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# A TEXT-BOOK OF
# INORGANIC CHEMISTRY.
## VOLUME VII. PART I.

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# A TEXT-BOOK OF
# INORGANIC CHEMISTRY.

EDITED BY

J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,
Carnegie Gold Medallist

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## THE PERIODIC TABLE.*

| PERIODS. | GROUP O. | GROUP I | GROUP II. | GROUP III. | GROUP IV. | GROUP V. | GROUP VI. | GROUP VII. | GROUP VIII |
|---|---|---|---|---|---|---|---|---|---|
| First short period | *2*<br>He<br>4 00 | *1*<br>H<br>1 008<br>*3*<br>Li<br>6·94 | *4*<br>Gl<br>9·1 | *5*<br>B<br>11 0 | *6*<br>C<br>12·005 | *7*<br>N<br>14·01 | *8*<br>O<br>16 00 | *9*<br>F<br>19·0 | |
| Second short period | *10*<br>Ne<br>20 2 | *11*<br>Na<br>23 00 | *12*<br>Mg<br>24·32 | *13*<br>Al<br>27·1 | *14*<br>Si<br>28·3 | *15*<br>P<br>31·04 | *16*<br>S<br>32 06 | *17*<br>Cl<br>35 46 | |
| First long period Even series | *18*<br>A<br>39 88 | *19*<br>K<br>39·10 | *20*<br>Ca<br>40·09 | *21*<br>Sc<br>44·1 | *22*<br>Ti<br>48 1 | *23*<br>V<br>51 0 | *24*<br>Cr<br>52·0 | *25*<br>Mn<br>54·93 | *26*<br>Fe<br>55·85<br>*27*<br>Co<br>58 97<br>*28*<br>Ni<br>58 68 |
| Odd ,, | | *29*<br>Cu<br>63·57 | *30*<br>Zn<br>65 37 | *31*<br>Ga<br>69 9 | *32*<br>Ge<br>72 5 | *33*<br>As<br>74·96 | *34*<br>Se<br>79·2 | *35*<br>Br<br>79 92 | |
| Second long period Even series | *36*<br>Kr<br>82·9 | *37*<br>Rb<br>85·45 | *38*<br>Sr<br>87·63 | *39*<br>Y<br>89·0 | *40*<br>Zr<br>90·6 | *41*<br>Cb<br>93 5 | *42*<br>Mo<br>96·0 | *43*<br>. | *44*<br>Ru<br>101 7<br>*45*<br>Rh<br>102 9<br>*46*<br>Pd<br>106 7 |
| Odd ,, | | *47*<br>Ag<br>107·88 | *48*<br>Cd<br>112·4 | *49*<br>In<br>114 8 | *50*<br>Sn<br>119·0 | *51*<br>Sb<br>120·2 | *52*<br>Te<br>127 6 | *53*<br>I<br>126·92 | |
| Third long period Even series | *54*<br>X<br>130·2 | *55*<br>Cs<br>132 81 | *56*<br>Ba<br>137·37 | *57–71*<br>THE RARE EARTH METALS. | *72*<br>. | *73*<br>Ta<br>181·5 | *74*<br>W<br>184 0 | *75*<br>. | *76*<br>Os<br>190 9<br>*77*<br>Ir<br>193 1<br>*78*<br>Pt<br>195 2 |
| Odd ,, | | *79*<br>Au<br>197·2 | *80*<br>Hg<br>200 6 | *81*<br>Tl<br>204 0 | *82*<br>Pb<br>207 20 | *83*<br>Bi<br>208·0 | *84*<br>Po | *85* | |
| Fourth long period | *86*<br>Nt<br>222·4 | *87*<br>.. | *88*<br>Ra<br>226·0 | *89*<br>Ac | *90*<br>Th<br>232 4 | *91*<br>Pa | *92*<br>U<br>238 2 | . | ... . |
| Formulæ of oxides | ... | $R_2O$ | $RO$ | $R_2O_3$ | $RO_2$ | $R_2O_5$ | $RO_3$ | $R_2O_7$ | $RO_4$ |
| Formulæ of hydrides | ... | $RH$ | $RH_2$ | $RH_3$ | $RH_4$ | $RH_3$ | $RH_2$ | $RH$ | .. |
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* The International Atomic Weights for 1918 are adopted in this Table Atomic numbers are in italics.

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

## VOLUME VII. PART I.

---

## OXYGEN.

BY

J. NEWTON FRIEND, AND DOUGLAS F. TWISS,
D.Sc.(B'ham), Ph.D.(Würz.), F.I.C. D.Sc.(B'ham), 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 0, 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 radicles 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 in 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 list.

The addition of the *Table of Dates of Issue of Journals* (pp. xix-xxvi) 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 Author desires to express his 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 and Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

*November* 1923.

# PREFACE.

OXYGEN is generally recognised as one of the most important elements known to science, and the literature referring to it is extraordinarily voluminous. Although the original intention was to issue Volume VII of this series in one part, it has been found necessary to divide it into three, the First Part dealing with oxygen alone, the Second with sulphur, selenium, and tellurium, whilst the remaining elements of Group VI are relegated to the Third Part.

The Authors desire to express their sincere thanks to many friends who have assisted them in one way or another in the preparation of this work. In particular they would thank Mr. J. H. Coste, who has afforded considerable assistance in the sections dealing with the solubilities of gases in water, and last, but not least, Professor Wheeler and the Council of the Chemical Society for permission to reproduce the very beautiful photographs in Plate I.

J. N. F.
D. F. T.

*November* 1923.

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# LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

| Abbreviated Title. | Journal. |
|---|---|
| *Afhandl. Fys. Kem.* | Afhandlingar 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, a 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, Beiblatter. |
| *Ann. Sci. Univ. Jassy* | Annales scientifiques de l'Université de Jassy. |
| *Arbeiten Kaiserl. Gesundheitsamte* | Arbeiten aus dem Kaiserlichen Gesundheitsamte. |
| *Arch. exp. Pathol. Pharmak.* | Archiv fur experimentelle Pathologie und Pharmakologie. |
| *Arch. Pharm.* | Archiv der Pharmazie. |
| *Arch Sci. phys. nat.* | Archives des Sciences physique et naturelles, Genève. |
| *Atti Acc. Torinò* | Atti della Reale Accademia delle Scienze di Torinò. |
| *Atti R. Accad. Lincei* | Atti della Reale Accademia Lincei. |
| *B.A. Reports* | British Association Reports. |
| *Ber.* | Berichte der Deutschen chemischen Gesellschaft. |
| *Ber. Deut. physikal. Ges.* | Berichte der Deutschen physikalischen Gesellschaft. |
| *Bot. Zeit.* | Botanische Zeitung. |
| *Bull. Acad. Sci. Cracow* | Bulletin international de l'Académie des Sciences de Cracovie. |
| *Bull. Acad. roy. Belg.* | Académie royale de Belgique—Bulletin de la Classe des Sciences. |
| *Bull. de Belg.* | Bulletin de la Société chimique Belgique. |
| *Bull. Soc. chim.* | Bulletin de la Société chimique de France. |
| *Bull. Soc. franc. 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 fur Mineralogie. |
| *Chem. Ind.* | Die Chemische Industrie. |
| *Chem. News* | Chemical News. |
| *Chem. Weekblad.* | Chemisch Weekblad. |
| *Chem. Zentr.* | Chemisches Zentralblatt. |
| *Chem. Zeit.* | Chemiker Zeitung (Cöthen). |
| *Compt. rend.* | Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris). |
| *Crell's Annalen* | Chemische Annalen fur die Freunde der Naturlehre, von L. Crelle. |
| *Dingl. poly. J.* | Dingler's polytechnisches Journal. |
| *Drude's Annalen* | Annalen der Physik (1900–1906). |
| *Electrochem. Met. Ind.* | Electrochemical and Metallurgical Industry. |

| ABBREVIATED TITLE. | JOURNAL. |
|---|---|
| *Eng. and Min. J.* | Engineering and Mining Journal. |
| *Gazzetta* | Gazzetta chimica italiana. |
| *Gehlen's Allg. J. Chem* | Allgemeines Journal der Chemie. |
| *Gilbert's Annalen* | Annalen der Physik (1799–1824). |
| *Giorn di Scienze Naturali ed Econ.* | Giornale di Scienze Naturali ed Economiche. |
| *Geol. Mag.* | Geological Magazine. |
| *Int. Zeitsch. Metallographie* | Internationale Zeitschrift fur Metallographie. |
| *Jahrb kk. geol. Reichsanst.* | Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt. |
| *Jahrb. Miner.* | Jahrbuch fur Mineralogie. |
| *Jahresber.* | Jahresbericht uber 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 fur 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. |
| *Mém. Paris Acad.* | Mémoires présentés par divers savants à l'Académie des Sciences de l'Institut de France. |
| *Mon. scient.* | Moniteur scientifique. |
| *Monatsh.* | Monatshefte fur Chemie und verwandte Theile anderer Wissenschaften. |
| *Munch. Med. Wochenschr.* | Munchener Medizinische Wochenschrift. |
| *Nature* | Nature. |
| *Nuovo Cim.* | Il nuovo Cimento. |
| *Öfvers. K. Vet.-Akad Forh.* | Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar. |
| *Oesterr. Chem. Zeit.* | Oesterreichische Chemiker-Zeitung. |
| *Pfluger's Archiv* | Archiv fur die gesammte Physiologie des Menschen und der Thiere. |
| *Pharm. Zentr.-h..* | Pharmazeutische Zentralhalle. |
| *Pharm. Post* | Pharmazeutische Post. |
| *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. |
| *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. |
| *Sitzungsber. K. Akad. Wiss. Berlin.* | Sitzungsberichte der Königlich Preussischen Akademie de Wissenschaften zu Berlin. |

| Abbreviated Title. | Journal. |
|---|---|
| *Sitzungsber. K. Akad. Wiss. Wien* | Sitzungsberichte der Koniglich bayerischen Akademie der Wissenschaften zu Wien. |
| *Sci. Proc. Roy. Dubl. Soc.* | Scientific Proceedings of the Royal Dublin Society. |
| *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* | Wiedermann'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 fur 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.

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| 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. |
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| 86 | 177 | ... | 2 | 40, 41 | . | 5 | 93, 94 | 6 | 27–29 | 25 | | 11, 12 | |
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| 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 |

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| 1890 | 12 | 39, 40 | 15 | 256–260 | 19–21 | 17, 18 | 228 | 23 | 3, 4 | 61, 62 | 6, 7 | ... | 14 | 110, 111 |
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| 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 |
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| 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 |
| 01 | 25, 26 | 11, 12 | 26 | 314–319 | 22–24 | 19, 20 | 239 | 34 | 25, 26 | 83, 84 | 28, 29 | ... | 25 | 132, 133 |
| 02 | 27, 28 | 13, 14 | 27 | 320–325 | 25–27 | (10) 1, 2 | 240 | 35 | 27, 28 | 85, 86 | 30, 31 | | 26 | 134, 135 |
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| 04 | 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 |
| 06 | 35, 36 | 21, 22 | 31 | 344–350 | 7–9 | 9, 10 | 244 | 39 | 35, 36 | 93, 94 | 38, 39 | | 30 | 142, 143 |
| 07 | 37, 38 | 23, 24 | 32 | 351–357 | 10–12 | 11, 12 | 245 | 40 | (4) 1, 2 | 95, 96 | 40, 41 | 4 | 31 | 144, 145 |
| 08 | 39, 40 | 25, 26 | 33 | 358–363 | 13–15 | 13, 14 | 246 | 41 | 3, 4 | 97, 98 | 42, 43 | 5 | 32 | 146, 147 |
| 09 | 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 |
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| 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 |
| 01 | 316 | 31 | 23 | 79, 80 | . | 13, 14 | 5 | 63, 64 | 33 | 20 | 22 | 57 | 63, 64, 65 | (6) 1, 2 |
| 02 | 317 | 32 | 24 | 81, 82 | | 15, 16 | 6 | 65, 66 | 34 | 21 | 23 | 58 | 65, 66, 67 | 3, 4 |
| 03 | 318 | 33 | 25 | 83, 84 | .. | 17, 18 | 7 | 67, 68 | 35 | 22 | 24 | 59 | 67, 68, 69 | 5, 6 |
| 04 | 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 |
| 06 | 321 | 36 | 28 | 89, 90 | . | 23, 24 | 10 | 73, 74 | 38 | 25 | 27 | 64, 65 | 73, 74, 75 | 11, 12 |
| 07 | 322 | 37 | 29 | 91, 92 | . | 25, 26 | 11 | 75, 76 | 39 | 26 | 28 | 66, 67 | 75, 76, 77 | 13, 14 |
| 08 | 323 | 38 | 30 | 93, 94 | .. | 27, 28 | 12 | 77, 78 | 40 | 27 | 29 | 68, 69 | 77, 78, 79 | 15, 16 |
| 09 | 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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| 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 |
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| 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 |
| 01 | 196, 197 | 2 | 17 | 68, 69 | 20 | 110 | 21 |  | 40 | 14 | 26–29 | 7 | 34–36 | 36–38 |
| 02 | 198, 199 | 3 | 18 | 69, 70 | 21 | 111 | 22 |  | 41 | 15 | 29–33 | 8 | 36, 37 | 39–42 |
| 03 | 200–202 | 4 | 19 | 71, 72 | 22 | 112 | 23 |  | 42 | 16 | 33–37 | 9 | 37–39 | 43–46 |
| 04 | 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 |
| 06 | 206 | 7 | 22 | A. 77. 78 | 25 | 115 | 26 |  | 45 | 19 | 48–52 | 12 | 42, 43 | 54–57 |
| 07 | 207 | 8 | 23 | 78, 79, 80 | 26 | 116 | 27 |  | 46 | 20 | 52–56 | 13 | 43 44 | 58–60 |
| 08 | 207–209 | 9 | 24 | 80, 81 | 27 | 117 | 28 |  | 47 | 21 | 56–60 | 14 | 44–46 | 61–64 |
| 09 | 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 |
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* Remainder of vol. 55 appeared in 1920.

A TEXT-BOOK OF

# INORGANIC CHEMISTRY.

VOLUME VII. PART I.

# A TEXT-BOOK OF INORGANIC CHEMISTRY.

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## VOL. VII. PART I.

## OXYGEN.

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## CHAPTER I.

## GENERAL CHARACTERISTICS OF THE ELEMENTS OF GROUP VI.

The elements of the sixth vertical group of the Periodic Table resemble those of the seventh in that they can be divided into two sections possessing non-metallic and metallic properties respectively. But whereas in Group VII. the non-metals—the so-called halogens—are sharply divided from the metals, in Group VI. the non-metals, beginning with oxygen, gradually acquire decidedly metallic properties as the atomic weight increases on passing through sulphur to selenium and tellurium. Although all the elements in Group VI. possess certain characteristics in common, or manifest interesting gradations in properties, the general relationships are not so marked as are those observed in each subsection.[1]

| Group VI. | |
|---|---|
| A. Chromium Group. | B. Oxygen Group. |
| | O |
| | S |
| Cr | |
| | Se |
| Mo | |
| | Te |
| W | |
| U | Po<br>(RaF) |

**Chemical Properties of Group VI.**—With the exception of oxygen, all the elements in Group VI. are solid at the ordinary temperature. Oxygen is a typical non-metal, but as passage is made through sulphur to selenium and tellurium, metallic properties become increasingly pronounced, the two latter elements being usually regarded as metalloids. All the elements in the chromium subsection are characteristically metallic, but, in common with most metals of more or less high atomic weight, they yield, in addition to basic oxides, others that can form fairly powerful acids, which yield well-defined salts. Such, for example, are the chromates, the molybdates, the tungstates, and the uranates.

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[1] The main characteristics of the elements of the chromium subdivision are dealt with in Chapter I. of Vol. VII., Part III. Those of sulphur, selenium, and tellurium are discussed in Volume VII., Part II. Polonium (Radium F) is dealt with in Vol. III.

