corresponding to 67 per cent. neutralisation is being removed from a liquid corresponding to 45 per cent. The precipitation may be delayed until about $1\frac{1}{2}$ equivalents of lime have been added and the *p*H value has become 6·7.[2] Further addition of lime then produces a gradual increase in alkalinity, absolute neutrality ($p\text{H} = 7$) being reached after the addition of about 2 equivalents, *i.e.* at 67 per cent. neutralisation. A slight further addition of lime then produces a sharp drop in the alkalinity, which is not observed however when the neutralisation is carried out in the presence of dissolved sucrose.[2] This " kink " in the curve is probably due to supersaturation. The process of deposition with increase of acidity in the presence of precipitated solids would probably continue much further if sufficient time were allowed, since it has been calculated from the results of Bassett that the solution in equilibrium with dicalcium phosphate or even with tricalcium phosphate has a much greater acidity (*p*H approximately 5·5) than the solutions in which these precipitates are first produced. A continuation of the titration with lime up to 3 equivalents (100 per cent. neutralisation) gives only a slight increase in alkalinity, which becomes somewhat greater after the addition of 3 equivalents. In contradistinction then to the alkalies and even baryta and strontia, calcium hydroxide apparently does not give high alkalinities when in the presence of precipitated calcium phosphate. This is due not only to the sparing solubility of $Ca(OH)_2$, but also to its combination with $Ca_3P_2O_8$ to give hydroxyapatite, $3Ca_3P_2O_8.Ca(OH)_2$.

The practical significance of these observations is that phosphates can only remain freely soluble in soils with a relatively high acidity (*p*H less than 5·5); the solid present in contact with such solutions is either $CaH_4P_2O_8.H_2O$ or $Ca_2H_2P_2O_8$ in a finely divided and anhydrous state. Neutral or even faintly acid solutions (*p*H 5·5 to 7·0) will contain but little dissolved phosphate, being in equilibrium with $CaHPO_4.2H_2O$, $Ca_3(PO_4)_2$ or $Ca(OH)_2.3Ca_3P_2O_8$, or a mixture of these solids. The solubility of these solids is however sufficient for the requirements of plants, since it is found that the amount of phosphorus in the extract even of a rich soil is only of the order of 1 milligram per litre, while soils of average fertility may contain only 0·1 to 0·2 milligram per litre. The fact that this very low concentration appears to be sufficient for the growth of plants makes it probable that these are able to use insoluble phosphate,[3] as has also been pointed out by N. M. Comber and others. It is important that there should be a sufficient reserve of phosphate in the soil which may gradually become available. The removal of phosphoric acid by plants increases the amount of basic phosphate and should be compensated by the addition of an acid-producing fertiliser such as ammonium sulphate. The value of phosphates in a really soluble form has long been recognised.

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[1] Farnell, *J. Soc. Chem. Ind.*, 1926, 45, 343T.

[2] Britton, *Trans. Chem. Soc.*, 1927, p. 614.

[3] Tidmore, *J. Amer. Soc. Agron.*, 1930, 22, 481.

The Acid Phosphates.—On account of the relatively higher degree of dissociation of sulphuric acid it is capable of liberating phosphoric acid from phosphates, and the reaction is favoured by the low solubility of calcium sulphate.

$$Ca_3P_2O_8 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

This probably is the first stage of the reaction by which superphosphates are produced. It is succeeded by

$$Ca_3P_2O_8 + 4H_3PO_4 = 3CaH_4P_2O_8$$

When two mols of sulphuric acid are added to one of the tribasic phosphate more than 96 per cent. of the phosphate is rendered freely soluble in water, superphosphate being formed as follows :—

$$Ca_3P_2O_8 + 2H_2SO_4 = 2CaSO_4 + CaH_4P_2O_8$$

In practice it is arranged that a little of the tribasic phosphate is left undecomposed, and this then reacts according to the equation

$$Ca_3P_2O_8 + CaH_4P_2O_8 = 4CaHPO_4$$

The amount of freely soluble phosphate is thus reduced. When the superphosphate is brought into contact with water the insoluble part is increased by the production of a solution containing from 12 to 5½ times as much phosphoric acid as lime (see p. 220), or about 4 times as much when $CaHPO_4$ is present as a solid. The presence of $CaSO_4$ in commercial phosphate does not much alter these ratios, as is shown by the following solubilities :—[1]

Solid Phases.	P_2O_5, grams/litre.	CaO grams/litre.
$CaSO_4.2H_2O$, $CaHPO_4.2H_2O$, $CaH_4P_2O_8$	317	77
$CaSO_4.2H_2O$, $CaSO_4$, $CaH_4P_2O_8.H_2O$	545	38

The ratio P_2O_5/CaO is 4·1 in the solutions which are in contact with solid "reverted" phosphate and sulphate of lime, and 14 in the solutions which are in contact with solid superphosphate and sulphate of lime.

The Manufacture of Superphosphate.

The finely ground rock is mixed with sulphuric acid in the proportions required by the equations

$$CaCO_3 + H_2SO_4 + H_2O = CaSO_4.2H_2O + CO_2$$
$$Ca_3P_2O_8 + 2H_2SO_4 + 5H_2O = CaH_4P_2O_8.H_2O + 2[CaSO_4.2H_2O]$$

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[1] Cameron and Bell, *J. Amer. Chem. Soc.*, 1906, 28, 1220.

The evolution of carbon dioxide plays an important part in keeping the mass porous ; if a sufficient proportion of carbonate is not present in the rock it may be supplied by blending. The heat evolved by the reaction is used to evaporate the surplus water. This heat depends on the composition of the rocks—those which contain much carbonate evolve more heat and may be treated with cold acid, while those which contain little may require hot acid. Chamber acid of density 1·53 to 1·61 is used ; this is also the chief source of the water required. The hydrates retain their water when dried at 100° C., or even to a great extent up to 150° C.* If artificial drying is used the temperature should not rise over 150° C. or else an undue proportion becomes insoluble. The loss in weight is 10 to 12½ per cent. The product hardens on cooling and is cut out and powdered by a mechanical disintegrator (see p. 226). It contains, when freshly made, 30 to 45 per cent. of phosphate (calculated as $Ca_3P_2O_8$) soluble in water, according to the composition of the rock used. A more concentrated form (" double superphosphate ") is made by adding sulphuric acid sufficient in amount to set free all the phosphoric acid, which, after filtration, is concentrated to a syrup and used to decompose more phosphate according to the equation

$$Ca_3P_2O_8 + 4H_3PO_4 + 3H_2O = 3(CaH_4P_2O_8 + H_2O)$$

The manufacture has been of great value as an outlet for surplus sulphuric acid, of which 11 cwt. (69 per cent. acid) is required for every ton of (ordinary) superphosphate.