In the accompanying table are listed a few of the more important types of compounds yielded by these elements. It will be observed that the maximum valency of the elements with regard to oxygen is numerically equal to six. An interesting link between tellurium—a heavy member of the oxygen subdivision—and uranium—the last of the chromium subdivision—is afforded by their union with sulphuric acid to form sulphates of the type $M(SO_4)_2$. The heaviest members of both subdivisions exhibit radioactivity.

| Type. | Oxygen | Sulphur. | Selenium. | Tellurium. | Chromium. | Molybdenum. | Tungsten. | Uranium. |
|---|---|---|---|---|---|---|---|---|
| $MH_2$ | $OH_2$ | $SH_2$ | $SeH_2$ | $TeH_2$ | .. | .. | .. | .. |
| MO | O.O | .. | ? SeO | TeO | CrO | .. | .. | .. |
| $MO_2$ | $O.O_2$ | $SO_2$ | $SeO_2$ | $TeO_2$ | $CrO_2$ | $MoO_2$ | $WO_2$ | $UO_2$ |
| $M_2O_3$ | . | $S_2O_3$ | ? $Se_2O_3$ | .. | $Cr_2O_3$ | .. | .. | .. |
| $MO_3$ | .. | $SO_3$ | $SeO_3$ | $TeO_3$ | $CrO_3$ | $MoO_3$ | $WO_3$ | $UO_3$ |
| $MCl_2$ | $OCl_2$ | $SCl_2$ | .. | $TeCl_2$ | $CrCl_2$ | $MoCl_2$ | $WCl_2$ | .. |
| $MCl_3$ | .. | .. | .. | .. | $CrCl_3$ | $MoCl_3$ | $(WCl_3)$ * | $UCl_3$ |
| $MCl_4$ | . | $SCl_4$ | $SeCl_4$ | $TeCl_4$ | .. | $MoCl_4$ | $WCl_4$ | $UCl_4$ |
| $MF_6$ | .. | $SF_6$ | $SeF_6$ | $TeF_6$ | .. | $MoF_6$ | $WF_6$ | $UF_6$ |
| $MOF_4$ | .. | .. | .. | .. | .. | $MoOF_4$ | $WOF_4$ | .. |
| $MOCl_2$ | .. | $SOCl_2$ | $SeOCl_2$ | $TeOCl_2$ | .. | .. | .. | .. |
| $MO_2Cl_2$ | .. | $SO_2Cl_2$ |  | .. | $CrO_2Cl_2$ | $MoO_2Cl_2$ | $WO_2Cl_2$ | $UO_2Cl_2$ |
| $H_2MO_3$ | .. | $H_2SO_3$ | $H_2SeO_3$ | $H_2TeO_3$ | .. | .. | .. | .. |
| $H_2MO_4$ | .. | $H_2SO_4$ | $H_2SeO_4$ | $H_2TeO_4$ | $H_2CrO_4$ | $H_2MoO_4$ | $(H_2WO_4)$† | $(H_2UO_4)$† |
| $M(SO_4)_2$ | .. | .. | .. | $Te(SO_4)_2$ | .. | .. | .. | $U(SO_4)_2$ |
| $MAg_2$ | $OAg_2$ | $SAg_2$ | $SeAg_2$ | $TeAg_2$ | .. | .. | .. | .. |
| $M_2C$ | $O_2C$ | $S_2C$ | .. | .. | .. | .. | .. | .. |
| MN | ON | $(SN)_4$ | SeN | TeN | .. | .. | .. | .. |

## THE OXYGEN SUBDIVISION.

**Atomic Weights.**—When the elements are arranged in the order of their atomic weights, several arithmetical regularities become apparent. As long ago as the beginning of last century the attention of chemists had been drawn to the fact that certain triads of elements exist which exhibit not only a close similarity in their chemical and physical properties, but also an interesting regularity in their atomic weights.[1] For several years, however, the subject was allowed to drop into abeyance until Dumas, in 1851, again brought it to the fore,[2] and both he and other chemists rapidly added to the list of regularities. Sulphur, selenium, and tellurium were typical. At first it was hoped that all the elements might ultimately be grouped into triads, and that in this way a complete system of classifying the elements might be evolved, inasmuch as the Periodic Classification had not as yet been introduced. These hopes were, however, doomed to failure, and a severe blow was struck at the utility of the triads when Cooke[1] showed that some of them actually broke into natural groups of elements. The halogens are a case in point, for chlorine, bromine, and iodine are but three out of four closely similar elements, and no system of classification that deals with these to the exclusion of fluorine can be regarded as satisfactory. A similar objection applies to the elements now under discussion, for whilst it is true that sulphur, selenium, and tellurium resemble each other very closely, a remarkable analogy exists between them and oxygen, these four elements thus constituting a natural tetradic group.

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* In combination only. † Salts are well known.

[1] Doebereiner, *Gilbert's Annalen*, 1817, 57, 436; *Pogg. Annalen*, 1829, 15, 301. See also *Gilbert's Annalen*, 1816, 56, 332, which contains a report by Wurzer on Doebereiner.

[2] Dumas, *British Assoc. Reports*, 1851, *Compt. rend.*, 1857, 45, 709; 1858, 46, 951; 1858, 47, 1026.

Many triads exhibit an interesting relationship between the numerical values of their atomic weights, the mean of the first and third being almost identical with the middle value. The sulphur triads are no exception to this rule as is evidenced by the following table:

| Element. | Atomic weight. | Difference. | Mean of extreme atomic weights. |
|---|---|---|---|
| Lithium . . . | 6·94 | 16·06 | **23·02** |
| Sodium . . . | **23·00** | 16·10 | |
| Potassium . . | 39·10 | | |
| Calcium . . . | 40·07 | 47·56 | **88·72** |
| Strontium. . . | **87·63** | 49·74 | |
| Barium . . . | 137·37 | | |
| Sulphur . . . | 32·06 | 47·14 | **79·78** |
| Selenium . . . | **79·2** | 48·3 | |
| Tellurium . . . | 127·5 | | |
| Chlorine . . . | 35·46 | 44·46 | **81·19** |
| Bromine . . . | **79·92** | 47·00 | |
| Iodine . . . | 126·92 | | |

Dumas also noticed that, if oxygen and the sulphur triads are considered together, the approximate atomic weights may be arranged as follow:

| O | S | Se | Te |
|---|---|---|---|
| 16 | 16+16 | 16+16+3×16 | 16+16+2×3×16 |

Such arithmetical connections might be regarded as a curious chance, were it not for the fact that many other analogous relationships occur amongst the elements.

**Physical Properties.**—Oxygen, in common with most of the elements in the first short horizontal series of the Periodic Table, exhibits several marked contrasts with the remaining elements in its own vertical group, and to these attention is directed in the sequel. Tellurium, again, is not typical of the group, partly in consequence of its increased tendency to resemble the metals. There is thus the most marked resemblance between sulphur and selenium. The following table indicates a series of interesting gradations in physical properties with increasing atomic weight.

---

[1] J. P. Cooke, *Amer. J. Sci.*, 1854, 17, 387.

| | Oxygen. | Sulphur. | Selenium. | Tellurium. |
|---|---|---|---|---|
| Atomic weight . | 16 00 | 32·06 | 79·2 | 127·5 |
| Colour (solid) . | Bluish | Pale yellow | Red and grey | Silvery grey |
| Density (solid) . | 1·426 | 1·96–2·07 | 4·8 (grey) | 6·2 (approx.) |
| Melting-point, ° C. | –219 | 110–119 | 217 (grey) | 455 |
| Boiling-point, ° C. | –183 | 444 | 690 | At bright red heat |

**Allotropy.**—All of the elements exhibit allotropy. Oxygen yields two gaseous allotropes, namely, ordinary oxygen and ozone. These can co-exist at room temperatures for indefinite periods without manifesting any tendency to reach a stage of chemical equilibrium.

Sulphur does not exhibit allotropy in the gaseous condition in the ordinary acceptation of the term, although vapour density measurements indicate considerable polymerisation at temperatures near the boiling-point, the vapour apparently consisting of $S_8$, $S_6$, $S_4$, $S_2$, and even $S_1$ molecules in varying proportions according to circumstances.[1] Selenium vapour yields closely similar results; below 550° C. it contains a small proportion of $Se_8$; between 550° and 900° C. it consists essentially of $Se_2$ and $Se_6$ molecules; above 900° C. it is mostly $Se_2$, with possibly a few $Se_1$ molecules.[2]

Liquid oxygen does not appear to manifest additional allotropy, but three allotropes of sulphur are recognised as existing in equilibrium in the liquid state. This phenomenon is termed *dynamic* allotropy, the allotropes being designated as $S\lambda$, $S\mu$, and $S\pi$ respectively. $S\lambda$ is a yellow, mobile liquid containing, it is believed, eight atoms within its molecule, whilst $S\mu$ is a thick, viscous liquid, formula $S_6$. $S\pi$ is probably tetratomic, $S_4$. The percentage of $S\mu$ rises with the temperature.[3] Thus:

| Temperature, ° C. . | 120 | 140 | 180 | 220 | Boiling-point |
|---|---|---|---|---|---|
| $S\mu$ per cent. . . | 0·1 | 1·3 | 20·4 | 32·2 | 36·9 |
| $S\lambda$ do. . . . | 96·4 | 93·7 | 73·1 | 62·7 | 59·1 |

The freezing-point of the liquid accordingly varies both with the nature of the solid phase that separates and with the percentage of $S\mu$ and in $S\pi$ the liquid.

Liquid selenium appears to exhibit allotropy, but tellurium does not.

In the solid form all four elements exhibit allotropy. Three forms of oxygen are recognised, namely, $\alpha$, $\beta$, and $\gamma$, the transition points being as follow:[4]

$$\alpha \underset{-249\cdot5^\circ\text{ C.}}{\rightleftharpoons} \beta \underset{-230\cdot5^\circ\text{ C.}}{\rightleftharpoons} \gamma$$

---

[1] Preuner and Schupp, *Zeitsch. physikal. Chem.*, 1909, 68, 129.

[2] Preuner and Brockmöller, *ibid.*, 1912, 81, 129.

[3] See this Vol., Part II. Also this series, Vol. I., p. 67.

[4] See p. 48.

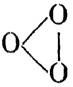
Sulphur exists in a variety of forms, two of which are crystalli namely, the rhombic and monoclinic allotropes.

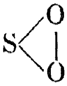
Solid selenium likewise exists in several allotropic forms. The crystalline variety is labile, and may possibly occur in two modification both of which are monoclinic.[2] The grey crystalline form appears consist of two varieties, $Se_A$ and $Se_B$, in dynamic equilibrium with ea other.[1] Solid tellurium manifests allotropy, but to a much less p nounced degree.

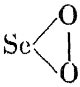
**Chemical Properties.**—Sulphur, selenium, and tellurium bu with blue flames yielding dioxides. If ozone is regarded as a dioxi the series may be represented as follows :

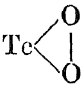
$$O{=}O{=}O \qquad O{=}S{=}O \qquad O{=}Se{=}O \qquad O{=}Te{=}O$$

in which the central atoms are regarded as tetravalent. Cyclic schen may, however, be preferred :









The dioxides (save ozone) dissolve in water to form weak aci $H_2SO_3$, $H_2SeO_3$, and $H_2TeO_3$, the salts of which may be regarded analogous to the ozonates. Thus :

| $K_2O.O_3$ | $K_2SO_3$ | $K_2SeO_3$ | $K_2TeO_3$ |
|---|---|---|---|
| Potassium ozonate, $K_2O_4$. | Potassium sulphite. | Potassium selenite. | Potassium tellurite. |

The dioxides vary considerably in stability, ozone, $O.O_2$, t analogue of $SO_2$, etc., being exceptionally unstable. The heats formation of aqueous solutions of sulphurous, selenous, and tellur acids are as follow :[3]

$$(S, O_2, Aq.)=78{,}780 \text{ calories.}$$
$$(Se, O_2, Aq.)=56{,}160 \quad ,,$$
$$(Te, O_2, Aq.)=77{,}180 \quad ,,$$

The heats of formation of aqueous solutions of the more hig oxygenated acids manifest a similar minimum with selenium :

$$(S, O_3, Aq.)=142{,}410 \text{ calories.}$$
$$(Se, O_3, Aq.)=\ 76{,}660 \quad ,,$$
$$(Te, O_3, Aq.)=\ 98{,}380 \quad ,,$$

The dioxides of sulphur, selenium, and tellurium admit of oxidati to the trioxides $SO_3$, $SeO_3$, and $TeO_3$, which dissolve in water to yi the corresponding acids, sulphuric acid being the strongest and tellu the weakest. An analogy may be found with oxygen in the case of oxozonides. Oxygen is strictly non-metallic, but selenium, and t greater extent tellurium, possess many pronounced metallic properti and are thus amphoteric elements. Thus the dioxide $TeO_2$ can funct as an acidic oxide, as mentioned above, or as a basic oxide, yield with sulphuric acid, tellurium sulphate $Te(SO_4)_2$. The gradual tr sition from non-metallic to metallic properties is evidenced in interesting manner by the gradual fall in the heat of union of the elements with hydrogen. Thus :[1]

---

[1] Kruyt, *Zeitsch. anorg. Chem.*, 1909, 64, 305.

[2] Muthmann, *Zeitsch. Kryst. Min.*, 1890, 70, 353.

[3] Thomsen, *Thermochemistry.* Translated by Burke (Longmans, 1908).

| Element . . . . | O | S | Se | Te |
|---|---|---|---|---|
| Heat of combination (Calories) | 68·4[2]<br>58·0[3] | 4·8[4]<br>2·7[5] | −25·1 | −34·9 |

With positive elements, other than hydrogen, definite compounds are usually formed, analogous in composition to oxides. Thus, with silver—

| $Ag_2O$ | $Ag_2S$ | $Ag_2Se$ | $Ag_2Te$ |
|---|---|---|---|
| Oxide. | Sulphide. | Selenide. | Telluride. |

The sulphur triads combine with fluorine to yield well-defined hexafluorides, but oxygen appears to be entirely unable to unite with fluorine to form any kind of compound.

| Element . . . | Oxygen | Sulphur | Selenium | Tellurium |
|---|---|---|---|---|
| Compound . . . | .. | $SF_6$ | $SeF_6$ | $TeF_6$ |
| Boiling-point ° C. . | .. | −62 | 39 | 35·5 |

All of these compounds are stable gases, exhibiting the maximum valency of the elements. They neither attack glass nor decompose spontaneously. The selenium and tellurium fluorides attack mercury making it adhere to glass, and in this respect they resemble ozone. Sulphur hexafluoride does not do this.

**Isomorphism.**—Although potassium tellurate, $K_2TeO_4$, is not isomorphous with the corresponding sulphate,[6] the hydrogen rubidium salts of selenic and telluric acids are isomorphous.[7]

Sulphuric, selenic and telluric acids yield double salts with alkali and certain divalent metals, which salts have the general formula

$$M_2'RO_4 \cdot M''RO_4 \cdot 6H_2O$$

where R stands for chromium or a sulphur triad ; M′ for ammonium or an alkali metal, and M″ for iron (ferrous), cobalt, nickel, manganese, copper, cadmium, magnesium, or zinc. These are isomorphous with one another. Both sulphur and selenium (but not tellurium) yield alums which are isomorphous, and of the general type

$$M_2'RO_4 \cdot M_2''(RO_4)_3 \cdot 24H_2O$$

where R stands for sulphur or selenium.

**Valency.**—All the elements have a valency of two in respect to hydrogen; that is, they possess two free negative valences, as witness the compounds

$$H_2O \qquad H_2S \qquad H_2Se \qquad H_2Te.$$

These exhibit a steady fall in stability with rise in molecular weight.

The following *per* derivatives are also known :

$$H_2O_2 \qquad H_2S_2.$$

[1] Thomsen, *Thermochemistry.* Translated by Burke (Longmans, 1908).

[2] To water at 18° C.

[3] To water-vapour at 18° C.

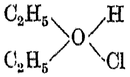
[4] From amorphous sulphur.

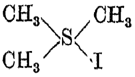
[5] From rhombic sulphur.

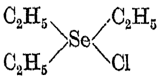
[6] Staudenmaier, *Zeitsch. anorg. Chem.*, 1895, **10**, 189.

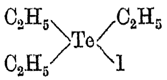
[7] Pellini, *Atti R. Accad. Lincei*, 1906, [5], **15**, i., 629, 711 ; ii. 46.

The elements yield tetravalent derivatives in special circumstances, in which they function as the basic elements. In the case of oxygen they are termed *oxonium* salts ; sulphur yields sulphonium salts ; whilst selenium and tellurium offer an even wider range of derivatives. Thus, the following types of compounds are now well known :


Di-ethyl
oxonium
chloride.


Tri-methyl
sulphonium
iodide.


Tri-ethyl
selenium (or selenonium)
chloride.


Tri-ethyl
tellurium
iodide

**Contrasts.**—Whilst these undoubted analogies exist between oxygen and the sulphur triads, there are many directions in which oxygen differs from these elements. This is by no means an uncommon phenomenon in connection with the first element and its successors in a vertical column of the Periodic Table.

Thus, for example, the boiling-points of the hydrides of sulphur, selenium, and tellurium steadily fall with the atomic weights of the electro-negative elements :

| | $H_2Te$ | $H_2Se$ | $H_2S$ |
|---|---|---|---|
| Boiling-point ° C. . | 0 | −42 | −62 |

The boiling-point of water, therefore, should be, if the analogy were followed, of the order of −70° C. instead of its actual value of 100° C. This is undoubtedly due to association (see Chap. X.).

# CHAPTER II.

## OXYGEN.

Symbol, O. Atomic weight, 16·000.

**Occurrence.**—Oxygen is the most abundant element in the earth. It is present in the uncombined state in the atmosphere to the extent of approximately 23 per cent. by weight (see Chap. VI.), but this amount is relatively minute when the immense quantities of oxygen in various forms of combination are considered. The sea contains roughly 86 per cent. and the earth's crust nearly 48 per cent. by weight of this element; indeed, it has been computed that almost exactly one-half of the mass of the whole earth (including the ocean and the atmosphere) is due to oxygen.[1] From the results of spectrum analysis it is probable that uncombined oxygen is also present in the sun.[2]

**History.**—From ancient writings it appears that the Chinese, already in the eighth century, recognised that a substance, on burning, combined with one of the constituents of the air; it was also realised that this constituent of the atmosphere was present in water, and that it could be obtained in a pure condition by heating certain minerals.[3] In Europe it was not until the middle of the seventeenth century that the atmosphere was regarded as a mixture of which one of the ingredients played an important part in combustion, respiration, and the change in colour of the blood. It was understood by Hooke (1665) and Mayow (1674) that saltpetre contains a substance of somewhat similar properties, but although the observation that saltpetre, when heated to decomposition, gives a vigorous evolution of gas was made only a little later, the actual discovery of oxygen was delayed until the next century, when the experimental methods first introduced by Mayow in 1674[4] for the collection of gases began to bear fruit. The gas was first prepared and recognised as a new substance[5] by the Swedish chemist Scheele[6] about the year 1771 as the result, amongst other methods, of heating red mercuric oxide or "mercurius calcinatus per se" by concentrating the sun's rays upon it with a lens. He termed the gas *empyreal* or *fire air*, and also showed that the same gas could be obtained from the yellow oxide produced by precipitation of a mercuric salt from aqueous solution on addition of an alkali. Unfortunately for himself these results were not published for some four years after their discovery, and in the meantime, namely on 1st August 1774, the English chemist Priestley,[1] independently discovered oxygen, likewise by heating mercuric oxide. He communicated his results to Lavoisier in Paris in October of the same year, and shortly afterwards his discovery received general publication.

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[1] Stoney, *Phil. Mag.*, 1880, [5], 47, 565; Clarke (this series, Vol. I., p. 8) gives 19·8 per cent.; Fersmann (*Bull. Acad. Sci. Petrograd.*, 1912, p. 367) estimates 53·81 per cent.

[2] Draper, *Amer. J. Sci.*, 1877, 14, 89; Trowbridge, *Phil. Mag.*, 1902, 4, 156; Meissner, *Physikal. Zeitsch.*, 1914, 15, 668.

[3] Duckworth, *Chem. News*, 1886, 53, 250.

[4] See *Alembic Club Reprints*, No. xvii.

[5] Hales had, as early as 1727, prepared oxygen by heating potassium nitrate, but although he collected the gas over water and measured its volume, he did not recognise it as a new gas or determine its properties.

[6] Scheele, *Crell's Annalen*, 1785, 2, 229, 291; *Chemische Abhandlung von der Luft und dem Feuer* (Upsala, 1777). See *Alembic Club Reprints*, No. viii. (1891); Ortwed, Speter, and Jorgensen, Ahren's *Sammlung*, 1909, 14, 111. Scheele, *Nachgelassene Briefe und Aufzeichnungen*, Nordenskiold (Stockholm, 1892).

**The Theory of Phlogiston.**—In order to appreciate the enormous influence which the discovery of oxygen was destined to exert upon the further progress of chemistry, it is necessary to gain some idea of the views then prevalent as to the nature of combustion.

It is undoubtedly a fact that neither Scheele nor Priestley realised the important part played in combustion processes by the gas they had discovered.

By gradual modification the ancient Aristotelean idea of fire, as one of the four "elements" of nature, had merged into the assumption that all substances capable of burning contained a common combustible constituent or "principle." For several centuries sulphur appears to have been regarded as this principle, and its presence was postulated in all metals capable of being burnt or calcined in air. Becher,[2] however, in 1669 took exception to this latter view, maintaining that sulphur owed its combustibility to the fact of its containing a large amount of combustible principle, but that sulphur itself was not that principle. He therefore gave the name *terra pinguis* or "oily earth" to the last named, and explained the calcination of metals by heating in air as due to the expulsion of terra pinguis. What, precisely, this terra pinguis might be, whether of a material or non-material nature, Becher did not say. Perhaps he regarded it as of a spiritual nature, like flame itself, and somewhat defying conventional definition. His views were accepted and amplified by Stahl, who, *c.* 1697, introduced the word *phlogiston* (Greek *φλογίζειν*, to set on fire) to denote the active principle producing fire. Like Becher, Stahl hesitated to define exactly the nature of his phlogiston. It corresponded to the terra pinguis of Becher and the sulphur of the earlier chemists. Any substance that would burn was regarded as being rich in phlogiston, and carbon was considered to be nearly pure phlogiston.

When metals are calcined in air, oxides are usually produced. This was explained by Stahl on the supposition that the metal, on being heated, parted with its phlogiston, leaving a residue of *calx*.[3]

In the light of this idea a metallic calx or oxide was of simpler composition than the metal itself. Thus

$$\text{metal} = \text{calx} + \text{phlogiston}.$$

Further, reducing agents such as charcoal were substances which, being rich in phlogiston, could restore this to the metallic oxide and so regenerate the metal. In accordance with these views, Priestley named the gas which he obtained from mercuric oxide, *dephlogisticated air* as an expression of the readiness with which substances burned in or imparted phlogiston to it; nitrogen, on the other hand, which appeared incapable of supporting combustion, was regarded as being already saturated with phlogiston, and was termed by Priestley *phlogisticated air.*

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[1] Priestley, *Experiments and Observations on Different Kinds of Air*, 1774, ii., 28. See *Alembic Club Reprints*, No. vii. (1894); Freund, *The Study of Chemical Composition*, chapter i. (Camb. Univ. Press, 1904).

[2] Becher, *Physica Subterranea*, 1669.

[3] Latin, *calx*, lime. The process of "burning" chalk to form lime was known to the ancients, and as the result of analogy the term calx was used to designate the residue of oxide obtained after "burning" a metal.

The theory of phlogiston was, during the eighteenth century, exceedingly popular amongst chemists, despite the fact that it was full of anomalies. For example, if phlogiston were a material substance it is evident, from the equation given above, that a metal must weigh more than its calx. If phlogiston were non-material, the metal and calx would possess equal weight. But Jean Rey[1] had already, in 1630, shown that lead and tin *increase* in weight when calcined, and Bayen,[2] in 1774, found that on heating mercury calx to a sufficiently high temperature, metallic mercury is obtained, accompanied by a *diminution* in weight.[3] Both of these facts are in direct opposition to the phlogistic theory.

Again, Stahl himself was not unaware of the fact that carbon would not burn in the absence of air, although, as mentioned above, he regarded it as almost pure phlogiston. The explanation offered was that phlogiston could not leave a substance unless it had somewhere to go. The air, however, could act as a sponge and absorb the phlogiston, and thus enable combustion to proceed. Such an explanation is, of course, inadequate in the case of the calcination of metals since no account is taken of the reduction in volume that invariably ensues.

It was reserved for Lavoisier to discover the true cause of combustion. Having satisfied himself that metals do increase in weight upon calcination, he definitely proved that this is due to their combining with Priestley's dephlogisticated air, and was thus led to discard the idea of a special principle of combustibility such as phlogiston. A new name was therefore necessary for Priestley's gas, and Lavoisier first called it "eminently pure air," but later *oxygen* (French *oxygène*), in his belief that the element was an essential constituent of all acids.[4] The German name *Sauerstoff* embodies the same idea. Although subsequent research has demonstrated the inaccuracy of this assumption, the names have retained their popularity.

## PREPARATION OF OXYGEN.

**Physical Processes.**—The atmosphere, as a comparatively simple gaseous mixture, naturally suggests itself as a source of oxygen. There are various physical methods available for the separation of two such gases as nitrogen and oxygen, chief among which are the following:

1. *Liquefaction.*—When liquid air is allowed to evaporate, the escaping vapour is exceedingly rich in nitrogen since this gas has a lower boiling-point (namely, 195·67° C.) than oxygen (b.-pt., 182·9° C.).

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[1] See *Alembic Club Reprints,* No. xi.

[2] Bayen, *J. Physique,* 1774, 3, 135, 281.

[3] Bayen did not examine the gas evolved in this process, or he would probably have recognised it as a new gas, and thus forestalled Priestley's discovery of oxygen.

[4] From the Greek, ὀξύς, sour, and γεννάω, I produce.

The residual liquid in consequence becomes increasingly richer in oxygen as evaporation proceeds. This has been made the basis of a very successful commercial method for the preparation of oxygen.[1]

2. *Solubility.*—Oxygen is approximately twice as soluble in water as nitrogen, hence it follows that water, upon exposure to air, will absorb twice as much oxygen in proportion to nitrogen as corresponds to the partial pressures of these gases. If now the dissolved gases are expelled from the water by boiling or by the aid of a vacuum pump the resulting "air" will contain roughly one part of oxygen to two parts of nitrogen by volume. By repeating these processes several times, fairly pure oxygen can be isolated. Mallet,[2] in 1869, took out a patent for the commercial preparation of oxygen based on the foregoing principle. He found that after eight absorptions with water under pressure, a gas containing 97·3 per cent. of oxygen could be obtained. His results for successive absorptions were as follows:

| No. of absorptions | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| Percentage of oxygen | 21 | 33·3 | 47·5 | 62·5 | 75·0 | 85·0 | 91·0 | 95·0 | 97·3 |
| Percentage of nitrogen, etc. | 79 | 66·7 | 52·5 | 37·5 | 25·0 | 15·0 | 9·0 | 5·0 | 2·7 |

At the present time this method does not appear to have any commercial importance.[3] The relative solubilities of oxygen and nitrogen in various other solvents have been determined,[4] but the results do not encourage the idea that oxygen can be obtained any more readily than by the employment of water.

3. *Transfusion.*—Thin layers of caoutchouc allow oxygen to diffuse through them about $2\frac{1}{2}$ times as rapidly as nitrogen, and a rough separation of the gases can be effected in this manner.[5]

4. *Absorption in Charcoal.*—When coconut charcoal is cooled to −185° C., and exposed to pure, dry air, it absorbs oxygen more readily than nitrogen, and the gas recovered at 15° C. contains some 56 per cent. of oxygen. If allowed to escape slowly, the absorbed gas can be fractionated, the later fractions containing as much as 84 per cent. of oxygen.[6]

It is also possible to separate oxygen and nitrogen by taking advantage of their differences in density as, for example, by direct diffusion through some inert, porous material, when the gases pass through at rates consonant with Graham's Law; or by centrifugal force.[7]

**Chemical Processes.**—The majority of the methods for obtaining oxygen fall into this category, and may be classified according to whether the parent substance is a normal oxide, a higher oxide, or a more complex oxygenated compound. Several of the processes can be extended to serve as methods for the extraction of atmospheric oxygen.

A. *Preparation of Oxygen from Normal Oxides.*—Water.—Perhaps the most important process by which water can be made to yield its oxygen in a free state consists in electrolysis in the presence of an alkaline substance such as potassium carbonate or an alkali hydroxide. The oxygen obtained in this manner, if due precautions are observed, presents a high degree of purity, and is hence particularly suitable for metal cutting and welding (see p. 135). Care must be taken to avoid contamination with hydrogen during the process, owing to the dangerously explosive nature of the mixture.

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[1] For details see p. 31.

[2] Mallet, *Dingl. Poly. J.*, 1871, 199, 112; *English Patent*, 2137 (1869).

[3] See also Kubierschky, *English Patent*, 17780 (1899); Humphrey, *ibid.*, 14809 (1905); Lévy, *ibid.*, 5931 (1909).

[4] Claude, *Compt. rend.*, 1900, 131, 447.

[5] Graham, *J. Chem. Soc.*, 1865, 18, 9. See also d'Arsonval, *Compt. rend.*, 1899, 128, 1545. Several processes based on this principle have been patented. See Hélouis, *English Patent*, 2080 (1881); Neaver, *ibid.*, 6463 (1890); de Villepique, Fournier, and Shenton, *ibid.*, 19044 (1896); Bartelt, *ibid.*, 24428 (1906).

[6] Dewar, *Compt. rend.*, 1904, 139, 261; *Ann. Chim. Phys.*, 1904, [8], 3, 12. See also Montmagnon and de Laire, *Bull. Soc. chim.*, 1869, 11, 261.

[7] Bredig, *Zeitsch. physikal. Chem.*, 1895, 17, 459.

For laboratory purposes a glass apparatus after the principle of a Kipp may be conveniently used. The electrolyte consists of a 30 per cent. solution of sodium hydroxide, whilst sheet-nickel plates serve as electrodes. The inner electrode functions as anode and the supply of oxygen regulates itself automatically, the liquid in the inner space surrounding the anode being gradually expelled, as in Kipp's apparatus, as the pressure of the gas above increases, until the anode is left high and dry, when, of course, electrolysis ceases.[1] Very pure oxygen may be obtained by the electrolysis of barium hydroxide solution. To a certain extent the electrolysis of water is used for the commercial preparation of oxygen.[2] To this end, containing vessels of iron are used, the electrodes consisting of this metal or of nickel. The electrolyte consists of 15 per cent. caustic soda solution, and the liberated hydrogen and oxygen are collected in separate dome-shaped vessels under a pressure of some 60 mm. of water. A higher pressure cannot safely be employed owing to the danger of mixing. By means of a metallic partition between the electrodes, this danger is still further minimised. The containing vessels are packed in wooden boxes with sand, whereby the heat of the reaction is conserved, the temperature rising to about 70° C. Each vessel yields 110 litres of oxygen per hour of purity 97 per cent.[3] Dilute solutions of acids, particularly sulphuric acid, may be employed instead of alkalies, but the latter are preferable.

Electrolytic oxygen may contain as much as 4 per cent. of hydrogen. This may be removed as water by passage over platinised asbestos.[4]

Attempts have been made to cheapen the process by producing electrolytic oxygen without the simultaneous liberation of hydrogen by the adoption of depolarising electrolytes, or cathodes; also of cathodes which absorb hydrogen and may subsequently be employed as elements in gas cells.[5]

At high temperatures steam dissociates into hydrogen and oxygen, and these gases admit of isolation by taking advantage of the greater velocity of diffusion of the hydrogen as explained on p. 287. This by no means constitutes a convenient method of preparing oxygen, but the process may be facilitated by the introduction of some substance capable of uniting with the hydrogen. Thus steam is readily decomposed by chlorine when the two are passed through a red-hot porcelain tube. The reaction is accelerated by the presence of fragments of porcelain in the tube to increase the heating surface.

$$2H_2O + 2Cl_2 = 4HCl + O_2.$$

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[1] See Ruhstrat, *Zeitsch. angew. Chem.*, 1912, 25, 1277.

[2] See *Zeitsch. Elektrochem.*, 1901, 7, 857.

[3] The resistance of each cell is 2·8 volts. A current of 600 amperes is supplied, the theoretical yield of oxygen from which is 125 litres per hour.

[4] Moser, *Zeitsch anorg. Chem.*, 1920, 110, 125.

[5] See Coehn, *German Patent*, 75930 (1893); Brianchon, *French Patent*, 439737 (1912).

The hydrochloric acid may be absorbed by passage of the resulting gases through water or caustic soda solution.

Silver oxide, $Ag_2O$, is readily decomposed by heat, evolving oxygen, and the characteristic change in colour from brown to silver-white renders the reaction particularly suitable for lecture demonstration. The equilibrium pressures of oxygen have been measured up to 800° C., and are found to conform with the following law :

$$\log p = 6{\cdot}2853 - 2859/T$$

where $p$ is the pressure in atmospheres, and T the absolute temperature.[1]

The decomposition of mercuric oxide by heat has already been mentioned as the method by which Priestley was led to the discovery of oxygen. The oxide, which is yellow or brick red in colour, first becomes black—a reversible, physical effect. Oxygen is then evolved and a sublimate of mercury collects on the cooler parts of the containing vessel. The reaction is reversible, thus :

$$2HgO \rightleftharpoons 2Hg + O_2.$$

In the following table are given the dissociation pressures of mercuric oxide between 360° and 480° C.[2]

| Temperature, ° C. | Pressure, mm. | Temperature, ° C. | Pressure, mm. |
|---|---|---|---|
| 360 | 90 | 440 | 642 |
| 380 | 141 | 460 | 1017 |
| 400 | 231 | 480 | 1581 |
| 420 | 387 | .. | .. |

The rate of decomposition is accelerated by suitable catalysts such as finely-divided platinum, ferric oxide, and manganese dioxide. Aluminium and stannic oxides are apparently without effect.

The normal oxides of several other metals behave in an analogous manner to mercuric oxide. Thus palladous oxide, PdO, decomposes when heated, yielding metallic palladium and oxygen,[3] the reaction being reversible :

$$2PdO \rightleftharpoons 2Pd + O_2.$$

At 877° C. the dissociation pressure of the oxide is 760 mm.

In the case of auric oxide, $Au_2O_3$, the reaction is not reversible. When heated at 150° to 165° C., oxygen is evolved and aurous oxide, AuO, remains. At 250° C. this latter oxide is completely converted into metallic gold.[4] Similarly, platinum dioxide, $PtO_2$, upon ignition evolves oxygen, a residue of metallic platinum being obtained together with a solid solution of either the monoxide or sesqui-oxide in the dioxide.[5]

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[1] Keyes and Hara, *J. Amer. Chem. Soc.*, 1922, 44, 479 ; Lewis, *Zeitsch. physikal. Chem.*, 1906, 55, 449.

[2] Taylor and Hulett, *J. Physical Chem.*, 1913, 17, 565.

[3] Wöhler, *Zeitsch. Elektrochem.*, 1906, 12, 781 ; 1905, 11, 836.

[4] See Krüss, *Annalen*, 1887, 237, 296 ; *Ber.*, 1886, 19, 2541.

[5] Wöhler and Frey, *Zeitsch. Elektrochem.*, 1909, 15, 129.

When chlorine is passed over zinc oxide at a high temperature oxygen is evolved, zinc chloride remaining behind.

$$2ZnO+2Cl_2=2ZnCl_2+O_2.$$

Oxides of the alkaline earth metals, namely $CaO$, $SrO$, and $BaO$, may be similarly employed, as also litharge, $PbO$, and cadmium oxide, $CdO$.[1]

B. *Preparation of Oxygen from Higher Oxides.* In addition to their normal ones, many metals yield oxides in which the percentages of oxygen are greater than correspond to the valencies of the metals as manifested in their more common salts. Such compounds are conveniently termed *higher oxides*, and may usually be made to part with their excess of oxygen either by heating alone or with sulphuric acid.

Manganese dioxide, $MnO_2$, when heated to moderate redness, evolves oxygen and leaves a residue of the sesqui-oxide $Mn_2O_3$.

$$4MnO_2=2Mn_2O_3+O_2.$$

The reaction begins at 530° C. in air,[2] and if the temperature is raised to 940° C. the sesqui-oxide in turn decomposes, yielding a further supply of oxygen and a residue of trimanganic tetroxide, $Mn_3O_4$.

$$6Mn_2O_3=4Mn_3O_4+O_2.$$

The foregoing reactions at one time offered one of the cheapest methods of preparing oxygen for commercial purposes. The source of the dioxide was the mineral pyrolusite, but the high temperature required to extract the oxygen led to the superseding of this method by other more convenient processes.