"*Retrogression.*"—Superphosphate may require to be stored for several months, and during this time insoluble $CaHPO_4$ is formed according to the equation on p. 222 from the small amount of undecomposed $Ca_3P_2O_8$. Even a week after manufacture the soluble phosphate may have diminished by about 2 to 4 per cent. This " retrogression " is particularly marked when the phosphatic material contains more than 2 per cent. of iron plus alumina. The excess of these bases reacts with the $CaH_4P_2O_8$ to give insoluble phosphates of iron and aluminium according to the equation

$$\begin{aligned} &CaH_4P_2O_8.H_2O + Fe_2(SO_4)_3 + 5H_2O \\ &\qquad = 2[FePO_4.2H_2O] + CaSO_4.2H_2O + 2H_2SO_4 \end{aligned}$$

The phosphates of iron and aluminium form gelatinous precipitates which are insoluble in weak acids, or in hydrolysed acid phosphates or sulphates. Ferric phosphate may be decomposed, using up more sulphuric acid, as in the equation

$$3FePO_4 + 3H_2SO_4 \rightleftharpoons FePO_4.2H_3PO_4 + Fe_2(SO_4)_3$$

or it may easily lose its water, becoming insoluble, thus :

$$FePO_4.2H_2O + CaSO_4 = CaSO_4.2H_2O + FePO_4$$

If the original rock contains up to 2 per cent. of iron oxide the resulting phosphate of iron is soluble, but with more than 4 per cent. of iron oxide the phosphate is insoluble—hence such a rock is considered unsuitable for the manufacture of superphosphate. The "regression" of the phosphate by the iron salt just described may be avoided if the rock is dissolved in ammonium sulphate solution and then treated with sulphur dioxide; the iron is then converted into $(NH_4)_2SO_4.FeSO_4.6H_2O$.

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* At this temperature, however, retrogression is liable to occur, and also the formation of pyro- or meta-phosphate.

The Treatment of Special Ores.—Alumina does not appear to induce "retrogression." It may be removed by caustic alkalies or hot alkali carbonate solutions. Redonda phosphate ($AlPO_4$) may be made soluble by fusion with ammonium bisulphate, giving a dry powder which is a mixture of ammonium alum, ammonium bisulphate and biphosphate.

Rocks which contain calcium chloride or fluoride (apatites) are decomposed according to the equations

$$CaCl_2 + H_2SO_4 = 2HCl + CaSO_4$$
$$CaF_2 + H_2SO_4 = 2HF + CaSO_4$$

The corrosive gases which are liberated are absorbed in towers containing water and furnish solutions of hydrochloric or hydrofluosilicic acid by reaction with the silica of the phosphate rock. Thus

$$4HF + SiO_2 = SiF_4 + 2H_2O$$
$$SiF_4 + 2HF = H_2SiF_6$$

By addition of common salt silicofluoride may be precipitated and the filtrate may be worked up for hydrochloric acid. Thus

$$H_2SiF_6 + 2NaCl = Na_2SiF_6 + 2HCl$$

Apatite may be treated by the following process (Palmer):—[1] Perchloric or chloric acid made by electrolysis of the sodium salts is mixed with the coarsely ground rock. The liquid, containing H_3PO_4, is precipitated by the alkaline kathode liquors so as to give a slightly acid precipitate of the composition $CaHPO_4.2H_2O$, which is soluble to the extent of 95 per cent. in ammonium citrate—see Phosphate Analysis (p. 225).[2]

Phosphoric Acid.—By using three mols of sulphuric acid instead of two, the whole of the lime is converted into sulphate and the whole of the phosphoric acid set free according to the equation

$$Ca_3P_2O_8 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4$$

The raw material should contain at least 50 per cent. of $Ca_3P_2O_8$ and be as free as possible from sesquioxides. It may be ignited if high in organic matter, reduced to a fine powder, and fed continuously into tanks lined with wood or hard lead alloy, where it meets on the counter current principle hot sulphuric acid of about 5 per cent. concentration. The reaction is quickly completed and the precipitated calcium sulphate is allowed to settle and filtered off continuously through filter presses. This sulphate is "phosphatic gypsum" and contains 3 to 4 per cent. of phosphoric acid of which 1 per cent. is soluble in water. The solution is evaporated in wrought-iron pans up to a concentration of 50 per cent. phosphoric acid, which may be further refined for use in pharmaceutical products or foods.

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[1] *Imperial Mineral Resources Bureau Publication*, "*Phosphates, 1913–1919*," H.M. Stationery Office, 1921; *Chemical Age*, 1926, 14, 93.

[2] A full account of the technical preparation of phosphorus products with abstracts of patents will be found in "*Phosphor, Phosphorsäure und Phosphate*," Dr Oscar Kausch, Springer, Berlin, 1929.

The crude phosphoric acid is also used in the manufacture of "high analysis" or "triple superphosphate." The solution containing about 45 per cent. of H_3PO_4 is mixed with more of the ground rock and evaporated. The product, distinguished from ordinary superphosphate by freedom from gypsum, sets to a tough mass. It is broken up while comparatively fresh and dried at about 200° C. It contains $CaH_4P_2O_8$ mixed with sandy crystals, is non-hygroscopic and may have the following composition:—

Total P_2O_5	48·0–49·0	CaO	20·80
Water-soluble P_2O_5	41·0–42·0	$Fe_2O_3 + Al_2O_3$	2·25
Citrate-soluble P_2O_5	4·0– 5·0	$Na_2O + K_2O$	2·0
Citrate-insoluble P_2O_5	2·0– 3·0	SiO_2	1·4

together with fluoride, sulphate, other bases (Cu, etc.) and about 2 per cent. of water.[1]

Electrolytic Methods.—If apatite or other phosphatic material is placed round the anode in a solution of sodium chloride which is being electrolysed, a citrate-soluble calcium phosphate is precipitated. Or perchloric acid may be made separately in the anode compartment and mixed with the alkali produced at the kathode, giving a precipitate of $Ca_2H_2P_2O_8$.[2]

Alkali Treatment.—Phosphate rock may also be made soluble by heating the powdered material with soda ash, carbon and silica, thus :

$$Ca_3(PO_4)_2 + 3SiO_2 + 3Na_2CO_3 = 3CaSiO_3 + 2Na_3PO_4 + 3CO_2$$

The History and Technology of Superphosphate Manufacture.

Allusion has already been made to the suggestion of Liebig that bones could be made more available for agriculture by fine grinding and treatment with acid. This treatment of bones and other phosphoritic materials was patented by J. B. Lawes in 1842, but the claim was modified later to cover only minerals such as apatite, phosphorite, etc. A paper published by the Rev. Henslow called attention to the use of crag coprolites from Suffolk, which with guano and bones were used by Lawes in his factory at Deptford. From 1842 to 1854 the manufacture was essentially a British industry and in the early period, until about 1870, the plant was of the simplest description. The right quantity of acid, determined by trial and error, was run on to a heap of ground phosphatic material in a "den" made of tarred pitch pine or tarred bricks secured by cast-iron plates, and mixed by means of rakes and shovels. The mass soon set and dried itself by the heat of the reaction, and after storing for a month or so was broken up, screened and bagged. The only machinery used consisted of stone mills for grinding the rock. Rotary stirrers operated by hand were sometimes installed and were in service into the twentieth century. The production of 1 ton of superphosphate requires about 11 cwt. of chamber acid, 69 per cent. H_2SO_4, and the weight of superphosphate from a good grade of rock, containing about 32 per cent. P_2O_5, is rather less than twice the weight of the rock. This industry helped to absorb some of the large excess of sulphuric acid which became available after the decline of the Leblanc process.

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[1] Larison, *Ind. Eng. Chem.*, 1929, **21**, 1172.