When heated with concentrated sulphuric acid, manganese dioxide evolves oxygen, leaving a residue of manganese sulphate. The reaction takes place in two stages,[3] namely:

(1) At 110° C.

$$4MnO_2+6H_2SO_4=2Mn_2(SO_4)_3+6H_2O+O_2.$$

(2) At the boiling-point of sulphuric acid

$$2Mn_2(SO_4)_3=4MnSO_4+2SO_3+O_2.$$

Lead dioxide, $PbO_2$, when heated above 310° C., decomposes, yielding oxygen and lead monoxide.

$$2PbO_2=2PbO+O_2.$$

Similarly red lead, $Pb_3O_4$, when strongly heated evolves oxygen, a residue of lead monoxide remaining. This reaction is reversible.[4]

$$2Pb_3O_4\rightleftharpoons 6PbO+O_2.$$

At 530° C. the red lead may be completely converted into monoxide in a vacuum, but in the presence of air a higher temperature is essential, as is evident from the following data.[1]

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[1] See Gay Lussac, and Thénard, *Recherch. physicochim.*, 1800, 2, 143; Weber, *Pogg. Annalen*, 1861, 112, 619.

[2] Meyer and Rötgers, *Zeitsch. anorg. Chem.*, 1908, 57, 104. See also this series, Vol. VIII., Chap. 6.

[3] Carius, *Annalen*, 1856, 98, 53.

| | | | | |
|---|---|---|---|---|
| Temperature ° C. . . . . . . | 445 | 500 | 555 | 636 |
| Dissociation pressure of $Pb_3O_4$ in mm. . | 5 | 60 | 183 | 763 |

Alkali peroxides are rapidly decomposed by water, oxygen being evolved. In the case of sodium peroxide the reaction proceeds according to the following equation :

$$2Na_2O_2+2H_2O=4NaOH+O_2.$$

The reaction is conveniently carried out in a flask fitted with a drop funnel through which the water is slowly admitted. Some hydrogen peroxide is simultaneously produced. The evolution of oxygen is facilitated by the addition of a catalyst, such as a salt of nickel, cobalt, or copper. When pressed into small blocks or cubes, the mixture of sodium peroxide and catalyst may be placed in a Kipp or other gas-generating apparatus based on a similar principle, and a steady supply of oxygen obtained. The commercial commodity known as "oxylithe" has the following composition :

| | |
|---|---|
| Sodium peroxide . . . . | 98·32 per cent. |
| Oxide of iron . . . . | 1·00 ,, |
| Copper sulphate . . . . | 0·68 ,, |

and is very suitable for this type of reaction.[2]

The preparation of small quantities of oxygen for laboratory purposes may be conveniently effected by gently warming a mixture of fused sodium peroxide with some salt containing water of crystallisation. For this purpose crystals of sodium carbonate or sulphate are very suitable. The oxygen is evolved in a steady stream which is readily kept under control.[3]

By the action of acids upon alkali or alkaline earth peroxides, hydrogen peroxide is liberated, which immediately undergoes partial or complete decomposition according to circumstances. Thus oxygen is readily obtained[4] by the employment in a Kipp of lumps of the mixture obtained by adding 100 parts of sodium peroxide and 25 parts of magnesium oxide to 100 parts of molten potassium nitrate. The liquid reagent consists of dilute hydrochloric acid. The magnesia does not serve as a catalyst ; on the contrary, it is added as an inert diluent to moderate the violence of the reaction.

Hydrogen peroxide readily yields up its oxygen either under the influence of heat or of a catalyst. As examples of the last named, colloidal solutions of the platinum metals may be mentioned.

In neutral solution hydrogen peroxide is decomposed catalytically by lead dioxide, but in acid solution the action is different and quantitative.[5] Thus, in the presence of nitric acid,

$$PbO_2+H_2O_2+2HNO_3=Pb(NO_3)_2+2H_2O+O_2.$$

Manganese dioxide behaves similarly in acid solution, and, if charged in lump form into a Kipp and subjected in the usual manner to the action of commercial hydrogen peroxide acidified with sulphuric acid, a steady stream of oxygen is obtained.[1]

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[1] Le Chatelier, *Bull. Soc. chim.*, 1897, [3], 17, 791. See also this series, Vol. V.

[2] See Hanman, *English Patent*, 9783 (1903).

[3] H. J. Turner, *Amer. Chem. J.*, 1907, 37, 106.

[4] Wolter, *Chem. Zeit.*, 1908, 32, 1066.

[5] Schlossberg, *Zeitsch. anal. Chem.*, 1902, 41, 735.

Instead of using free hydrogen peroxide, barium peroxide may be used, lumps of a mixture of barium peroxide, gypsum, and manganese dioxide being introduced into the Kipp, the liquid reagent consisting of hydrochloric acid.[2]

Hydrogen peroxide reacts with potassium permanganate in acid solution evolving oxygen. In the presence of dilute sulphuric acid the reaction proceeds along the lines indicated by the equation

$$2KMnO_4+5H_2O_2+3H_2SO_4=K_2SO_4+2MnSO_4+8H_2O+5O_2.$$

For laboratory purposes [3] a steady evolution of oxygen may be obtained by allowing a solution of 25 grams of potassium permanganate in 500 c.c. of water and 50 c.c. of concentrated sulphuric acid to flow from a dropping funnel into a litre flask containing 500 c.c. of hydrogen peroxide solution (10 vol.).[4] No heat is required.

Hydrogen peroxide reacts in an analogous manner with potassium bichromate, evolving oxygen. A convenient way of preparing the gas in small quantities consists in adding 150 grams of concentrated sulphuric acid to hydrogen peroxide solution (10 vol.) [4] and allowing the mixture to come into contact with crystals of potassium bichromate [5] in a Kipp's apparatus. The crystals should be large and the process carried out with care in the cold, as otherwise the reaction is liable to be very violent. In order to prevent small pieces of the bichromate from falling into the lower chamber of the Kipp, a layer of small pieces of pumice may be introduced into the middle chamber prior to the admission of the salt. The reaction proceeds according to the equation

$$K_2Cr_2O_7+4H_2SO_4+3H_2O_2=K_2SO_4+Cr_2(SO_4)_3+7H_2O+3O_2.$$

In alkaline solution potassium ferricyanide and hydrogen peroxide also yield a steady stream of oxygen which can be immediately checked by the addition of an acid.[6]

The reactions involved appear to be represented by the following equations:

$$\begin{gathered}2K_3Fe(CN)_6+2KHO=2K_4Fe(CN)_6+H_2O+O\ \text{(nascent)}\\ O+H_2O_2=H_2O+O_2.\end{gathered}$$

Experiment shows that it is the amount of alkali present that controls the reaction—an observation in harmony with the above equation.

With bleaching powder, hydrogen peroxide in acidified solution readily yields oxygen gas,[7]

$$Ca(OCl)Cl+H_2O_2=CaCl_2+H_2O+O_2.$$

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[1] See Baumann, *Ber.*, 1890, **23**, 324; *Zeitsch. angew. Chem.*, 1890, p. 72.

[2] Neumann, *Ber.*, 1887, **20**, 1584.

[3] Gähring, *Chem. Zeit.*, 1889, **13**, 264; Seyewetz and Poizat, *Compt. rend.*, 1907, **144**, 86; Mossler, *Chem. Zentr.*, 1909, ii., 785; from *Zeitsch. Allg. Oesterr. Apoth. Ver.*, 1909, **43**, 301.

[4] That is a solution of hydrogen peroxide, yielding upon decomposition into water and oxygen ten times its own volume of the latter.

[5] Blau, *Monatsh*, 1892, **13**, 281; Erdmann and Bedford, *Ber.*, 1904, **37**, 1184.

[6] Kassner, *Chem. Zeit.*, 1889, **13**, 1302, 1338, 1407; *Arch. Pharm.*, 1890, **228**, 432.

[7] Volhard, *Annalen*, 1889, **253**, 246; Lunge, *Zeitsch. angew. Chem.*, 1890, p. 7; Vanino, *ibid.*, 1890, p. 80.

Barium peroxide is readily decomposed by heat, the reaction being reversible:

$$2\mathrm{BaO}_2 \rightleftharpoons 2\mathrm{BaO} + \mathrm{O}_2.$$

By continuous removal of the oxygen, therefore, decomposition will continue at constant temperature until the whole of the solid phase has been converted into the monoxide.

If, on the other hand, the pressure of oxygen in contact with the solid phase is increased beyond the dissociation pressure at a given temperature, the barium peroxide is regenerated, the foregoing reaction now proceeding from right to left.[1]

In the following table are given the dissociation pressures of barium peroxide in contact with moisture[2] at various temperatures ranging from 618° to 868° C.

| Temperature ° C. . . | 618 | 655 | 697 | 737 | 794 | 835 | 853 | 868 |
|---|---|---|---|---|---|---|---|---|
| Oxygen pressure (cm. mercury) | 11·3 | 26·8 | 65·4 | 141 | 378 | 718 | 937 | 1166 |
| Water-vapour (cm. mercury) | 7·3 | 13·7 | 26·3 | 47 | 98 | 159 | 195 | 231 |

Boussingault attempted to use the foregoing reactions for the preparation of oxygen on a commercial scale, but found that after several reheatings the barium oxide lost its power of absorbing oxygen. This difficulty was eventually overcome by the brothers Brin,[3] who formed a company for the preparation of oxygen for industrial purposes.[4]

The barium oxide was obtained in a hard and porous condition by ignition of the nitrate. Pieces about the size of a walnut were heated to 600° C. in vertical steel retorts into which air, purified from carbon dioxide and from most of its moisture, was conducted under a pressure of about 10 lb. per sq. inch. After seven minutes the pressure was reduced to 4 inches (10 cm.) of mercury, the temperature remaining constant, whereon the absorbed oxygen was evolved. This process was repeated four times per hour, and a gas of 95 per cent. purity obtained.[5]

As late as 1907 three works were producing 30,000 cubic feet of oxygen per day by this process, which is now, however, obsolete in Great Britain, having been superseded by the liquid-air process,[6] which not only yields a cheaper but a purer gas, namely, 97 per cent. oxygen.

In 1913 a process was patented[7] by which the oxygen of the air could be obtained by alternate oxidation and reduction of oxides of nitrogen. Vapour of nitric acid is passed over heated sulphuric acid whereby oxygen is liberated and water and nitrosulphuric acid are produced. The latter is treated with water yielding sulphuric acid and a mixture of nitric oxide and nitrogen peroxide, the last named being reconverted into nitric acid by solution in water in presence of air. The reactions may be represented as follows:

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[1] See Boussingault, *Ann. Chim. Phys.*, 1852, [3], 35, 5; 1880, [5,] 19, 464; Gondolo, *Compt. rend.*, 1868, 66, 488. The velocity of formation of barium peroxide has recently been studied by Sasaki, *Mem. Coll. Sci Kyoto*, 1921, 5, 9.

[2] Which is necessary for the reaction. See Hillebrand, *J. Amer. Chem. Soc.*, 1912, 34, 246. Compare Le Chatelier, *Compt. rend.*, 1892, 115, 654.

[3] Brin, *Mém. Soc. Ing. civ.*, 1881, p. 450; *English Patent*, 1416 (1880).

[4] The velocity of formation of barium peroxide has been studied by Sasaki, *Mem. Coll. Sci. Kyoto*, 1921, 5, 9.

[5] See *English Patents*, 1416 (1880); 4955 (1889); 4292 (1891); 17298 (1891); 14918 (1893). Also Murray, *Proc. Inst. Mech. Eng.*, 1890, p. 131; Thorne, *J. Soc Chem. Ind.*, 1890, 9, 246.

[6] See p 31.

[7] Bergfeld, *English Patent*, 21211 (1913); *J. Soc. Chem. Ind.*, 1914, 33, 831.

(i) $4HNO_3 = 4NO_2 + 2H_2O + O_2$.
(ii) $4H_2SO_4 + 4NO_2 = 4H(NO)SO_4 + 2H_2O + O_2$.
(iii) $2H(NO)SO_4 + H_2O = 2H_2SO_4 + N_2O_3$.
(iv) $N_2O_3 + O_2 + H_2O = 2HNO_3$.

C. *Preparation of Oxygen from more Complex Compounds.* Many oxygenated salts and other compounds yield oxygen when subjected to the influence of heat, either alone or in contact with other substances. They may even yield oxygen at ordinary temperatures in contact with suitable catalysers.

When metallic chlorates are gently heated, oxygen is evolved, a chloride being generally left behind. The salt which, for various reasons, has been studied most carefully in this connection is potassium chlorate. The decomposition of this salt is liable to be explosive if the heating is carried out suddenly.[1] This is readily demonstrated by allowing very small drops of molten chlorate on the end of a glass rod to fall on to the bottom of a test-tube heated to redness. Sharp detonations result. When heated to 357° C. this salt undergoes no perceptible decomposition, but the powder cakes together and when examined under the microscope shows signs of incipient fusion.[2] The salt becomes liquid at a slightly higher temperature,[3] and at 370° to 380° C. there is a rapid evolution of oxygen.[4] Several reactions now begin to take place:

(1) The formation of perchlorate. This is a case of autoxidation, one molecule of chlorate oxidising three other molecules of chlorate to perchlorate and being itself reduced to chloride. Thus:

$$KClO_3 + 3KClO_3 = KCl + 3KClO_4.$$

This reaction is exothermic, evolving 61,300 calories.[5]

The velocity of formation of potassium perchlorate has been measured at 395° C. and the reaction shown to be tetramolecular and to proceed in accordance with the above equation.[6]

(2) In addition to the foregoing reaction, potassium chlorate undergoes decomposition into oxygen and potassium chloride. This is a monomolecular reaction [7] and proceeds according to the equation

$$2KClO_3 = 2KCl + 3O_2.$$

(3) If the temperature is raised sufficiently the potassium per-

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[1] Berthelot, *Compt. rend.*, 1899, **129**, 926.

[2] M'Leod, *Trans. Chem. Soc.*, 1889, **55**, 184.

[3] Using an electrical method, C. D. Carpenter (*Chem. Met. Eng.*, 1921, **24**, 569) has determined the melting-point as 357·10° C.

[4] Oxygen is very slowly evolved at temperatures below the melting point of the chlorate (Rilliet and Crafts, *B.A. Reports*, 1882, p. 493).

[5] In many textbooks this reaction is described as taking place according to the equation

$$2KClO_3 = KClO_4 + KCl + O_2.$$

It has long been known, however, that this is incorrect (Marignac, *Jahresber.*, 1845, **24**, 192; Teed, *Proc. Chem. Soc.*, 1885, **1**, 105; 1886, **2**, 141; *Trans. Chem. Soc.*, 1887, **51**, 283; Frankland and Dingwall, *ibid.*, 1887, **51**, 274). The formation of perchlorate is not *per se* accompanied by the evolution of oxygen. See Sodeau, *Trans. Chem. Soc.*, 1902, **81**, 1066; Fowler and Grant, *ibid.*, 1890, **57**, 279.

[6] Scobai, *Zeitsch. physikal. Chem.*, 1903, **44**, 319.

[7] Scobai, *loc. cit.*

chlorate formed in the first reaction begins to decompose, in the main according to the equation

$$KClO_4 = KCl + 2O_2.$$

This reaction is inappreciable even at 411° C.,[1] but readily proceeds to completion at 445° C.[2] A small quantity of potassium chlorate is simultaneously regenerated.[3]

A trace of chlorine is usually found in the oxygen obtained by heating potassium chlorate in glass apparatus, a larger amount being obtained with Jena glass than with either soda or Bohemian combustion glass. When the chlorate is decomposed in platinum vessels, however, chlorine is either not evolved, or only in infinitesimal quantities whether at atmospheric or under reduced pressure.[4]

Sodium chlorate decomposes in a precisely similar manner to the potassium salt.[5]

The foregoing method of preparing oxygen possesses two disadvantages. Not only is the evolution of the gas inclined to be violent and difficult to control, but the temperature at which the reaction takes place is too high to be satisfactorily carried out in a glass vessel. These difficulties are overcome by mixing the chlorate with manganese dioxide prior to heating, a procedure first described by Doebereiner[6] in 1832. Under these conditions the evolution of oxygen is steady and commences at about 240° C. instead of 370° C.

It is important to remember that commercial manganese dioxide is occasionally contaminated with carbonaceous material such as coal dust. Such a mixture is very liable to explode when heated with potassium chlorate owing to the rapid combustion of the carbon in the oxygen. Manganese dioxide should, therefore, always be tested beforehand and rejected for the preparation of oxygen if it is found to contain any carbonaceous matter.

The manner in which the manganese dioxide assists the decomposition of the chlorate has been made the subject of considerable controversy. The oxide may be used over and over again without any measurable diminution of its activity.[7] It has been suggested from time to time that its action is purely mechanical[8] analogous to that of sand, etc., in promoting the boiling of water. The analogy, however, is misleading, for reduction of pressure does not materially facilitate the evolution of oxygen from potassium chlorate, although it greatly reduces the boiling-point of water.[9] Again, were the action purely mechanical, all other finely-divided substances, irrespective of their chemical composition, might be expected to act in a similar manner just as they are known to do in the case of boiling water. This, however, is not the case, for although oxides of iron, cobalt, nickel, cerium,[1] and copper facilitate the reaction, the oxides of zinc, magnesium, etc., appear incapable of doing so.