[2] Palmaer, *United States Patent*, 748523 (1903); Wiborgh and Palmaer, *ibid.*, 707886 (1902).

The necessity of mixing in a closed room by external power became urgent with the introduction of rocks which evolved hydrochloric or hydrofluoric acid when treated with sulphuric acid. Machinery suited to these operations has now been devised.[1] The stone grinders were replaced by ball mills and later by rotary crushers and roll-jaw crushers which will reduce 90 per cent. of the material to a fine powder which will pass through a sieve having 10,000 meshes to a square inch. Hand labour was employed at first for the mixing. Charges of sulphuric acid and phosphates were weighed into a closed "den" and, after the reaction was completed, were dug out with the aid of gravity. These reaction chambers were replaced by mechanically operated "dens," some of which could be rotated. Various types of mechanical excavators are used. In one the block of superphosphate is forced by a ram against tearing and cutting wheels, and the broken material after falling through a grid is elevated to the storage rooms. Or the fixed chambers, each holding 150 to 200 tons, are emptied by grab-buckets which are let down into the mass. The reaction in modern plant, aided by fineness of grinding and good mixing, is complete in a few minutes.

Mixed and Concentrated Phosphoric Fertilisers.

The manufacture of fertilisers containing potassium or ammonium or both in addition to phosphoric acid has called for an accurate knowledge of the interaction of the salts concerned and also for the greatest refinements of chemical engineering in order to produce a material of uniform, dry and yet not dusty character.

Potassium Phosphates.—Basic or neutral phosphates (Rhenania phosphates) may be made directly from rock phosphate by mixing it with potassium chloride, some form of carbon and soda, and heating to over 1000° C. in an electric furnace.[2] One of these products has the composition $Ca_2KNaP_2O_8$, with some silica. Such products may contain 23 to 31 per cent. of soluble phosphoric acid. Potassium superphosphate has been made by mixing potassium sulphate and calcium carbonate with concentrated phosphoric acid in a lead-lined vessel.[3] The $CaSO_4.2H_2O$ is separated and the filter-pressed solution is evaporated to dryness by steam heat. The residue may be treated with more phosphoric acid and again evaporated. The reaction is expressed by the equation

$$K_2SO_4 + 2H_3PO_4 + CaCO_3 = 2KH_2PO_4 + CaSO_4 + CO_2 + H_2O$$

Ammonium Phosphates.—Ordinary superphosphate may be treated with aqueous ammonia up to 3 per cent. without any marked increase in the citrate-insoluble proportion.[4] The calcium salt is present as $CaH_4P_2O_8$ and $CaHPO_4$ up to 2 per cent. of ammonia, but is wholly converted into $Ca_3P_2O_8$ at 6 per cent. ammonia.[1]

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[1] Parrish and Ogilvie, "*Artificial Fertilisers,*" vol. i., Benn, 1927.

[2] Wedge, *United States Patent,* 1624195 (1927).

[3] "*Annual Reports of Applied Chemistry,*" 1922, p. 434.

[4] Jacob, *Ind. Eng. Chem.,* 1931, 23, No. 1, 14.

The ground rock may be treated directly with 2 mols of sulphuric acid and 1 mol of ammonium sulphate, which react according to the equation

$$Ca_3P_2O_8 + (NH_4)_2SO_4 + 2H_2SO_4 = 3CaSO_4 + 2(NH_4)H_2PO_4$$

The solution is filtered from calcium sulphate and more ammonia is added until the phosphates of aluminium and iron settle. On concentrating the filtrate phosphates and sulphates of ammonia may be crystallised.[2]

In another process crude calcium acid phosphate is mixed with ammonium sulphate solution below 80° C., and the mixture concentrated and filtered, when $(NH_4)H_2PO_4$ crystallises. $(NH_4)_2HPO_4$ is made from ammonia, fumes of phosphoric acid and water.[3] Or calcium phosphate is just dissolved in sulphuric acid, the calcium sulphate filtered off and the acid solution treated with ammonia and carbon dioxide. The ammonium sulphate and phosphate form a good mixed fertiliser.[4]

Very soluble fertilisers are prepared by reactions between phosphoric acid and ammonia or its salts. Thus, if ammoniacal gas liquor is mixed with crude phosphoric acid, diammonium phosphate, $(NH_4)_2HPO_4$, may be crystallised in the anhydrous state.[5] The composition of such products may range from 45 per cent. P_2O_5 and 14 per cent. nitrogen to 18 per cent. P_2O_5 and 18 per cent. nitrogen. By varying the proportions, monoammonium phosphate, $(NH_4)H_2PO_4$, may be obtained as a white granular solid, which is non-hygroscopic and stable under ordinary conditions. The product prepared by evaporation down to 2–3 per cent. of water and grinding contains about 53 per cent. P_2O_5 (of which 48 per cent. is soluble in water), with 13·3 per cent. of ammonia and up to 3 or 4 per cent. of a mixture of iron and aluminium, magnesium and the alkali metals.[6]

Various "sulphophosphates" are made by mixing ammonium (also alkali) sulphate solution with 55 per cent. H_3PO_4 at 80° C., thus :

$$(NH_4)_2SO_4 + H_3PO_4 = (NH_4)HSO_4 + (NH_4)H_2PO_4$$
$$K_2SO_4 + H_3PO_4 = KHSO_4 + KH_2PO_4$$

The products may be obtained in a dry form and are easily soluble in water. On account of their high proportion of free acid they may be mixed with basic slag or phosphatic chalk and still retain a large proportion of soluble phosphate.

By starting with a purer phosphoric acid, ammonium salts may be obtained in a purer state. If ammonia gas is passed into 75 per cent. phosphoric acid a reaction takes place with great heat evolution, and on cooling acid ammonium phosphate, $(NH_4)H_2PO_4$, crystallises in the anhydrous state. Further saturation with ammonia yields a mixture of the mono- and di-ammonium salts, and on further addition of concentrated ammonia solution, or by carrying out the whole reaction in more dilute solution, the salt $(NH_4)_2HPO_4$ may be obtained as white non-hygroscopic crystals containing 53·8 per cent. P_2O_5 and 25·8 per cent. NH_3.

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[1] Ross, *Ind. Eng. Chem.*, 1931, 23, No. 1, 19.
[2] Gordon, *English Patent*, 316428 (1928).
[3] Peacock, *United States Patent*, 995898 (1911).
[4] Liljenroth, *English Patent*, 275843 (1926); see also *English Patent*, 252953 (1925).
[5] *Chemical Age*, 1929, 21, 602.
[6] Larison, *loc. cit.*

By suitable combinations of the methods just described, mixtures of potassium and ammonium phosphates may be prepared. The preparation of very concentrated fertilisers containing potassium and ammonium phosphates has been described by Ross and Merz, 1916,[1] Ross, Jones and Mehring, 1926.[2]

Mixed fertilisers containing ammonium phosphate with other salts have been made in the form of cylindrical granules like smokeless powder.[3] The slower operations of solution, neutralisation, evaporation and crystallisation are avoided, the bases, acids and neutral components being combined, ground, mixed and kneaded in one operation. Salts of potassium or other base are passed through valve-locked mains into a mixing pan which contains scrapers and muller mechanisms enclosed in a gas-tight hood. Liquid phosphoric acid and gaseous ammonia are admitted simultaneously with the salts and combine under pressure in about ten minutes to form diammonium hydrogen phosphate. The sticky mass is removed by means of a vertical screw and passes into an extruding machine which had to be designed specially to deal with non-plastic masses. The extruded sections are dried, first with cold air, then at a temperature below 70° C. They are then cut into pieces about 1½ diameters or 1/8 inch long, screened and polished. The product is uniform, non-hygroscopic and is easily drilled into the land.

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[1] *United States Patent,* 1191615 (1916).

[2] *United States Patent,* 1598259 (1926).

[3] Klugh; reported in *Chemical Age,* 1932, 26, 274.

NAME INDEX.

Abbott, 165, 171, 172.
Abel, 62.
Adair, 157.
Adie, 143.
Adlucary, 133.
Agruss, 179.
Albert, 157.
Albinus, 5.
Allison, 42.
Amagat, 91.
Amat, 142, 145, 147.
Amato, 75.
André, 173.
Andrews, 157, 158.
d'Ans, 184.
Antoine, 91.
Arbuzov, 55, 144, 146, 167.
Archibald, 73.
Arctowski, 39.
von Arend, 29, 125, 135, 136, 140.
Armstrong, 92.
Arnold, 66.
Arrhenius, 136, 162, 164.
Arseneeff, 179.
Aston, 23, 49.
Atkins, 209.
Auger, 147.
Auren, 42.

Bailey, 134.
Baker, 119.
Bakunin, 97.
Balard, 76, 101, 103, 143, 144.
Balareff, 170, 174.
Ball, 179.
Banthien, 123, 127.
Barnett, 131, 174.
Bassett, 209, 219, 220.
Baudrimont, 92, 93, 96–98, 190.
Bauer, 12, 61, 62.
Bausa, 150, 153.
Baxter, 44, 45, 47, 48.
Beatty, 101, 102.
Beck, 41, 131.
Becker, 146.
Beckmann, 23.
Bell, 11, 219, 222.
Bergegren, 41.
Berger, 133.
Berthelot, D., 43, 52.
Berthelot, M., 76, 86, 87, 93, 96, 98, 101, 158, 164, 167, 173.
Berthier, 67.
Berzelius, 42, 155, 170, 186, 189, 192.
Besson, 63, 64, 76, 77, 89, 93, 98, 101, 125, 174, 189, 190, 192, 205, 206.
Beyers, 168.
v. Bezold, 187, 190, 191.
Bhandakar, 74.
Billandot, 9.
de la Billardière, 75, 78.
Biltz, 23, 96, 101.
Bineau, 77.
Bird, 28.
Blackwelder, 3, 208.
Blake, 176.
Blanc, 141, 165.
Bleckrode, 73.
Bloch, L. and E., 97, 121, 122.
Blondlot, 64, 65.
Blunt, 61.
Blyth, 71.
Bock, 169.
Boeseken, 16, 31.
Bokhorst, 21–23, 25, 35, 38, 40.
Booge, 157, 158.
Bordet, 72.
Bose, 42.
Bossuet, 61.
Böttger, 11, 62, 72, 81.
Boulouch, 186, 187, 190.
Bowen, 26.
Boyle, 5, 116, 155.
Boylston, 45.
Braun, 171.
Bray, 165, 171, 172.
Bredig, 83, 137.
Brenner, 71.
Breuning, 123.
Bridgman, 16–18, 40, 41, 91.
Brieglieb, 206.
Briggs, 182.
Briner, 71, 73, 77.
Britton, 165, 166, 179, 220, 221.
Brodie, 31.
de Broglie, 41.
Brown, 182.
Bruhl, 63.
Brukl, 28.
Bryant, 11.
Buck, 81.
Budnikoff, 89.
Buff, 90.
Bunsen, 61.
Burgess, 125.
Burke, 93, 96.
Busse, 123.

CABELL, 127.
Cahours, 94, 95.
Cailletet, 72.
Cain, 78.
Calvert, 80, 95.
Cameron, 219, 222.
Carius, 191.
Carpenter, 157.
Carrara, 93.
Carré, 167.
Casselmann, 95.
Cavalier, 150, 173.
Cavazzi, 62, 65, 67, 76, 143.
Caven, 56.
Centnerszwer, 21, 116, 124.
Chalk, 125.
Chancel, 10.
Chanton, 120.
Chapman, 33, 125.
Chappuis, 120.
le Chatelier, 66.
Chevrier, 113, 114, 203.
Chrétien, 168.
Christomanos, 19, 20, 62, 63, 99–101, 122.
Clark, 3, 34, 42, 71, 155, 163, 165.
Clarke, 67, 208.
Clarkson, 168.
de Claubry, 89.
Clausius, 122.
Clayton, 188.
de Clermont, 173.
Clever, 195.
Cloez, 114.
Cohen, 15, 20, 32, 75, 119, 192.
Colson, 32.
Compton, 19.
Cooper, 162.
Corenwinder, 103.
Corne, 150.
Cornec, 150, 153, 163, 175.
Cowper, 126.
Crafts, 84.
Cronander, 98.
Croullebois, 80.
Curie, 18.
Cushman, 66.
Cuthbertson, 25, 55.

DAGHLIEN, 53.
Dale, 17, 92, 169.
Dalton, 75, 76.
Damien, 17, 18, 54.
Darrin, 168.
Dauvillier, 41.
Davidson, 208.
Davy, H., 60, 68, 75, 76, 86, 89, 93, 94, 133, 140.
Davy, J., 116.
Defacqz, 65.
Déjardins, 26.
Demole, 101.
Dennis, 66.
Dervin, 92, 190.
Desch, 61.
Deschamps, 121.
Deville, 23, 94.
Dickinson, 78.
Dieckmann, 7, 66.
Dieterici, 161.
Dixon, 11, 29, 119.
Dobbie, 26.
Dodge, 194.
Doughty, 102.
Downey, 116, 120, 121, 123, 124, 128.
Dragunov, 176.
Drawe, 153.
Drechsel, 80.
Drummond, 76, 169.
Dufet, 145.
Duffendack, 26.
Dulong, 70, 125, 135, 138, 140.
Dumas, 43, 61, 68–70, 75, 86, 90.
Duncan, 21.
Dusart, 25.
Dushman, 75.

EASTMAN, 162.
Eder, 26.
Edwards, 61.
Efremoff, 65, 66.
Egidi, 173.
Elster, 122.
Emeléus, 121.
Emmerling, 62–64.
Engels, 78.
Ephraim, 194.
Epperson, 179.
Étard, 69.
Ewan, 118.
Ewing, 88.
Eydmann, 120.

FADAKOWSKY, 123.
Fair, 131, 134.
Fairweather, 157.
Faraday, 17, 18, 186.
Farnell, 220, 221.
Favre, 93, 164.
Federlin, 143, 144.
Ferrand, 193, 194.
Fichter, 184, 185.
Field, 169.
Finch, 131.
Finck, 143, 149.
Fireman, 103.
Firth, 139.
Fleitmann, 174, 177, 178.
Folie-Desjardins, 7.
Fonzes-Diacon, 63.
Foote, 18, 19.
de Forcrand, 23, 76, 164.
Fourcroy, 133, 145.
Fournier, 89.
Foussereau, 17.
Fowler, 134.
Fox, 26, 71.
de Franchis, 20.
Franck, 63.
Francke, 82.
Frank, 7.
Frankenheim, 39.
Fraser, 131.