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[1] Scobai, *loc. cit.*

[2] That is, at the boiling-point of sulphur. See Frankland and Dingwall, *Trans. Chem. Soc.*, 1887, **51**, 279.

[3] Teed, *loc. cit*; Frankland and Dingwall, *loc. cit.*

[4] Sodeau, *Trans. Chem. Soc.*, 1900, **77**, 137. Compare Williams, *Proc. Chem. Soc.*, 1889, **5**, 26.

[5] Scobai, *Zeitsch. physikal. Chem.*, 1903, **44**, 319.

[6] Doebereiner, *Annalen*, 1832, **1**, 236.

[7] M'Leod, *Trans. Chem. Soc.*, 1889, **55**, 184.

[8] Veley, *Phil. Trans.* 1888, [A], **179**, 270.

[9] Sodeau, *Trans. Chem. Soc.*, 1900, **77**, 144; 1901, **79**, 939.

The most probable explanation is that alternately higher and lower oxides of manganese are formed[2]—the higher oxide by the oxidising action of the heated chlorate, and the lower oxide by the decomposition of the higher, either alone or in contact with a further supply of chlorate. Mention has already been made of the fact that, when potassium chlorate is heated alone, some perchlorate is formed through self-oxidation simultaneously with the evolution of oxygen. This reaction does not occur in the presence of manganese dioxide,[3] since this oxide effects the decomposition of the chlorate into chloride and oxygen at a temperature considerably below that at which autoxidation of the chlorate proceeds at an appreciable rate.[4]

That several other minor or side reactions should take place, in addition to the main cycle indicated above, is only to be anticipated. Thus the fact that the oxygen invariably contains traces of chlorine[5] suggested that a peculiar form of ozone was produced rather than chlorine; but this is negatived by the results of M'Leod.[6] Small quantities of potassium permanganate are also undoubtedly formed in the solid mass, for when potassium chlorate is fused with a very small quantity of manganese dioxide a pink colour is observable on cooling. When this pink mass is fused over a flame, oxygen is evolved, but the colour persists until nearly all the chlorate is decomposed; it then becomes greenish and ultimately brownish. If the dioxide is present in considerable quantity any pink colour is masked by the blackness of the mixture.

M'Leod explains these changes as follows:[7]

(1) The dioxide acts on the chlorate forming permanganate, chlorine, and oxygen.

$$2KClO_3+2MnO_2=2KMnO_4+Cl_2+O_2.$$

(2) The permanganate then undergoes decomposition by the heat yielding potassium manganate, manganese dioxide, and oxygen.

$$2KMnO_4=K_2MnO_4+MnO_2+O_2.$$

This reaction begins at about 200° C., and is rapid at 260° C.[8]

(3) The manganate is decomposed by chlorine yielding potassium chloride, manganese dioxide, and oxygen.

$$K_2MnO_4+Cl_2=2KCl+MnO_2+O_2.$$

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[1] Namely cerium dioxide; *German Patent*, 1915, No. 299505.

[2] Sodeau, *Trans. Chem. Soc.*, 1902, 81, 1066.

[3] Eccles, *J. Chem. Soc.*, 1876, 29, 857; Teed, *Trans. Chem. Soc.*, 1887, 51, 283.

[4] Sodeau, *loc. cit.*

[5] Brunck, *Ber.*, 1893, 26, 1760; *Zeitsch. anorg. Chem.*, 1895, 10, 222.

[6] M'Leod, *Trans. Chem. Soc.*, 1894, 65, 202; 1896, 69, 1015.

[7] M'Leod, *ibid.*, 1889, 55, 184. For further details of the discussions on the decomposition of potassium chlorate the reader is referred to the following references in addition to those already cited: Berthelot, *Compt. rend.*, 1899, 129, 926; Warren, *Chem. News*, 1888, 58, 247; Hodgkinson and Lowndes, *Chem. News*, 1888, 58, 309; 1889, 59, 63; Bottomley, *ibid.*, 1887, 56, 227; Maumené, *ibid.*, 1886, 53, 145; Jungfleisch, *Bull. Soc. chim.*, 1871, [2], 15, 6; *J. Pharm. Chim.*, 1871, 14, 130; Baudrimont, *ibid.*, 1871, 14, 81, 161; Debray, *Ber.*, 1870, 3, 247; Wiederhold, *Ann. Phys. Chem.*, 1862, 116, 171.

[8] See p. 24.

Oxygen may also be obtained by heating the chlorates of other metals, notably barium,[1] calcium,[2] strontium,[3] lead,[4] and silver,[5] or by decomposition of metallic bromates and iodates.[6]

Aqueous solutions of alkali hypochlorites readily yield oxygen at the boiling-point under the influence of catalysers. This is easily accomplished by passing a current of chlorine through a concentrated solution of caustic soda at the boiling-point, to which a small quantity of a cobalt salt has been added.[7] The cycle of reactions involving the liberation of oxygen may be represented as follows:

$$2NaOH + Cl_2 = NaClO + NaCl + H_2O$$
$$NaClO + CoO = NaCl + CoO_2$$
$$2CoO_2 = CoO + O_2.$$

An aqueous solution of bleaching powder, to which a trace of a cobalt salt has been added to serve as catalyst, readily evolves oxygen when warmed to about 80° C. The procedure may be varied by using a thin cream of bleaching powder in water and warming this on a water-bath to 70° or 80° C. in the presence of a small quantity of a cobalt salt. The mixture froths excessively, but this tendency may be overcome by addition of a little paraffin oil.

The mechanism of the process consists in the immediate conversion of the cobalt salt into an oxide which undergoes alternate reduction and oxidation. What the composition of the higher oxide may be is uncertain; probably it is either the sesqui-oxide, $Co_2O_3$, or the dioxide, $CoO_2$.[8] Assuming it to be the latter, the reactions taking place may be represented as follows:

$$2Ca(OCl)Cl + 2CoO = 2CaCl_2 + 2CoO_2$$
$$2CoO_2 = 2CoO + O_2.$$

The velocity of reaction indicates it to be monomolecular.[9] Salts of nickel, copper, or iron may be used instead of those of cobalt, but are less active. The theory that the catalyst effects the decomposition by its own alternate oxidation and reduction is supported by the result of passing chlorine into a 50 per cent. solution of sodium hydroxide containing dissolved copper hydroxide; the blue solution at first deposits a yellow copper peroxide, which rapidly decomposes, evolving oxygen and regenerating the original solution.[10] The effect of adding two catalysts to bleaching powder is remarkable. If the bleaching powder is made into a cream with water, oxygen may be liberated at the ordinary temperature by addition of a ferrous or manganous salt and in the presence of a copper or nickel compound. The best result is obtained with a mixture of ferrous and copper sulphates.[1]

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[1] Potilitzin, *J. Russ. Chem. Soc.*, 1887, p. 339; *Ber.*, 1887, **20**, Ref. 769, Schulze, *J. prakt. Chem*, 1880, [2], **21**, 407. See also Sodeau, *Trans. Chem. Soc.*, 1900, **77**, 137.

[2] Sodeau, *Trans. Chem. Soc.*, 1901, **79**, 247; Potilitzin, *J. Russ. Phys. Chem. Soc.*, 1890, **22**, 333.

[3] Potilitzin, *loc. cit*, 1889, **21**, 451.

[4] Sodeau, *Trans. Chem. Soc.*, 1900, **77**, 717; Wächter, *J. prakt. Chem.*, 1843, **30**, 329; Schulze, *loc. cit.*; Spring and Prost, *Bull. Soc. chim.*, 1889, [3], **1**, 340.

[5] Sodeau, *ibid.*, 1901, **79**, 249.

[6] E. H. Cook, *ibid.*, 1894, **65**, 802

[7] See Bleaching Powder below.

[8] See Carnot, *Compt. rend.*, 1889, **108**, 610; Schroder, *Chem. Zentr.*, 1890, i, 931; Hüttner, *Zeitsch. anorg. Chem.*, 1901, **27**, 81; M'Leod, *Brit. Assoc. Reports*, 1892, p. 669.

[9] Bell, *Zeitsch. anorg. Chem.*, 1913, **82**, 145

[10] See Fleitmann, *Annalen*, 1865, **134**, 64; Bottger, *J. prakt. Chem.*, 1865, **95**, 309, 375; Stolba, *ibid.*, 1866, **97**, 309; Winkler, *ibid*, 1866, **98**, 340; Denigès, *J. Pharm. Chim.*, 1889, **19**, 303; Bell, *Zeitsch. anorg. Chem.*, 1913, **82**, 145.

Practically the same reaction takes place when a stream of chlorine gas is passed through boiling milk of lime containing a trace of cobalt oxide as catalyst. The oxygen is steadily evolved.

$$2Ca(OH)_2 + 2Cl_2 = 2CaCl_2 + 2H_2O + O_2.$$

Oxygen is readily evolved at the ordinary temperature on adding water to a mixture of bleaching powder and an alkali or alkaline earth peroxide in the presence of a catalyst such as ferrous or copper sulphate. If the solid mixture is pressed into small lumps or cubes, it may be used in a Kipp's apparatus and thus afford a convenient method of preparing the gas for lecture or laboratory purposes.[2]

$$Ca(OCl)Cl + Na_2O_2 + H_2O = Ca(OH)_2 + 2NaCl + O_2.$$

Concentrated sulphuric acid, when strongly heated, decomposes into water and a mixture of sulphur dioxide and oxygen.

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2.$$

To this end the acid is allowed to drop on to a red-hot surface and the resultant gases treated with suitable absorbents to remove the sulphur dioxide and steam.[3]

Concentrated nitric acid readily decomposes, when heated, into water, nitrogen dioxide, and oxygen. The two former are readily converted again into nitric acid by the action of the atmospheric air.[4]

Alkali nitrates, when heated above their melting-points, yield the corresponding nitrite and oxygen; but the gas is contaminated with nitrogen resulting from partial decomposition of the nitrite. In the case of potassium nitrate the reaction may be represented by the equation:[5]

$$2KNO_3 = 2KNO_2 + O_2.$$

Priestley had noticed as early as 1772 that, when a lighted candle is lowered into the gas obtained by heating potassium nitrate, the flame "increased," indicating more intense combustion.[6]

The decomposition of alkali nitrates appears to be a reversible reaction. When heated in oxygen at a pressure of 175 atmospheres at a temperature gradually rising from 395° to 530° C. during nine hours, sodium nitrite is almost completely oxidised to nitrate. Thus:

$$2[NaNO_2] + (O_2) = 2[NaNO_3] + 45,000 \text{ calories}.$$

Calcium nitrite undergoes oxidation to nitrate in similar circumstances.[7]

Potassium permanganate decomposes when gently heated. The pure, dry salt shows signs of decomposition at 200° C.[8] The reaction is appreciable at 215° C. and is complete at 240° C. The oxygen pressure of the residue corresponds with that of pure manganese dioxide up to 185° C. The heat of dissociation of potassium permanganate is 60,000 calories.[1]

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[1] Jaubert, *German Patent*, 157171 (1905).

[2] Jaubert, *Compt. rend.*, 1902, 134, 778; *English Patent*, 11466 (1901); 14848 (1901).

[3] This process is used commercially, not for the preparation of oxygen, but for preparing a mixture of sulphur dioxide and oxygen in the requisite proportions to yield sulphur trioxide.

[4] See Bergfeld, *J. Soc. Chem. Ind.*, 1914, 33, 831.

[5] Lang, *Ann. Phys. Chem.*, 1863, [2], 118, 282.

[6] Priestley, *Phil. Trans.*, 1772, 62, 245.

[7] Matignon and Monnet, *Compt. rend.*, 1920, 170, 180.

[8] Moles and Crespi, *Zeitsch. physikal. Chem.*, 1922, 100, 337.

The reaction proceeds *approximately* according to the equation

$$2KMnO_4=K_2MnO_4+MnO_2+O_2,$$

a residue of potassium manganate and manganese dioxide being obtained.[2]

When a mixture of manganese dioxide and sodium hydroxide is heated to dull redness in a current of air, sodium manganate is formed:[3]

$$4NaOH+2MnO_2+O_2=2Na_2MnO_4+2H_2O.$$

The absorption of oxygen begins at 240° C., the rate of absorption increasing with the temperature, the optimum temperature being 600° C. The product, on treatment with steam at 450° C., evolves oxygen, sodium hydroxide and manganese dioxide being regenerated:

$$2Na_2MnO_4+2H_2O=4NaOH+2MnO_2+O_2.$$

The foregoing reactions were made the basis of a commercial method for the preparation of oxygen from the air, but, owing to the short life of the solid phase, the process has not proved particularly successful.[4]

Teissier and Chaillaux[5] suggest the employment of barytes and manganous oxide which are heated together to redness with the production of manganese dioxide and barium sulphide:

$$BaSO_4+4MnO=BaS+4MnO_2.$$

The temperature is now raised to white heat, whereby the dioxide dissociates. Thus:

$$4MnO_2=4MnO+2O_2.$$

Finally steam is injected under pressure, reconverting the barium sulphide into sulphate and liberating hydrogen:

$$BaS+4H_2O=BaSO_4+4H_2.$$

These reactions are interesting as constituting one of the few commercial processes in which hydrogen is simultaneously obtained in equivalent quantity to the oxygen.

The alkali bichromates, when gently heated with concentrated sulphuric acid, are converted into chromium salts with liberation of oxygen.[6] Thus:

$$2K_2Cr_2O_7+8H_2SO_4=2K_2SO_4+2Cr_2(SO_4)_3+8H_2O+3O_2.$$

The change in colour undergone by the mixture during the reaction is very marked, the deep red of the bichromate giving place to the deep green of chromic sulphate.

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[1] Moles and Crespi, *loc. cit.*

[2] See Askenasy and Solberg, *Festschrift W. Nernst.*, 1912, p. 53; Tessié du Motay and Maréchal, *Dingl. Poly. J.*, 1870, **196**, 230; Rousseau, *Compt. rend.*, 1886, **103**, 261; M'Leod, *Trans. Chem. Soc.*, 1889, **55**, 184.

[3] See this series, Vol. VIII., Chap. 6

[4] Tessié du Motay and Maréchal, *English Patent*, 85 (1866); Parkinson, *ibid.*, 14925 (1890); Bowman, *ibid.*, 7851 (1890); Fanta, *ibid.*, 3034 (1891); Chapman, *ibid.*, 11504 (1892).

[5] Teissier and Chaillaux, *French Patent*, 447688 (1912).

[6] Balmain, *J. Pharm.*, 1842, **2**, 499.

Upon exposure to moist air cuprous chloride absorbs oxygen, being converted into the basic oxide $Cu_2OCl_2$. This, on heating to 400° C., yields free oxygen and a residue of cuprous chloride, from which the basic salt can be obtained again as indicated above. The initial supply of basic cuprous chloride may be conveniently obtained by heating a moist mixture of cupric chloride, sand, and clay in a current of steam at 100° to 200° C.[1]

Other processes that have been suggested involve the use of nitrosulphonic acid [2] and hæmoglobin.[3]

*Plumboxan*, a mixture of the manganate and meta-plumbate of sodium, namely, $Na_2MnO_4 . Na_2PbO_3$, readily evolves oxygen when heated in a current of steam at 430° to 450° C. The plumboxan is regenerated at the same temperature by replacing the steam with air, the issuing gas, during the initial stages of regeneration, consisting of a fairly pure nitrogen.[4]

The oxygen obtained by this process is very pure if the precaution is taken to remove the last traces of nitrogen from the pores of the plumboxan after regeneration by connecting to a vacuous vessel before introducing the steam. The chemical reactions taking place are very complex, and but imperfectly understood.

*Orthoplumbates* of the alkaline earth metals yield oxygen when strongly heated. The calcium salt, $Ca_2PbO_4$, is readily obtained by heating calcium carbonate and lead oxide in the presence of air [5] at about 600° C. When heated more strongly, the salt dissociates, yielding free oxygen, the dissociation pressures being as follow : [6]

| Temperature, ° C. . | 880 | 940 | 1020 | 1060 | 1100 | 1110 |
|---|---|---|---|---|---|---|
| Pressure in mm. . | 47 | 112 | 350 | 557 | 940 | 1040 |

Although a higher temperature is required for the preparation of oxygen by this method than is the case with barium peroxide (see p. 19), the calcium plumbate is more rapidly regenerated in the presence of air when the temperature is lowered ; furthermore, it is not necessary to remove the carbon dioxide from the air as in Brin's process.

The reactions entailed may be represented by the equation

$$4CaCO_3+2PbO+O_2(\text{from air})\rightleftharpoons 2Ca_2PbO_4+4CO_2$$
$$2Ca_2PbO_4\rightleftharpoons 4CaO+2PbO+O_2.$$

The oxygen may be derived from calcium plumbate, however, in other ways than by heat alone. One method consists in heating to about 700° C. in carbon dioxide :

$$4CO_2+2Ca_2PbO_4\rightleftharpoons 4CaCO_3+2PbO+O_2.$$

The residue is then heated successively in steam and air whereby the plumbate is reformed.[7]

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[1] Mallet, *Compt. rend.*, 1867, **64**, 226 ; 1868, **66**, 349 ; *English Patent*, 2934 (1864) ; 3171 (1866).

[2] Bergfeld, *English Patent*, 21211 (1913) ; see also p. 19.

[3] Sinding-Larsen and Storm, *ibid.*, 8211 (1910) ; 12728 (1910).

[4] Kassner, *Arch. Pharm.*, 1913, **251**, 596.

[5] Kassner, *ibid.*, 1890, **228**, 109 ; 1894, **232**, 375.