Freese, 66.
Friedel, 193.
Friedrich, 194.
Frumkin, 27.

Garmendia, 165.
Garrison, 120, 123.
Gattermann, 80, 81.
Gautier, 61, 69, 82, 103.
Gay-Lussac, 60, 89, 102.
Gazarian, 70, 71.
Geibel, 165.
Geitel, 122.
Gengembre, 68.
Gerhardt, 199.
Germann, 103.
Geuther, 26, 93, 97, 99, 129, 138, 141, 170, 173, 177, 206.
Gewecke, 64.
Gibson, 24, 54.
Gill, 209.
Giran, 20, 23, 132, 158, 160, 171, 172, 175, 176, 187, 189.
Gladstone, 17, 54, 76, 89, 92, 97, 98, 101, 114, 163, 175, 189, 198, 199, 201–204.
Glatzel, 178, 191–194, 203.
Glühmann, 174.
Goldschmidt, 97, 190.
Gomolka, 33, 34, 64.
Gordon, 227.
Gore, 134.
Görlacher, 121.
Graham, 68, 75, 125, 155, 163, 170, 172, 177.
de Gramont, 26.
Granger, 61, 62, 65, 66, 87.
Gregoire, 182.
Gregory, 155, 170.
Grosheintz, 41, 141.
v. Grotthus, 64.
Grüneberg, 207.
Guldberg, 100.
Guntz, 86, 87.
Gustavson, 98, 133, 143, 174.
Gutzwiller, 185.
Guye, 73.

Haagen, 54.
Hackspill, 61, 82.
Hager, 160.
Hahn, 166, 195.
Hambly, 133.
Harkins, 3.
Harries, 126.
Hartley, 25, 124, 132.
Hatchett, 66.
Hausknecht, 80, 81.
Hautefeuille, 32, 62, 90, 130, 132, 168.
Heimann, 177.
Helff, 187, 188, 190, 191.
v. Helmholtz, 34, 37, 122.
Hempel, 8.
Henderson, 169.
Henneberg, 174, 177.
Henning, 73.
Henry, 113.
Henstock, 128.
Heraeus, 168.
Hernette, 131, 134.
Herscovici, 187, 190–192.
Hertz, 23.
Hess, 16, 17.
Hetherington, 168.
Heumann, 89, 97.
Heyn, 12, 61, 62.
Hicks, 26.
Hill, 169.
Hilpert, 66.
Hinshelwood, 75.
Hiorns, 62.
Hittorf, 25, 29, 31–33, 39.
Hoeflake, 131.
van't Hoff, 76, 77.
Hofmann, 69, 70, 75–78, 80, 82, 85, 113, 140, 187, 203, 207.
Holborn, 162.
Holland, 96.
Holleman, 181.
Holmes, 97, 114, 199, 201–204.
Holroyd, 58, 96.
Holt, 78, 158, 171, 174.
Honda, 18.
Hopkin, 132.
Houdremont, 7.
Huff, 151, 153.
Hughes, 165.
Hugot, 60, 70, 104, 197.
Hunter, 72, 191.
Huntingdon, 61, 62.
Hurtzig, 97, 141.
Husain, 184, 185.
Huthsteiner, 26.
Hvoslef, 66.

Ikeda, 118.
Inouye, 20.
Ipatieff, 27, 68.
Isambert, 79, 186–189.
Italiener, 142.
Ivanov, 55.

Jaboin, 61.
Jackson, 15, 35, 132.
Jacob, 8, 157, 226.
Jacobsohn, 150, 152.
Jäger, 91, 99, 100, 104.
Jakovlev, 26.
Janneret, 168.
Janowsky, 65, 93.
Jeep, 101.
Joannis, 60.
Johansen, 32, 207.
Johnson, 54, 77, 79, 80, 104.
Jokote, 71.
Jolibois, 16, 21, 22, 32, 33, 63, 64.
Joly, 150, 151, 158, 160.
Jones, 44, 76, 157, 158.
Jones, H. C., 158.
Joslin, 67.
Joubert, 117.

Jowett, 164, 165.
Juliusberger, 182.
Jung, 18, 41, 149, 154.

Kahlenberg, 133.
Kanonikoff, 54.
Kastle, 101, 102.
Katz, 62.
Kausch, 224.
Kayser, 26.
Kekulé, 99, 190–192.
Kempf, 131.
Kendall, 157, 158.
Kingzett, 120.
Kipping, 56.
Kirchmaier, 4.
Kirwan, 68.
Klockmann, 166.
Klugh, 228.
v. Knorre, 177, 178.
Knowlton, 161.
Köchlin, 89, 97.
Koerber, 90.
Kohler, 93.
Kohlrausch, 162.
Kohlschutter, 27, 140.
Kohn, 113.
Kolbe, 133.
Kolossowsky, 92.
Kolthoff, 137, 139, 141, 165, 172.
Konstantinoff, 66, 67.
Kooij, 74, 75.
Kopp, 15, 51.
Kowalski, 121.
Krafft, 5, 93, 189.
Kraut, 93.
Kremers, 97.
Kroll, 174, 179.
Kruger, 165.
Kubierschky, 194, 195.
Küchler, 203.
Kulisch, 28, 62, 63, 67.
Kunkel, 4.
Kuster, 165.

van Laar, 37.
Lampadius, 67.
Landgrebe, 64, 65.
Lange, 89.
Langheld, 175.
Larison, 213, 225.
Laurent, 204.
Lautemann, 133.
Lavoisier, 155, 156.
Leduc, 17, 73.
Leeuw, 15.
Lemoine, 40, 185, 186, 189, 193.
Lemoult, 76.
Lenard, 123.
Lenger, 72, 81, 82.
Leverrier, 81, 82, 125.
Levitsky, 144.
Lewes, 126.
Lichtenstadt, 56.
Lidbury, 125.
Lieben, 99.
Liebig, 204.
Liljenroth, 227.
Linck, 18, 41.
Lindboom, 177.
Lindgren, 3, 208, 209.
Linhart, 144.
Loessner, 138, 139.
Loew, 123.
Lomax, 157.
Lombard, 95, 96.
Lorah, 219.
Lubs, 165.
de Lucchi, 23.
Ludert, 178.
Ludlam, 119.
Luff, 56.
Luginin, 93, 96, 98, 101, 103, 164.
Lupke, 63, 70.
Luther, 142.

McIntosh, 73.
MacIvor, 65, 86, 114.
McLennan, 42.
Macleod, 53, 120.
MacRae, 21.
Maddrell, 177, 178.
Maggiacomo, 146.
Mahn, 76, 93.
Mai, 187, 189, 190, 196.
Major, 143, 144, 194.
Marckwald, 34, 37.
Marggraf, 155, 186.
Margottet, 168.
Marie, 135, 136.
Marini, 151.
Maronneau, 67.
Martens, 92.
Martres, 156.
van Marum, 116.
Mascart, 90.
Massini, 184.
Masson, 21, 52.
Mathias, 52.
Matignon, 63, 70.
Matteuci, 122.
Matthews, 209.
Matthiessen, 17.
Mawrow, 139.
May, 11.
Meekstroth, 169.
Mehring, 157.
Meisenheimer, 56.
Melcher, 162.
Mellman, 64.
Melville, 119, 121.
Mensching, 23.
Mente, 198, 199, 202.
Menzies, 158.
Messinger, 70, 78.
Metcalfe, 25, 55.
Meyer, 18, 23, 41, 190, 191, 195, 196.
Michaelis, 29, 92, 93, 97, 98, 114, 115, 125, 135, 136, 140, 146, 165, 195.
Mihr, 125, 127, 129.
Miller, 120, 130.
Millett, 164, 165.

Millikan, 26.
Miro, 184.
Mitchell, 93, 137, 139, 143, 144, 150.
Mohler, 19.
Moissan, 63, 70, 86, 134.
Montemartini, 173.
Moore, 45, 48, 162.
Moot, 92.
Morgan, 53.
Morton, 149, 172, 181.
Moser, 29.
Mounce, 161.
Muir, 11.
Muller, 29, 94, 97, 117, 177, 184, 203.
Mumford, 53.
Murphy, 61.
Murray, 208.
Muthmann, 139, 195.
Myers, 78, 139, 158, 174, 176.

van Name, 153, 157.
Neogi, 133.
Neumann, 83, 93, 95, 189.
Newman, 27.
Nikolaieff, 27, 68.
Norderskjold, 103.
North, 130, 144, 146.
Noyes, 162.
Nursey, 64.

Odling, 92.
Ogier, 76–78, 81, 93, 102, 103.
Ogilvie, 226.
Olie, 15, 32.
Olszewsky, 73, 91.
Oppenheim, 90.
Osann, 12.
Ossendowsky, 19.
Ostersetzer, 113.
Ostwald, 39, 120, 123, 136, 137, 141, 142, 167.
Oudlet, 117.
Ouvrard, 103, 104, 115, 189.

Palazzo, 146.
Palm, 153.
Palmaer, 225.
Palmer, 74.
Panormoff, 174.
Paquelin, 140.
Parkinson, 61.
Parravano, 151.
Parrish, 226.
Partington, 125, 184, 185.
Pascal, 18, 178.
Pauzer, 140.
Pawlesosky, 91.
Peacock, 227.
Pearson, 70.
Pelletier, 61, 68, 140, 186.
Percy, 62.
Perpérot, 94.
Perrey, 62, 130.
Person, 15, 16.
Personne, 29.
Persoz, 97.
Pessel, 176.
Peters, 4.
Petit, 76.
Peto, 131.
Petrikaln, 124.
Petterson, 16.
Philip, 12.
Phillips, 53, 161, 211.
Pickering, 92.
Pierre, 90, 99.
Pietvkowsky, 214.
Pinsker, 150, 151–154, 168.
Pisati, 16, 20.
Pischtschiminko, 192.
Pitsch, 125.
v. der Plaats, 43.
Plotnikoff, 143.
Plucker, 25.
Poggiale, 169.
Poleck, 62.
Polk, 140.
Pope, 163.
Poulenc, 87, 204.
Poundorf, 138.
Power, 168.
Prause, 168.
Preuner, 21, 22, 24, 25.
Prideaux, 21, 51, 58, 94, 95, 101, 102, 164, 165, 167, 175.
Prinvault, 92, 99.
Prinz, 113.
Pritze, 151, 173.
Purcell, 124.

Quincke, 18.

Rabinovitch, 161.
Railton, 146.
Rakusin, 179.
Ralston, 94, 97.
Ramme, 187, 188, 190.
Rammelsberg, 140, 144, 153.
Ramsay, 21, 23, 52–54, 91.
Ramsted, 137, 139.
Rankine, 71.
Raoult, 175.
Ratcliffe, 56.
Rathke, 113.
Rayleigh, 120.
Raymond, 68.
Readman, 7.
Rebs, 188, 190.
Recklinghausen, 190.
Reed, 53, 100.
Regener, 123.
Reglin, 152, 153.
Regnault, 15, 33, 90, 91.
Remsen, 92.
Renard, 208.
Renault, 61, 63.
Retgers, 17.
Reyher, 162.
Reynolds, 8.
Riban, 76, 90.
Richards, 15, 17.
Richarz, 122, 123.

Rinde, 129.
Ringer, 164.
Ritchie, 50.
Robinson, 7.
Robison, 169.
Rodger, 203.
Römer, 205.
Rosanovskaya, 176.
Rose, 61, 62, 64, 65, 75, 76, 81, 135, 138, 139, 145, 147.
Rosenheim, 147, 150–154, 168, 173.
Rosenstein, 29.
Rosin, 181.
Ross, 157, 158, 227.
Rossel, 63.
Rosset, 205.
Roy, 75.
Rudolph, 125, 187–189.
Rupp, 143, 149.
Russell, 119, 130.
Rutgers, 132.

SABANEEFF, 140, 145, 154, 198.
Sabatier, 63, 176.
Sacerdote, 73.
Sachs, 144.
le Sage, 125.
Sakalatwalla, 66.
Salm, 164.
Saltmarsh, 26.
Salzer, 150, 152, 153.
Salzmann, 199.
Sanfourche, 131, 134.
Sanger, 150.
Schacht, 19.
Scharfenberg, 191.
Scharff, 116, 122, 187, 189.
Scheele, 5, 155.
Scheffer, 77, 79, 131.
Schemtschuschny, 65–67.
Schenck, 16, 18, 29, 67, 81, 82, 99, 117, 123, 127, 140, 205.
Schepeleff, 67.
Schiff, 97, 134, 160, 198, 199, 203.
Schlundt, 18, 74, 100, 104.
Schmidlin, 184.
Schmidt, G. C., 123.
Schmidt, H., 123.
Schönbein, 116, 120, 122.
Schönn, 61.
Schönthan, 203.
Schreiner, 182.
Schroder, 30.
Schrötter, 29, 31, 33, 62–64.
Schuh, 153.
Schwarz, 174.
Seidell, 190, 219, 220.
Semenoff, 117, 118.
Senderens, 62.
Sérullas, 70, 77, 78, 80, 114, 189.
Sévène, 192.
Seyboth, 64.
Shenstone, 131.
Sherrill, 165.
Shields, 91.
Shiloff, 89.
Sidgwick, 58.
Sieverts, 138, 139, 143, 144.
Silbermann, 93, 164.
Silva, 84.
Skinner, 73, 77.
Slare, 116.
Smith, 71, 81, 95, 96, 132, 158.
Smits, 15, 21–23, 33, 37–40, 132.
Sommer, 140.
Sørensen, 164.
Springer, 189.
van de Stadt, 75, 147.
Stamm, 24, 25, 35, 40.
Stange, 174.
Stead, 64, 66.
Steel, 208.
Steele, 24, 25, 72, 73, 139, 143.
Stelling, 147.
Stern, 92, 98, 99.
Stiefelhagen, 92.
Stock, 72, 73, 80, 81, 114, 125, 187, 190, 191–195, 207.
Stoddard, 169.
Stokes, 197–202, 205.
Straub, 28.
Sugden, 52–54, 94, 100.
Svedberg, 30.