[6] Le Chatelier, *Compt. rend.*, 1893, **117**, 109.

[7] Kassner, *Chem. Zeit.*, 1898, **22**, 225 ; 1900, **24**, 615. See also Salamon, *English Patent*, 6553 (1890).

Another method consists in exposing the calcium plumbate to moist furnace gases at a temperature of about 80° to 100° C. The carbon dioxide is readily absorbed, the solid phase being converted into a mixture of calcium carbonate and lead dioxide. On raising the temperature, oxygen is evolved, the process being facilitated by the introduction of steam. The calcium plumbate is then regenerated by heating in air.

**Biological Processes.**—Under the influence of light the green parts of plants steadily assimilate carbon dioxide[1] and water, converting them into starch and evolving oxygen as a by-product. The volume of oxygen set free is approximately equal to that of the carbon dioxide absorbed, so that the initial and final stages of the very complex series of reactions involved may be represented by the equation

$$6CO_2+5H_2O=\underset{\text{(starch)}}{C_6H_{10}O_5}+6O_2.$$

The energy necessary for this reaction, which is endothermic, is obtained from the light, the most active rays being, curiously enough, those of the red, orange, and yellow portions of the spectrum,[2] and not the chemically reactive rays of the blue and violet end.

The evolution of oxygen from plants is readily demonstrated by placing fresh green leaves, such as those of mint or parsley, in a jar of water more or less saturated with carbon dioxide and exposed to sunlight. If the mouth of the jar is closed with an inverted funnel fitted with a tap, sufficient oxygen will collect in an hour or two to admit of being tested with a glowing splinter. The experiment may be carried out in a glass cell in a projecting lantern, an image of the whole being thrown on to the screen by means of electric light.[3] Bubbles of gas will be seen to collect rapidly on the leaves under the influence of the light.

This reaction is of particular interest inasmuch as it constitutes nature's method of replenishing the free oxygen content of the atmosphere. The efficiency of the process is evident when, to quote an example of medium assimilatory activity, it is remembered that one square metre of sunflower leaf can effect the decomposition of some 40 grams of carbon dioxide, and the simultaneous evolution of 30 grams of oxygen in one summer day of 15 hours' duration.

## LIQUID OXYGEN.

Oxygen was not obtained in the liquid state by Faraday in his classical investigations on the liquefaction of gases, because the refrigerating agents used by him did not suffice for the attainment of the critical temperature of the gas, above which it is impossible to effect liquefaction, no matter how great the pressure.

The gas was first reduced to the liquid state by Cailletet[4] in 1877, and almost simultaneously by Pictet.[5] The former investigator, who effected the cooling merely by the sudden expansion of the gas from a pressure of 300 atmospheres, obtained only a mist of small globules of liquid oxygen. Pictet, however, cooled the gas, already compressed to 320 atmospheres, to −140° C. in a bath of rapidly evaporating liquid carbon dioxide and was able to collect a small quantity of the liquid. Liquid oxygen was first produced in sufficient bulk for satisfactory examination by Wroblewski and Olszewski[1] who made use of liquid ethylene, boiling rapidly under reduced pressure, as a refrigerant. The rapid evaporation of liquid ethylene *in vacuo* leads to a temperature of −152° C, and Dewar[2] utilised this in preparing liquid air and oxygen in large quantities.

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[1] See Baly, Heilbron and Barker, *Trans. Chem. Soc.*, 1921, 119, 1025.

[2] See Pfeffer, *Pflanzen Physiol.*, 2nd ed., vol. i., sec. 60; Kohl, *Ber. deut. Bot Ges.*, 1897, Heft. 2.

[3] The rays should be first passed through a water cell to intercept the heat before entering the cell containing the leaves.

[4] Cailletet, *Compt. rend.*, 1877, 85, 1213, 1214.

[5] Pictet, *ibid.*, p. 1276.

**Production of Liquid Air.**[3]—The methods for the production of liquid air are divisible into two classes according to whether the cooling of the gases is due to the *external* or *internal* work performed by them.

The former method is based on the principle that the sudden, adiabatic expansion of gases against an external pressure causes external work to be done by them, accompanied by a proportional diminution in their own internal energy manifested by a reduction in temperature.[4] Although this method was introduced by Cailletet in 1877[5] and was successfully applied by him to the liquefaction of oxygen, nitrogen, and air, it was not until 1905 that it was successfully applied on a commercial scale, namely, in the *Claude Process*.[6]

The difficulty of lubrication appears to have been mainly responsible for the failure of previous attempts, and this was first overcome by the employment of petroleum ether which does not solidify, but merely becomes viscous at such low temperatures as −140° to −160° C. Later, however, it was found that leather retains its ordinary properties at these low temperatures, and in 1912 leather stampings were fitted to the working parts of the machinery to the entire exclusion of lubricants. Claude's apparatus is shown diagrammatically in fig. 1.

Air, compressed to 40 atmospheres, passes along the inner tube $T_1$ of the usual concentric system to the branched tube B, where it is placed in connection with a "liquefier" whilst much of the gas passes on through the expansion machine. Cooled by its loss of energy during expansion, it proceeds to the tubes inside the liquefier, and finally passes along the outer of the concentric tubes, thus cooling the oncoming air which reaches the expansion machine at −100° C. So cold does the expanded gas become that the compressed air in the liquefier finally condenses and is tapped off periodically, whilst the gas, after exerting this cooling effect, flows from the tubes of the liquefier into the outer tube $T_2$ and reduces to approximately −100° C. the temperature of the air reaching $T_1$.

The liquid air is usually collected and stored in Dewar vacuum flasks. These are double-walled glass vessels, the space between the walls being completely evacuated, so that the liquid in the flask is vacuum-jacketed. The heat conveyed by radiation across the vacuous space is only about one-sixth of that which would reach the liquid by conduction and convection if the space were filled with air; and this can be reduced to one-thirtieth by silvering the interior of the jacket. This latter procedure, however, is impracticable if for any purpose it is necessary to observe the contents of the flask.

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[1] Wroblewski and Olszewski, *Compt. rend.*, 1883, 96, 1140, 1225; *Wied. Annalen*, 1883, 20, 243; Wroblewski, *Compt rend.*, 1884, 98, 304, 982, 1885, 100, 979; 1886, 102, 1010; Olszewski, *ibid.*, 1885, 100, 350; *Monatsh.*, 1887, 8, 73.

[2] Dewar, *Phil Mag*, 1884, 18, 210; *Proc. Roy. Inst.*, 1886, p. 550.

[3] See discussion on the Generation and Utilisation of Cold, *Trans. Faraday Soc.*, 1922, 18, part ii

[4] See this series, Vol. I., 3rd ed., p. 40.

[5] See Cailletet, *Compt. rend.*, 1877, 85, 851, 1016, 1213, 1270; *Ann. Chim. Phys.*, 1878, 15, 132.

[6] Claude, *Compt. rend.*, 1902, 134, 1568; 1903, 136, 1359; 1905, 141, 762, 823; 1906, 143, 583.

The second method of producing liquid air is based on the internal work performed by a gas upon expansion during passage from a high to a low pressure, the work being mainly that necessary to overcome the attraction between the gaseous molecules. This work is carried out at the expense of the sensible heat of the gas, and the effect is the greater the lower the temperature. It would not exist in the case of a perfect gas upon free expansion, namely, into a vacuum, and must be carefully distinguished from the cooling already considered as the result of adiabatic expansion against the external atmospheric pressure, and as utilised in the Claude Process. This thermal effect was first studied by Joule and Thomson,[1] and is exhibited by oxygen and nitrogen and therefore by air, in the case of the last named, up to a temperature of 259° C. under normal pressure.[2] The cooling, which is a small effect, amounting in the case of air at the ordinary temperature to only about 0·255° C. for a fall in pressure of one atmosphere,[3] may be calculated from the expression

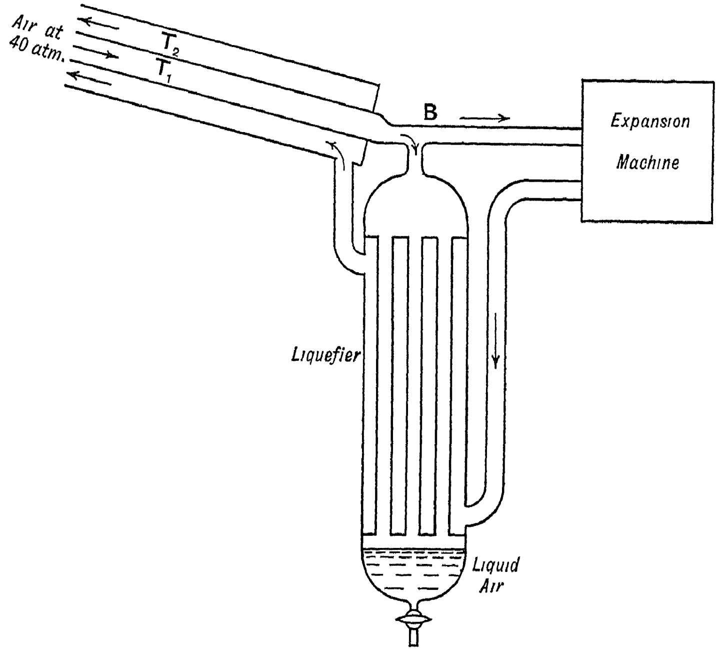

FIG. 1.—Claude's apparatus for the production of liquid air.

$$(t_1-t_2)=0{\cdot}276(p_1-p_2)\left(\frac{273}{T}\right)^2,$$

---

[1] Joule and Thomson, *Phil. Trans.*, 1853, 143, 357; 1854, 144, 321; 1862, 152, 579

[2] Olszewski, *Bull Acad Sci. Cracow*, 1906, p. 792.

[3] For discussions of this value, see Keyes, *J. Amer. Chem. Soc.*, 1921, 43, 1452; Hoxton, *Phys. Review*, 1919, 13, 438; Bradley and Hale, *ibid.*, 1904, 19, 391; 1909, 29, 258.

where $p_1$ is the initial high pressure, $p_2$ the final low pressure, and T the initial absolute temperature, the cooling being expressed in degrees centigrade. By employing high pressures the cooling effect is proportionately enhanced. Thus, if a pressure difference of 100 atmospheres is employed, working at 0° C., the fall in temperature is 27·6 centigrade degrees.

By allowing air to expand suddenly at ordinary temperatures a certain cooling is thus produced, and by applying this cooled gas to the reduction of the temperature of yet unexpanded gas, the latter after expansion will attain a still lower temperature. In this way it is possible to make the cooling effect cumulative so that at last the temperature of the air is reduced to the liquefying point. The Linde, Dewar, and Hampson liquefiers are based on this principle.[1]

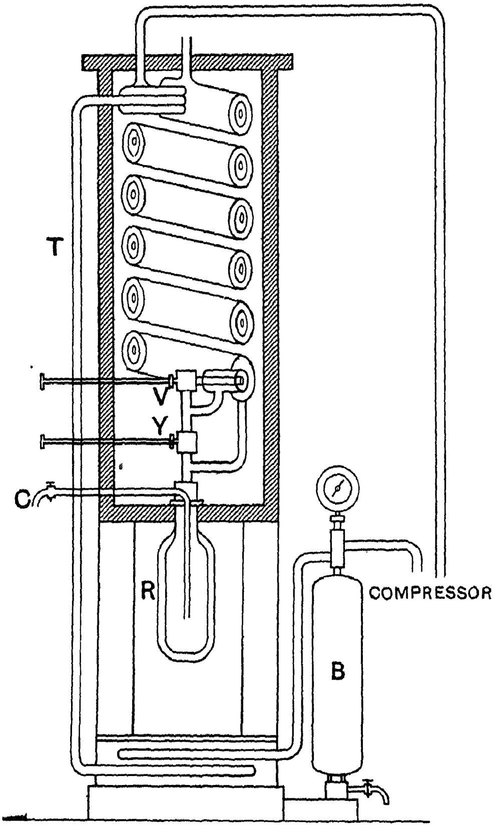

Fig. 2.—The Linde liquid-air machine.

A diagrammatic representation of the Linde machine is given in fig. 2. Air compressed to 200 atmospheres passes through the steel bottle B where it deposits its moisture, and thence proceeds to the worm surrounded by a refrigerating medium. Here the temperature is reduced to − 50° C. and the last traces of water-vapour are removed. The gas passes thence down the innermost of the concentric copper tubes T, by way of which it reaches the needle-valve V, where it expands to a pressure of 40 atmospheres. This limited expansion yields the major portion of the Joule-Thomson effect and at the same time reduces the subsequent necessary work of compression. The cooled expanded gas returns through the second concentric tube to the compressor, cooling the oncoming air as it passes. As this process is continued, the air reaching V steadily falls in temperature until at last it begins to condense to the liquid state, when the liquid is allowed periodically to pass through the valve Y where, on account of the further decrease of pressure to one atmosphere, the liquid evaporates vigorously until its temperature falls to its normal boiling-point for this pressure ; the cold gas from the evaporation passes away through the outermost concentric tube and so assists in cooling the compressed air, whilst the liquid air collects in the receiver R and can be drawn off as required by the tap C. The apparatus is enclosed in a packing of non-conducting material such as wool and is supported externally by a wooden or metallic case. In the earlier forms of this type of liquefier the process was somewhat simpler because the pressure was allowed to fall directly to the ordinary external atmospheric pressure by one expansion only. Machines of the more modern type have been constructed to yield over 50 litres of liquid air per hour.[1]

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[1] See Linde, *Ber.*, 1899, 32, 925; *Wied Annalen*, 1895, 57, 328; Olszewski, *Bull. Acad. Sci. Cracow*, 1902, p. 619; Hampson, *J. Soc. Chem. Ind.*, 1898, 17, 411; *English Patent*, 1895, No. 10165; also this series, Vol. I., p. 41.

**Production of Liquid Oxygen.**—On account of the great importance of oxygen and the increasing importance of nitrogen for industrial and other purposes, the liquid mixture of these elements provides a promising field for a successful process for the production of the gases on a large scale.

As is indicated by the curves in fig. 35 the vapour of boiling liquid air is richer in nitrogen than the liquid, hence careful fractional distillation or evaporation should finally yield the oxygen in a pure condition because the boiling-point rises steadily as the percentage of oxygen increases. Bearing in mind the proximity to the absolute zero, it will be easily recognised that the relative difference between the boiling-points of the two constituents, namely oxygen −182·9° C. and nitrogen −195 67° C., is very considerable and that the main difficulties are likely to be of a mechanical type.

Several forms of apparatus have been proposed. One of the earlier forms [2] suggested by Linde consisted of a modification of the apparatus represented in fig. 2 ; this was supplied with only one valve which allowed immediate expansion to atmospheric pressure, the liquid air produced by the cooling being collected in a suitable receiver. The compressed gas, before reaching the valve, was made to circulate through a copper coil actually inside the receiver so as to be covered by the liquid air already formed. The relative warmth of this gas caused an evaporation of the more volatile nitrogen, the liquid lost by evaporation being replaced by fresh liquid air produced by the expansion of the cooled gas. Proceeding in this way, the receiver soon contains fairly pure liquid oxygen which can be drawn off as necessary and transported, in the form of compressed gas, in steel cylinders. As the gaseous nitrogen which passes away from the apparatus is formed by the evaporation of a liquid containing at least 21 per cent. of oxygen, the nitrogen is not pure but must contain at least 7 per cent. of oxygen. A recent form of the Linde oxygen plant is shown in figs. 3 and 4.[3]

Prior to admission to the plant, the air is compressed to 135 atmospheres (2000 lb. per square inch), and cooled to −20° C. in an ordinary refrigerating apparatus. This serves to freeze out atmospheric moisture. Carbon dioxide is removed by passage through a slaked lime purifier.

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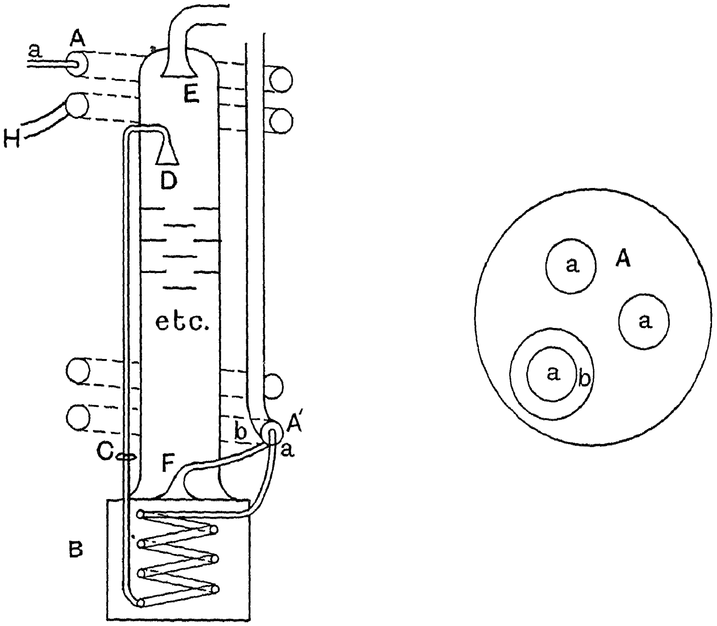
[1] The Hampson machine is described in this series, Vol. I., p. 41.

[2] See *British Patents,* 14111 (1902), 11221 (1903); 12528 (1895) The production of pure oxygen and impure nitrogen requires a slightly different plant from that for yielding pure nitrogen and impure oxygen. Hence slightly different forms of apparatus are used according to the object in view Griffiths (*Trans Faraday Soc*, 1922, 18, 224) discusses the production of liquid oxygen for use on air-craft

[3] See *Engineering,* 1915, 99, 155.