TAMMANN, 3, 15, 16, 77, 79, 161, 177, 178.
Tardieu, 13.
Tartar, 219.
Tassel, 88.
Tauchert, 28, 150.
Tausz, 121.
Terenin, 26.
Ter-Gazarian, 43.
Thénard, 60, 61, 69, 70, 80–82, 89.
Thiel, 190, 191.
Thomas, 157.
Thomlinson, 157.
Thomsen, 93, 96, 98, 132, 135, 136, 138, 141, 142, 158, 160, 164, 173.
Thomson, 76.
Thomson, J. J., 122.
Thorpe, T. E., 51, 70, 87, 88, 90, 91, 97, 99, 103, 113, 126, 127, 129, 130–133, 144, 146, 192, 197, 203.
Threlfall, 131.
Thummel, 62.
Tidmore, 221.
Tilden, 174.
Timmermann, 91.
Tivoli, 65.
Topley, 75.
Trautmann, 133.
Trautz, 74, 75.
Travers, 131.
Traxler, 103.
Treadwell, 182.
Troost, 23, 32, 90, 103.
Tucker, 61.
Turley, 157.
Turner, 42.
Tutin, 168.

Tutton, 70, 97, 103, 126–129, 131, 192, 197.
Twymann, 157.
Tyer, 121.

VANINO, 143.
Vauquelin, 145.
Veit, 66.
Vigier, 60.
Ville, 146.
Vitali, 62.
Vogel, 63, 176.
v. Vogel, 121.
Vogelis, 167.
Voigt, 96.

WAGGAMAN, 157.
Wagner, 78.
Wahl, 37.
Walden, 53, 91, 100, 139.
Walker, 11, 28, 104.
Wallsom, 194.
Walton, 120.
Ward, 165.
Warington, 219.
Warschauer, 177, 178.
Washington, 3, 208.
Weber, 4, 98, 113, 191.
Wedekind, 66.
Wedge, 226.
Weekhorst, 12.
v. Weimarn, 29.
Weiser, 120, 123.
West, 130, 131.
Weyl, 27.
Wiborgh, 225.
Wichelhaus, 92, 98, 99.
Wieland, 143.
Wiesler, 177.
Wigand, 33.
Wilkie, 181.
Wilkins, 53, 100.
Wilkinson, 94, 97.
Williams, 132.
Wingler, 143.
Winter, 70.
Wohler, 65, 113, 143.
Wolf, 42.
Wologdine, 66.
Wolter, 115.
Wood, 219.
Worms, 174.
Wrede, 207.
Wroblewsky, 91.
Wu, 168.
Wulf, 149, 154.
Wunder, 168.
Wurtz, 94, 102, 139, 143–145, 194.

YOUNG, 167.

ZOPPELARI, 93.

[SUBJECT INDEX.

SUBJECT INDEX.

Absorption of radiation by gaseous and combined phosphorus, 26.
Acids, Phosphorous, Phosphoric, etc., *see* under "Phosphorous," etc.
Alkali phosphides, 60.
Alkaline earth phosphides, 61.
Alkyl hypophosphites, 146.
— phosphates, 167.
— phosphites, 146.
Allotropic forms of phosphorus, 31 *et seq.*
Allotropy, Theory of, 38, 39.
Aluminium phosphides, 63.
Amidodiphosphoric acids, 200, 201.
Amidometaphosphoric acids, 198 *et seq.*
Amidophosphoric acids, 197, 198.
Animal body, Proportion of phosphorus, 4.
Antimony phosphides, 65.
Arsenic phosphides, 64, 65.
Atomic weight of phosphorus, 43–50.
Atomicity of gaseous phosphorus, 24, 25.

Barium phosphide, 61.
Basic slag, 216, 217.
Black phosphorus, Crystalline structure, 4.
— —, Preparation and properties, 40, 41.
Bone-ash, 5, 211, 213.
Bones, 4, 210.
Boron phosphide, 63.

Cadmium phosphides, 63.
Cæsium phosphides, 61.
Calcium phosphates, System lime-phosphoric acid, 218.
— phosphide, 61.
Chemical combinations of phosphorus, 27.
Chlorides of phosphorus, *see* "Phosphorus chlorides."
Chromium phosphides, 65.
Cobalt phosphides, 66.
Combined phosphorus, Physical properties, 51 *et seq.*
Condensation of phosphorus vapour, 40.
Copper phosphides, 61, 62.
— salts, Reactions with phosphorus, 28.
Critical constants of phosphorus, 37.
Crystalline forms of phosphorus, 17.

Densities of solid, liquid, and gaseous phosphorus, 16, 20, 24, 32, 33, 41, 42.

Detection of hypophosphites, etc., *see* "Hypophosphites," etc.
— — phosphorus, 30.
Dipole moment of phosphine, 57.

Electric furnace method for the preparation of phosphorus, 8.
Estimation of hypophosphites, 148 *et seq.*
— — phosphates, 180.
— — phosphites, 148 *et seq.*
— — phosphorus, 30.

Fertilisers, Phosphatic, Manufacture of, 225, 226.
—, —, Mixed, 227, 228.
Fireworks containing phosphorus, 12.
Fluophosphoric acid, 89, 106.
Fluorescence of phosphorus vapour, 26.
Fluorobromide, Fluorochloride, etc., *see* "Phosphorus fluorobromide," etc.

Glow of phosphorus, 116 *et seq.*
Gold phosphides, 61, 62.
Guanos, 215.

Heat of dissociation of gaseous phosphorus, 24.
— — fusion, Latent, of violet phosphorus, 37.
— — —, —, of white phosphorus, 15, 16.
— — sublimation, Latent, of phosphorus, 36, 37.
— — vaporisation, Latent, of liquid phosphorus, 23.
—, Latent, of hypophosphorous, phosphorous and phosphoric acids, 136, 141, 160, 171.
—, Specific, of white phosphorus, 15.
History of phosphorus, 2, 3.
— — — compounds, *see* under respective compounds.
Hydrogen phosphides, 68 *et seq.*; *see* also under "Phosphine," etc.
Hydroxyphosphines, 82.
Hypophosphates, 153, 154.
Hypophosphites, 139, 140.
—, Structure of, 145–147.
Hypophosphoric acid, 150–153.
Hypophosphorous acid, 135 *et seq.*
— —, Detection, 148–150.
— —, Estimation, 148–150.

Imido-derivatives of diphosphoric acid, 201, 202.

Ionisation of air by glowing phosphorus, 122, 123.
— potential of phosphorus, 18.
Iron phosphides, 66.

LATENT heats, *see* under "Heats."
Lead phosphides, 64.
Lime, Phosphates of, *see* under "Calcium."

MANGANESE phosphides, 65.
Mass spectrum of phosphorus, 49, 50.
Matches, Composition of, 11.
Melting-point of phosphorus compounds, *see* under respective compounds.
— — red phosphorus, 33.
— — violet phosphorus, 35.
— — white phosphorus, 14, 15.
Mercury phosphides, 63.
Metallic salts, Reactions with phosphorus, 27, 28.
Metaphosphoric acid, *see* "Phosphoric acid, Meta-."
Metaphosphorous acid, 147.
Metaphosphoryl bromide, 112.
— chloride, 110.
Mineral phosphates, 1, 211–216.
Molar weights in liquid phosphorus, 16.
— — of gaseous phosphorus, 24.
— — of phosphorus compounds, *see* under respective compounds.
Molybdenum phosphides, 65.

NICKEL phosphides, 67.
Nitrilodiphosphoric acids, 202.
Nitrilotrimetaphosphoric acid, 202.

OCEANIC deposits, 208, 209.
Organic compounds of phosphorus, 56.
Oxidation of phosphorus, 27, 116–124, 126, 131.
Oxygen, Rate of absorption by phosphorus, 118, 119.
Oxyhalides of phosphorus, 105–112; *see* also "Phosphorus oxyfluoride," etc.
Ozone, Production of, by oxidation of phosphorus, 120.

PACKING effect for phosphorus atom, 49.
Parachors of phosphorus compounds, 53.
Perphosphoric acids, 184, 185.
Phosphate minerals, 208, 211–215.
Phosphates, Assimilation by plants, 209.
—, Circulation of, 209–210.
—, Distribution of, 214, 215.
—, Meta, 176–179.
— of lime, 218–222.
—, Ortho-, meta- and pyro-, 155.
—, World's production, 215, 216.
Phosphatic fertilisers, 209–218, 225–228.
Phosphide, Hydrogen, Liquid, 80.
—, —, Solid, 81, 82.
Phosphides, Metallic, *see* under respective metals.
Phosphine, 68–76.
Phosphines, Alkyl, 82–85.
Phosphites, Detection, 148–150.
Phosphites, Primary and secondary, 144, 145.
Phosphonium halides, 76–80.
Phosphoric acid, Meta-, 174, 175.
— —, Ortho-, Chemical properties, 166–168.
— — —, Crystalline, 158.
— — —, History, 155.
— — —, Physical properties, 158–166.
— — —, Preparation, 156–157.
— —, Physiological action, 169.
— —, Pyro-, 171–174.
— —, Uses, 169.
Phosphoric acids, Complex hetero-, 168.
— —, Dehydration, 170.
— —, Detection, 179–180.
— —, Estimation, 180–184.
— —, Poly-, 174.
Phosphorous acid, Chemical properties, 142–144.
— —, Preparation and physical properties, 140, 141.
Phosphorus, Alloys, 12.
—, Assimilation by plants, 209.
—, Atomic weight, 42–50.
—, Black, 40–42.
— bromides, 99–102.
— bromonitrides, 206.
—, Chemical reactions, 27–30.
— chlorides, 77 *et seq.*; *see* also "Phosphorus trichloride," etc.
— chloronitrides, 204–206.
—, Colloidal, 29.
— compounds, Use in medicine, 13.
—, Critical constants, 37.
—, Detection, 30.
— dichloride, 89.
—, Discovery, 5.
—, Estimation, 30.
— fluorides, 86 *et seq.*
— fluoroammoniate, 88.
— fluorobromide, 88, 89.
— fluorochloride, 88.
— halides, 45, 48, 86 *et seq.*
— in animal body, 4.
— — bones, 4, 210.
— iodides, 102–104.
— nitride, 206.
— oxides, 125–134.
— oxybromides, 111.
— oxychlorides, 106–109.
— oxyfluoride, 105, 106.
— oxyhalides, 105–112; *see* also under "Meta-," "Pyro-."
— oxyiodide, 112.
— oxysulphides, 192.
— pentabromide, 101, 102.
— pentachloride, 96–98.
— pentafluoride, 87, 88.
— pentoxide, 131–134.
—, Physiological action, 12, 13.
—, Red, Preparation, 10, 31.
—, —, General properties, 28, 29.
—, —, Physical properties, 32, 33.
—, Reducing action on metallic salts, 27, 28.

Phosphorus, Reduction to, by carbon, 5, 6.
—, Scarlet, 29.
— selenide, 195, 196.
— sulphides, 186–192.
— sulphoselenides, 196.
— tetritadecasulphide, 190–192.
— tetritaheptasulphide, 189, 190.
— tetritahexasulphide, 189.
— tetritatrisulphide, 187, 188.
— tetroxide, 130.
— thioamides, 203, 204.
— thioamido-acids, 192, 193.
— thioiodides, 115.
— thiotriamide, 203.
— thiotribromide, 114.
— thiotrichloride, 112, 113.
— thiotrifluoride, 112.
— triamide, 197.
— tribromide, 99–101.
— trichloride, 89–93.
— trifluoride, 86, 87.
— triiodide, 103.
— trioxide, 125–130.
— vapour, 23–27.
—, Violet, 33–40.
Phosphoryl chlorodibromide, 111.
— dichlorobromide, 110.
— monochloride, 110.
— tribromide, etc., *see* "Phosphorus oxybromide," etc.
See also under "Metaphosphoryl," "Pyrophosphoryl."
Plants, Phosphorus as constituent in, 4.
Platinum phosphides, 67.
Potassium phosphides, 60.
Pressure, Effect on melting-point of phosphorus, 38.
—, Effect on oxidation of phosphine, 74, 75.
—, — — — — phosphorus, 123.
Pyrophosphoric acid, *see* "Phosphoric acid, Pyro-."
Pyrophosphorous acid, 147, 148.
Pyrophosphoryl chloride, 109, 110.

RED phosphorus, 28, 32; *see* also "Phosphorus, Red."
Refractivity, Atomic, of combined phosphorus, 55.
— of gaseous phosphorus, 25.
— of liquid phosphorus, 17.
— of solid phosphorus, 17.
Rubidium phosphide, 61.

SCARLET phosphorus, 42; *see* also "Phosphorus, Scarlet."
Selenides of phosphorus, 195.
Selenophosphates, 196.
Signal lights, 12.
Silver phosphides, 61, 62.
— salts, Reactions with phosphorus, 28.
Sodium phosphides, 60.
Soils, Content of phosphorus, 4, 209.
Solubilities of phosphorus compounds, *see* under respective compounds.
— of white phosphorus, 19, 20.
Spectra of phosphorus and its compounds, 26.
— — — glow, 123, 124.
Stereochemistry of phosphorus compounds, 55, 56.
Strontium phosphides, 61.
Structure of phosphorus compounds, 52; *see* also under the respective acids, etc.
Superphosphates, 222 *et seq.*
Surface tension of liquid phosphorus, 23.
— — — phosphorus compounds, *see* under respective compounds.

TETRAPHOSPHORUS heptasulphide, 189, 190.
— trisulphides, 187 *et seq.*
Thioamidophosphoric acids, 202, 203.
Thiohalides of phosphorus, 112–115; *see* also "Phosphorus thiofluoride," etc.
Thiohypophosphates, 193.
Thiophosphates, 193–195.
Thorium phosphide, 64.
Tin phosphides, 64.
Titanium phosphides, 63, 64.
Tungsten phosphides, 65.

USES of phosphorus, 4–13.

VALENCY of phosphorus, 58, 59.
Vapour density of phosphorus, 23, 24.
— pressures of liquid phosphorus, 22.
— — — red phosphorus, 32, 33.
— — — violet phosphorus, 35.
Violet phosphorus, 33–35.
Volumes, Molar, of combined phosphorus, 51–53.
—, Specific, of liquid phosphorus, 21.

WATER, Action on phosphorus, 27.
White phosphorus, *see* under "Phosphorus."

X-RAY absorption by phosphites, 147.
— diffraction by black phosphorus, 41.

ZINC phosphides, 63.
Zirconium phosphides, 64.

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