Thus treated, the air is admitted to the Linde plant at the mouth of the regenerator spiral AA′ through three small pipes a, one of which is surrounded by a wider concentric pipe b, as indicated in fig. 4. These small pipes continue, inside AA′, to encircle the rectifying column D and merge into the smaller spiral surrounded by liquid oxygen in B. The air on its passage becomes increasingly cooler, and escapes by way of the throttle-valve C to the top of the rectifying column D, a fall in temperature occurring at C owing to the Joule-Thomson effect. Ultimately a liquid rich in oxygen collects in B, whilst gas, rich in nitrogen and containing only about 7 per cent. of oxygen, escapes at E and leaves the apparatus through the regenerator spiral AA′, cooling in its passage, by conduction, the incoming air in a. The oxygen at F leaves through the tube b passing up inside A′A



Figs. 3 and 4.—The Linde oxygen plant.

When the apparatus has been at work a sufficient time to become steady, the liquid in B is continuously evaporated by the warmer air passing through the spiral, and the vapours escaping from B are rich in nitrogen, whilst the liquid remaining is rich in oxygen. The rectifying tower, with its baffle plates, reduces the amount of oxygen in the vapours escaping at E to about 7 per cent., for the ascending gases are constantly meeting liquids whose temperatures further up the rectifying column are increasingly lower. The oxygen thus condenses and joins the descending liquid stream. On the other hand, the nitrogen in that stream meets increasingly warmer gases as it falls, and having a lower boiling-point than the oxygen, it evaporates away and escapes at E. Liquid oxygen of 98 to 99 per cent. purity thus collects in B and is finally drawn off at H through b.

The efficiency of the apparatus depends upon the temperature gradient between D and F, and this is controlled by the throttle-valve C.

In practice it is found that a pressure of 50 to 60 atmospheres is sufficient, when the plant is in steady running, the temperature of the entering liquid air at D being −192° C., and at F −181·5° C.

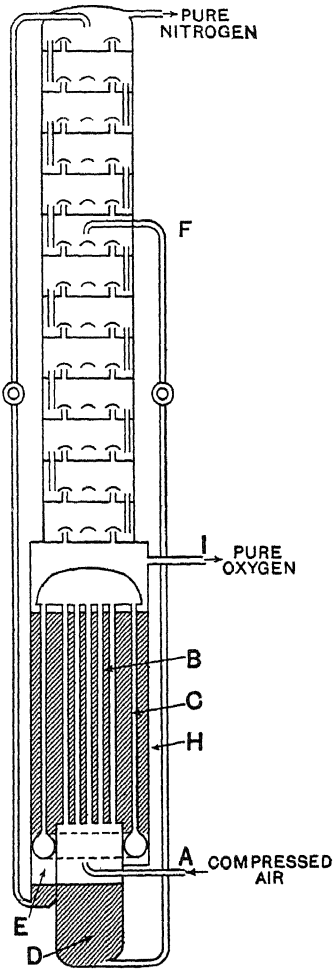


FIG. 5.—The Claude separator.

In Claude's[1] process compressed air, cooled by passage through a coil surrounded by the cold gases issuing from other parts of the apparatus, enters the lower portion of the apparatus (fig. 5) at A where it reaches the inner part of the tubular vessel B of annular cross-section; this vessel is surrounded by liquid oxygen. During its ascent through B, the air becomes partially condensed to a liquid which, as is shown by fig. 35, will contain up to 47 per cent. of oxygen. If the pressure of the incoming gas is correctly adjusted, the residual gas will consist of almost pure nitrogen, which will pass over into the external tubular space C, where it becomes entirely liquefied. The liquids condensed in D and E are therefore greatly enriched in oxygen and nitrogen respectively before admission to the "still" proper. The liquid collecting in D is caused by its pressure to rise through a regulating-valve into the fractionating column at F, and, overflowing downwards, meets the ascending gases from the liquid oxygen in H. On account of the contact between these two currents, the descending liquid grows steadily richer in oxygen until it reaches the vessel H, which is in connection with the tubes in B, as liquid oxygen. The gases rising up the column beyond F become submitted to further "scrubbing" by the liquid nitrogen reaching G from E, the effect of this being to condense any oxygen still remaining in the gas so that it returns to scrub the ascending gases in the lower portion of the column, whilst the gas issuing at the top is reduced to pure nitrogen. Gaseous oxygen can be drawn from I above the condensed liquid. Thus almost pure oxygen and nitrogen are simultaneously produced.[2]

Commercial liquid oxygen may contain argon. Morey[3] found the composition of liquid oxygen to be as follows:

| | |
|---|---|
| Oxygen . . . . . | 96·9 per cent. |
| Argon . . . . . | 2·8 ,, |
| Nitrogen . . . . . | 0·3 ,, |

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[1] Claude, *Compt. rend.*, 1905, 141, 823; also G. Claude, *Liquid Air, Oxygen, Nitrogen*, translated by H. E. P. Cottrell (Messrs J. & A. Churchill).

[2] For descriptions of *Pictet's process* reference may be made to *English Patent*, 27463 (1910); 9357 (1913); see also Maxted, *J Soc Chem. Ind.*, 1917, 36, 778.

[3] Morey, *J. Amer. Chem. Soc*, 1912, 34, 491. Compare Claude, *Compt. rend.*, 1910, 151, 752.

# CHAPTER III.

## THE PHYSICAL PROPERTIES OF OXYGEN.

GASEOUS oxygen is without colour, odour, or taste. The weight of 1 litre of the gas under standard conditions has been repeatedly determined, the more important results being given in the following table. The same result is reached irrespective of whether the gas is obtained chemically or from the atmosphere. As the result of a critical consideration of modern data Moles[1] concludes that the most probable value is 1·42891 ± 0·00003 grams.

**WEIGHT OF 1 LITRE OF OXYGEN IN GRAMS AT 0° C. AND 760 mm. PRESSURE.**

| Weight (grams). | Remarks. | Authority. |
|---|---|---|
| 1·42895 | Latitude 45° | Moles and Crespi, *Anal. Fís. Quím*, 1922, **20**, 190. Compare, Moles and Gonzalez, *ibid.*, 1922, **20**, 72. |
| 1·42889 | Mean of 45 determinations | Moles and Gonzalez, *Compt. rend.*, 1921, **173**, 355. |
| 1·42906 | Mean of 15 determinations at sea level and 45° latitude | Germann, *Compt. rend.*, 1913, **157**, 926. *J. Chim. phys.*, 1914, **12**, 66. |
| 1·42893 | .. | Jaquerod and Perrot, *Compt rend.*, 1905, **140**, 1542. |
| 1·4292 | .. | Jaquerod and Pintza, *ibid.*, 1904, **139**, 129. |
| 1·4293 | Paris[2] . . . | Leduc, *ibid.*, 1896, **123**, 805. |
| 1·42906 | Sea level, latitude, 45° . . . | Thomsen, *Zeitsch. anorg. Chem.*, 1896, **12**, 1. |
| 1·42954 | Paris[2] . . . | |
| 1·42900 | Mean of several series | Morley, *Zeitsch. physikal. Chem.*, 1896, **20**, 68. |
| 1·42952 | Paris[2] . . . | Rayleigh, *Proc. Roy. Soc.*, 1893, **53**, 134. |
| 1·42892 | Sea level, latitude, 45° . . . | Jolly, *Wied. Annalen*, 1879, **6**, 520. |
| 1·42939 | Paris[2] . . . | |
| 1·42971 | Paris[2] . . . | Jolly, corrected by Rayleigh, *l.c.* |
| 1·42980 | Paris[2] . . . | Regnault, 1847. |

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[1] Moles, *J. Chim. physique*, 1921, 19, 100.

[2] For Paris, the value of gravity $g = 980{\cdot}939$. Latitude, 48° 50′ N.

It may be mentioned that 1000 cubic feet of oxygen at 15° C. weigh 84·56 lb. (avoir.), whilst 1 lb. of the gas occupies 11·83 cubic feet.

Assuming the mean weight of a litre of air at Paris to be 1·2930 grams (see p. 191) and of oxygen 1·42891 grams, the relative density of the latter is 1·1051. Since the air is a mixture, and its composition subject to slight variation, its density is not perfectly constant, so that the above figure for the relative density of oxygen is merely a close approximation.

With reference to hydrogen as unity, the density of oxygen is 15·87.[1]

With reference to water at 4° C., the density of oxygen at N.T.P. is 0·00142952.[2]

Despite its greater density, oxygen transfuses through a caoutchouc membrane some 2½ times as rapidly as nitrogen [3] and a rough separation of the gases from ordinary air can be effected in this manner (see p. 13).

Oxygen, when subjected to increase of pressure, does not strictly obey Boyle's Law. At first the gas is slightly more compressible than the law demands, owing to the attraction between the gaseous molecules. Above 300 atmospheres, however, the product PV increases steadily as the influence of the dimensions of the molecules themselves begins to make itself felt. The gas thus becomes increasingly less compressible than the law requires. This is well shown by the numerical data given in the table on p. 194.

Considerable care must be exercised in compressing oxygen, for unless proper precautions are taken there is considerable danger of explosion. Thus the gauges must be particularly clean and free from oil and other organic matter, the only permissible lubricant being water.[4] Cylinders containing compressed oxygen are painted black; those with hydrogen, red; whilst nitrogen and air are stored in grey cylinders. This device tends to avoid confusion and explosions due to mixing the gases.

The diameter of a molecule of oxygen is given as 0·265 $\mu\mu$.[5]

**Solubility.**—Oxygen is slightly soluble in water and in aqueous solutions. Several methods have been devised for estimating the dissolved oxygen, and of these that due to Winkler is regarded as one of the most convenient and trustworthy.[6] As used by M'Arthur [7] the method consists in pouring the solution containing dissolved oxygen into a flask graduated to 250 c.c. and 252 c.c. respectively, as shown in fig. 6, until the former level is reached. One c.c. each of alkaline potassium iodide [8] and manganous chloride [9] solution are added, and the stopper

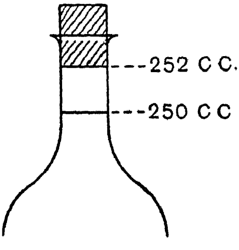

FIG. 6—Apparatus as used by M'Arthur (1916).

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[1] See this series, Vol. II., also this Vol, p. 35.

[2] Rayleigh, *loc. cit.*

[3] Graham, *J. Chem. Soc.*, 1865, 18, 9.

[4] Rasch, *Zeitsch komp. fluss. Gase*, 1904, p. 141; Wohler, *Zeitsch. angew. Chem.*, 1917, 30, 174.

[5] Keesom, *Proc. K. Akad. Wetensch. Amsterdam*, 1921, 23, 939.

[6] See Coste, *J. Soc. Chem. Ind.*, 1917, 36, 846.

[7] M'Arthur, *J. Physical Chem.*, 1916, 20, 495.

[8] Thirty-three grams NaOH, 10 grams KI. Dilute to 100 c.c.

[9] Forty grams $MnCl_2 . 4H_2O$ in 100 c.c. solution.

inserted to the 252 c.c. level. On shaking, the manganous hydroxide liberated by the sodium hydroxide is oxidised by the dissolved oxygen. The stopper is removed and the whole acidified with 3 c.c. of concentrated hydrochloric acid and well shaken. Titration of the liberated iodine, preferably in another flask or dish, with thiosulphate[1] gives the amount of oxygen.

Letts and Blake[2] use a large separating funnel (fig. 7), graduated to hold exactly 350 c.c. of liquid. It is filled with water, 7 c.c. removed and replaced by 5 c.c. of ferrous sulphate[3] solution and 2 c.c. of concentrated ammonia. The stopper is inserted, the whole well shaken and allowed to stand fifteen minutes. Upon inverting and filling the open tube with diluted sulphuric acid,[4] the tap may be opened. The acid enters owing to contraction caused by chemical action within the bulb, and, when all the ferrous hydroxide has dissolved, the solution is titrated with permanganate.[5]

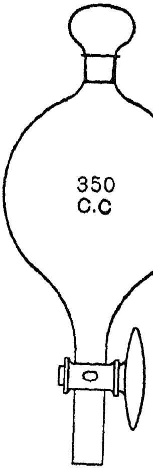

FIG. 7.—Apparatus as used by Letts and Blake (1899).

Volumetric methods are frequently adopted, the volume of gas absorbed by a given volume of gas-free liquid,[6] or, conversely, the volume expelled from the saturated solution being directly measured.

There are several ways in which the solubility of a gas may be expressed. By $\beta'$ is meant the volume of gas reduced to 0° C. and 760 mm. which is absorbed by one volume of the liquid under a total pressure of 760 mm., which includes the vapour pressure of the solvent.

$\beta$ is the volume of gas at N.T.P. absorbed by unit volume of the liquid under a partial pressure of the gas itself of 760 mm. irrespective of the vapour pressure of the liquid. It is known as *Bunsen's absorption coefficient.* Hence if $f$ is the vapour pressure of the solvent at any temperature

$$\beta' = \beta\frac{760-f}{760}.$$

*Ostwald's solubility product,* $l$, represents the ratio of the volume of absorbed gas to that of the liquid at the temperature and partial pressure of measurement. It is not reduced to 0° C. and 760 mm. Hence, if the measurements are made at atmospheric pressure

$$l = \beta(1+0{\cdot}00367t).$$

In the following table are given the results obtained by different modern investigators for the absorption coefficient, $\beta$, of oxygen in distilled water.

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[1] Preferably N/100.

[2] Letts and Blake, *Proc. Roy. Dublin Soc.*, 1899–1902, 9, 454.

[3] Twelve grams $FeSO_4$ per 250 c.c. of solution.

[4] Equal parts acid and water.

[5] A convenient strength is N/10.

[6] Winkler, *Ber.*, 1891, 24, 89; Estreicher, *Zeitsch. physikal. Chem*, 1899, 31, 176; Fox, *Trans. Faraday Soc.*, 1909, 5, 68.

## SOLUBILITY OF OXYGEN IN WATER.[1]

| Temperature, ° C. | Winkler,[2] 1891. | Bohr and Bock,[3] 1891. | Fox,[4] 1909. | Adeney and Becker,[5] 1919. |
|---|---|---|---|---|
| 0 | 0·04890 | 0·04961 | 0·04924 | 0·04660 |
| 10 | 0·03802 | 0·03903 | 0·03837 | 0·03620 |
| 20 | 0·03102 | 0·03171 | 0·03144 | 0·02965 |
| 30 | 0·02608 | 0·02676 | 0·02665 | 0·02479 |
| 40 | 0·02306 | 0·02326 | 0·02330 | .. |
| 50 | 0·02090 | 0·02070 | 0·02095 | .. |

Several complicated empirical formulæ have been given by means of which the solubility of oxygen may be calculated for any desired temperature. Winkler[6] gives, for temperatures between 0° and 30° C., the formula

$$\beta=0{\cdot}04890-0{\cdot}0013413t+0{\cdot}0000283t^2-0{\cdot}00000029534t^3.$$

Fox[7] gives an analogous expression for a temperature interval of 0° to 50° C.:

$$\beta=0{\cdot}049239-0{\cdot}0013440t+0{\cdot}000028752t^2-0{\cdot}0000003024t^3.$$

The solution of oxygen in water is accompanied by an expansion of the latter, 1 c.c. becoming 1·00115 c.c. on the absorption of 1 c.c. of oxygen.[8]

### *The Rate of Solution of Oxygen and Air in Water.*

Comparatively little work has been carried out on the velocity with which partially or completely de-aerated water reabsorbs oxygen and nitrogen from the atmosphere. Two cases merit consideration, namely:

(1) When the water is subjected to agitation so that fresh surface layers are continually formed, the rate of gaseous absorption is then at its maximum.

(2) When the water is quiescent. In this latter case the process is not purely one of absorption followed by diffusion[9] into the body of the liquid from the surface layers, as has generally been supposed. It is considerably more rapid than this. Experiment shows that the gases do not remain concentrated in the surface layers, but tend to "stream"[10] downwards under the influence of gravity, and thus to promote com-

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[1] For a general review, see Coste, *J. Soc. Chem. Ind.*, 1918, 37, 170 T.; 1917, 36, 846; also Carlson, *Zeitsch. angew. Chem.*, 1913, 26, 713

[2] Winkler, *Ber.*, 1891, 24, 3602; 1889, 22, 1764.

[3] Bohr and Bock, *Wied. Annalen*, 1891, 44, 318.

[4] Fox, *Trans. Faraday Soc*, 1909, 5, 68.

[5] Adeney and Becker (*Sci. Proc. Roy. Dublin Soc*, 1918, 15, 385, 1919, 15, 609) also discuss the rate of solution of oxygen in water, giving mathematical formulæ for determining the same at different temperatures (see below).

[6] Winkler, *Ber.*, 1889, 22, 1764.

[7] Fox, *Trans Faraday Soc*, 1909, 5, 68.

[8] Angstrom, *Wied. Annalen*, 1882, 15, 297.

[9] Adeney, *Phil Mag.*, 1905, 9, 360.

[10] Hüffner, *Wied. Annalen*, 1897, 60, 134. Compare Carlson, *Medd. K. Vetensk. Nobel-inst.*, 1911, 2, No. 6, 1.

paratively rapid mixing. This is a point of very great biological and economic importance.

Much of the modern research on the subject is due to Adeney and Becker,[1] whose initial researches were concerned with the rate of absorption of air by water under gentle agitation. They begin with the assumption that,[2] during the process of solution, the rate of passage, R, of gas into the liquid is proportional to the partial pressure of the gas, $p$, and the area, A, of the liquid exposed. Hence

$$R = uAp$$

where $u$ is the velocity of solution per unit area. Simultaneously with absorption, however, evaporation of the gas into the air takes place, with a rapidity proportional to the area A, and to the concentration, $w$, of the gas in the upper layers. If the coefficient of escape of the gas per unit area and volume of the liquid is denoted by $f$, the rate of escape, $R^1$, of the gas from the liquid is given by the expression

$$R^1 = fwA,$$

$w$ being expressed as grams of gas per c.c. of the upper layer.

The net rate of solution of the gas, therefore, is

$$R - R^1 = uAp - fwA,$$

and the two latter terms become equal upon saturation, when

$$fw = up.$$

Denoting the volume of the liquid by V, it follows that the rate of solution

$$\begin{aligned}\frac{dw}{d\theta} &= \frac{uAp}{V} - fw\frac{A}{V}\\ &= a - bw\end{aligned}$$

where $a = uAp/V$ and $b = fA/V$, time being expressed as $\theta$.

The above equation may, for the sake of convenience, be expressed somewhat differently. Writing

$$\frac{dw}{d\theta} = -b\left(w - \frac{a}{b}\right),$$

it follows that

$$\frac{dw}{w - a/b} = -bd\theta\,;$$

whence

$$\log_e (w - a/b) = -b\theta + \log_e C\,;$$

or, delogarising,

$$w - a/b = Ce^{-b\theta},$$

C being a constant. When $w=0$, $\theta=0$. Hence

$$C = -\frac{a}{b}$$

and

$$w = \frac{a}{b}(1 - e^{-b\theta}).$$

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[1] Adeney and Becker, *Sci. Proc. Roy. Dublin Soc*, 1918, 15, No. 31; 1919, 15, No. 44. Reprinted in *Phil. Mag.*, 1919, 38, 317; 1920, 39, 385; 1923, 45, 581. Adeney, Leonard, and Richardson, *Phil. Mag*, 1923, 45, 835.

[2] See Bohr, *Wied. Annalen*, 1899, 68, 500; 1897, 62, 644.

For practical purposes it is most convenient to express the results in terms of the percentage of saturation. So that if $w$ is the amount of gas in solution initially, expressed as a percentage of total saturation, the amount $w$ dissolved after a given time $\theta$ is

$$w=(100-w_1)(1-e^{-b\theta})=(100-w_1)(1-e^{-fA\theta/V}).$$

Now $f$ varies both with the temperature and the humidity. For an atmosphere saturated with moisture the following values for $f$ have been determined, the water being gently agitated to ensure thorough mixing :

For oxygen . . . $f=0{\cdot}0096\ (T-237)$
,, nitrogen . . . $f=0{\cdot}0103\ (T-240)$
,, air . . . . $f=0{\cdot}0099\ (T-239)$,

T being the absolute temperature, and $\theta$ expressed in minutes.

An example will make the value of the above equation quite clear.[1] Consider a cubic decimetre of water at 2·5° C. and containing 40 per cent. of its total saturation capacity for oxygen. If it exposes one side (100 sq. cm.) to oxygen, how much gas will be dissolved in one hour under gentle agitation ?

It is unnecessary to consider the pressure of the gas since Henry's Law is obeyed and the desired result is to be calculated in percentage of total saturation. Since $\theta=60$, $w_1=40$, $f=0{\cdot}0096\ (275{\cdot}5-237)$, it is easy to calculate that

$$w=11{\cdot}8.$$

In other words, after an hour the oxygen content will have risen from 40 to 51·8 per cent. of saturation.

The foregoing values for $f$ were determined experimentally for water under gentle agitation in an atmosphere saturated with moisture. Such conditions are largely artificial.

For quiescent bodies of water the following data have been obtained :[2]

| | Value of $f$ at 15° C. |
|---|---|
| Air dried over calcium chloride . . . | 0·61 |
| Air of average humidity[3] . . . . | 0·34 |
| Air nearly saturated with moisture . . | 0·23 |

These results are very striking, showing that dry air is much more rapidly absorbed than moist. This is interpreted as meaning that the process by which the dissolved gas is carried down into the body of the liquid is influenced by the rate of evaporation of the liquid surface, this being at a maximum when the air is dry. In the case of pure water this is merely a temperature effect, the evaporation causing a cooling of the surface layers and, at temperatures above 4° C., a gravitational circulation. In the case of solutions, such as sea-water, density changes, consequent upon variation in superficial concentration, are superimposed on the temperature effect, so that more rapid mixing is likely to occur. This is confirmed by experiments which yielded the following values for $f$ at 15° C. under similar conditions of average humidity :[1]

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[1] Taken from Adeney and Becker, *loc. cit.*

[2] Adeney and Becker, *Sci. Proc. Roy. Dublin Soc.*, 1920, 16, No. 20.

[3] The actual humidity is not stated.

| | |
|---|---|
| Tap-water . . . . | $f=0{\cdot}388$ |
| Sea-water . . . . | $f=0{\cdot}509$ |

The rate of solution of oxygen in water does not appear to be appreciably retarded by a thin layer of petroleum.[2]

As a general rule the presence of dissolved salts, chemically neutral towards oxygen, reduces the solubility of the gas. Thus, in the case of sea-water, the value for $\beta$ falls with rising chlorine content, as indicated in the following table :[3]

### SOLUBILITY OF OXYGEN IN SEA-WATER FROM A FREE, DRY ATMOSPHERE AT 760 mm.

(Fox, 1909.)

| Parts of Chlorine per 1000. | Temperature, ° C. | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 4. | 8. | 12. | 16. | 20. |
| 0 | 10·29 | 9·26 | 8·40 | 7·68 | 7·08 | 6·57 |
| 4 | 9·83 | 8·85 | 8·04 | 7·36 | 6·80 | 6·33 |
| 8 | 9·36 | 8·45 | 7·68 | 7·04 | 6·52 | 6·07 |
| 12 | 8·90 | 8·04 | 7·33 | 6·74 | 6·24 | 5·82 |
| 16 | 8·43 | 7·64 | 6·97 | 6·43 | 5·96 | 5·56 |
| 20 | 7·97 | 7·23 | 6·62 | 6·11 | 5·69 | 5·31 |

These results may be expressed mathematically by the equation

$$1000\beta''=10{\cdot}291-0{\cdot}2809t+0{\cdot}006009t^2+0{\cdot}0000632t^3$$
$$-\mathrm{Cl}(0{\cdot}1161-0{\cdot}003922t+0{\cdot}0000631t^2),$$

the chlorine being expressed as grams per litre.

The foregoing data have been recalculated to parts per million by Whipple.[4] Earlier data are those of Clowes and Biggs,[5] who show that the solubility of atmospheric oxygen in diluted sea-water falls regularly with the amount of sea-water present; the sodium chloride, as the predominant salt, has a determining effect upon the quantity of gas dissolved.

The following data, based on the results of M'Arthur,[6] give the actual and relative solubilities of oxygen in solutions of various salts at 25° C.

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[1] The actual humidity is not stated.

[2] Friend, *Carnegie Scholarship Memoirs*, Iron and Steel Institute, No. 3, 1911, p. 9; Stephenson, *Analyst*, 1919, 44, 288.

[3] Fox, *loc. cit.* The data, $\beta''$, give the number of c.c. of oxygen as measured at N.T.P. that would be absorbed under a total pressure of 760 mm. of dry air, but a partial oxygen pressure of $760\times0{\cdot}21$ mm

[4] Whipple, *J. Amer. Chem. Soc.*, 1911, 33, 362.

[5] Clowes and Biggs, *J. Soc Chem. Ind.*, 1904, 23, 358.

[6] M'Arthur, *loc. cit.* These data refer to oxygen as absorbed direct from the air at a partial pressure of $760\times0{\cdot}21$ mm.

## SOLUBILITY OF OXYGEN IN AQUEOUS SOLUTIONS.

(M'Arthur, 1916.)

| Salt. | Molecular Concentration | Grams per Litre. | Relative Density at 25° C. | c c. Oxygen per Litre. | Relative Solubility. |
|---|---|---|---|---|---|
| Water only | .. | .. | 1·0000 | 5·78 | 100 |
| NaCl | m/8 | 7·31 | 1·0022 | 5·52 | 95·5 |
| | m/4 | 14·62 | 1·0067 | 5·30 | 91·7 |
| | m/2 | 29·23 | 1·017 | 4·92 | 85·5 |
| | m | 58·46 | 1·038 | 4·20 | 72·7 |
| | 2m | 117·0 | 1·075 | 3·05 | 52·8 |
| | 3m | 175·5 | 1·112 | 2·24 | 38·8 |
| | 4m | 234·0 | 1·149 | 1·62 | 28·1 |
| KCl | m/8 | 9·32 | 1·003 | 5·52 | 95·5 |
| | m/4 | 18·64 | 1·0086 | 5·30 | 91·7 |
| | m/2 | 37·28 | 1·020 | 4·98 | 86·2 |
| | m | 74·56 | 1·042 | 4·26 | 73·7 |
| | 2m | 149·1 | 1·086 | 3·21 | 55·5 |
| | 3m | 223·7 | 1·134 | 2·36 | 40·8 |
| | 4m | 298·2 | 1·170 | 1·86 | 32·2 |
| KI | m/8 | 20·75 | 1·013 | 5·65 | 97·8 |
| | m/4 | 41·50 | 1·027 | 5·49 | 95·0 |
| | m/2 | 83·0 | 1·056 | 5·20 | 90·0 |
| | m | 166·0 | 1·116 | 4·75 | 82·2 |
| | 2m | 332·0 | 1·230 | 3·77 | 65·2 |
| | 5m | 830·0 | 1·460 | 1·81 | 31·3 |
| $NH_4Cl$ | m/8 | 6·69 | 1·0015 | 2·31 | 40·0 |
| | m/4 | 13·37 | 1·0025 | 1·16 | 20·1 |
| | m | 53·47 | 1·0014 | 0·07 | 0·1 |
| $KNO_3$ | m/4 | 25·28 | 1·015 | 5·49 | 95·0 |
| | m/2 | 50·56 | 1·029 | 5·11 | 88·4 |
| | m | 101·11 | 1·059 | 4·61 | 79·8 |
| | 2m | 202·22 | 1·110 | 3·65 | 63·1 |
| $Na_2SO_4$ | m/8 | 17·76 | 1·014 | 5·04 | 87·2 |
| | m/4 | 35·52 | 1·032 | 4·60 | 79·6 |
| | m/2 | 71·03 | 1·063 | 3·97 | 68·7 |
| | m | 142·06 | 1·13 | 3·00 | 51·9 |
| $K_2SO_4$ | m/8 | 21·78 | 1·016 | 5·11 | 88·4 |
| | m/4 | 43·57 | 1·032 | 4·66 | 80·6 |
| | m/2 | 87·13 | 1·060 | 3·89 | 67·3 |

### Solubility of Oxygen in Aqueous Solutions—(*continued*).

| Salt. | Molecular Concentration. | Grams per Litre | Relative Density at 25° C | c.c. Oxygen per Litre | Relative Solubility. |
|---|---|---|---|---|---|
| $MgCl_2$ | m/8 | 11·91 | 1·011 | 5·35 | 92·6 |
| | m/4 | 23·81 | 1·022 | 5·04 | 87·2 |
| | m/2 | 47·62 | 1·044 | 4·37 | 75·6 |
| | m | 95·24 | 1·085 | 3·18 | 55·0 |
| | 2m | 190·48 | 1·160 | 2·22 | 38·4 |
| | 4m | 381·0 | 1·284 | 0·78 | 13·5 |
| | 5m | 476·2 | 1·343 | 0·54 | 9·3 |
| $BaCl_2$ | m/8 | 26·04 | 1·019 | 5·40 | 93·4 |
| | m/4 | 52·08 | 1·042 | 5·04 | 87·2 |
| | m/2 | 104·15 | 1·082 | 4·27 | 73·8 |
| | m | 208·29 | 1·177 | 3·10 | 53·6 |
| $CaCl_2$ | m/4 | 27·75 | 1·022 | 5·08 | 87·9 |
| | m | 111·0 | 1·084 | 3·71 | 64·2 |
| | 5m | 555·0 | 1·340 | 2·14 | 37·0 |

The solubility of oxygen in aqueous solutions of acids and alkalies is given by Geffcken as follows: [1]

### SOLUBILITY OF OXYGEN IN DILUTE ACIDS AND ALKALIES. (Geffcken, 1904.)

| Solution. | Molecular Concentration. | Grams per Litre. | c.c. Oxygen per c.c. at | |
|---|---|---|---|---|
| | | | *l* (15° C.) | *l* (25° C.) |
| Water only | .. | .. | 0·0363 | 0·0308 |
| $H_2SO_4$ | m/4 | 24·52 | 0·0338 | 0·0288 |
| | m/2 | 49·04 | 0·0319 | 0·0275 |
| | m | 98·08 | 0·0285 [2] | 0·0251 |
| | 3m/2 | 147·12 | 0·0256 | 0·0229 |
| | 2m | 196·16 | 0·0233 | 0·0209 |
| | 5m/2 | 245·20 | 0·0213 | 0·0194 |
| HCl | m/2 | 18·22 | 0·0344 | 0·0296 |
| | m | 36·45 | 0·0327 | 0·0287 |
| | 2m | 72·90 | 0·0299 | 0·0267 |
| $HNO_3$ | m/2 | 36·52 | 0·0348 | 0·0302 |
| | m | 63·05 | 0·0336 | 0·0295 |
| | 2m | 126·10 | 0·0315 | 0·0284 |
| NaOH | m/2 | 20·03 | 0·0288 | 0·0250 |
| | m | 40·06 | 0·0231 | 0·0204 |
| | 2m | 80·12 | 0·0152 | 0·0133 |
| KOH | m/2 | 28·08 | 0·0291 | 0·0252 |
| | m | 56·16 | 0·0234 | 0·0206 |

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[1] Geffcken, *Zeitsch. physikal. Chem.*, 1904, 49, 257. Other data for sulphuric acid are given by Bohr (*ibid.*, 1910, 71, 47) and Christoff (*ibid.*, 1906, 55, 622).

[2] Calculated by the present authors. There is clearly a misprint in Geffcken's original paper at this point.

Oxygen is much more readily soluble in blood than in water; 100 c.c. of average human blood is able, when fully saturated in contact with air, to hold between 18 and 19 c.c. of oxygen measured at N.T.P. (see p. 135). In ethyl alcohol, oxygen is several times more soluble than in water.[1] Its solubility at any temperature may be calculated from the following equation: [2]

$$\beta = 0{\cdot}2337 - 0{\cdot}00074688t + 0{\cdot}000003288t^2.$$

The solubility of oxygen in aqueous solutions of ethyl alcohol at 20° C. is as follows: [3]

| Alcohol per cent. by weight | 9·09 | 16·67 | 23·08 | 28·57 | 33·33 | 50·00 | 66·67 | 80·00 |
|---|---|---|---|---|---|---|---|---|
| $l$ . . . . . | 2·78 | 2·63 | 2·52 | 2·49 | 2·67 | 3·50 | 4·95 | 5·66 |

It will be observed that there is a decided minimum solubility at about 30 per cent. of alcohol.

These data refer to an atmosphere of oxygen of partial pressure, 760 mm.

Oxygen is also soluble in certain molten metals,[4] *e.g.* platinum and silver, more than twenty times its own volume of the gas being absorbed in the case of the latter metal; the dissolved gas is largely, but not completely, restored at the moment of solidification of the metal, and the phenomenon of "spitting" is thus produced. The power of oxygen to diffuse through heated silver, whereas glass is impervious, is probably due to this solubility of oxygen in the metal.[5]

Certain finely divided metals, especially platinum black and palladium black, can absorb many times their own volume of oxygen. In the case of the latter metal [6] absorption is probably attended by the formation of an oxide or mixture of oxides, but in the case of the former, although the product may include an unstable oxide,[7] the oxygen can be entirely recovered by reducing the pressure.[8]

Wood charcoal can absorb eighteen times its own volume of oxygen at 0° C. and more than two hundred times its bulk at −185° C.; the absorbed gas is liberated if the charcoal is heated.[9]

By *thermal conductivity* is understood the quantity of heat [10] that would pass between the opposite faces of a unit cube with unit temperature difference between the faces. The value found [11] for oxygen at a

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[1] Carius, *Annalen*, 1855, 94, 134.

[2] Timofeieff, *Zeitsch. physikal. Chem.*, 1890, 6, 141.

[3] Lubarsch, *Wied Annalen*, 1889, 37, 525

[4] Deville, *Compt. rend.*, 1870, 70, 756; Levol, *Compt. rend*, 1852, 35, 63; Dumas, *Ann. Chim. Phys*, 1878, [5], 14, 289; Sieverts and Hagenacker, *Zeitsch. physikal. Chem.*, 1909, 68, 115; Donnan and Shaw, *J. Soc Chem. Ind.*, 1910, 29, 987.

[5] Bartoli, *Gazzetta*, 1884, 14, 544; Troost, *Compt. rend.*, 1884, 98, 1427; Graham, *Phil. Mag.*, 1866, [4], 32, 503.

[6] Neumann, *Monatsh.*, 1892, 13, 40; Willm, *Bull. Soc. chim.*, 1882, [2], 38, 611; Mond, Ramsay, and Shields, *Proc. Roy. Soc.*, 1897, 62, 290; *Zeitsch. physikal. Chem.*, 1898, 25, 657. See also this series, Vol. IX., Part I.

[7] Engler and Wohler, *Zeitsch. anorg. Chem.*, 1902, 29, 1; Mond, Ramsay, and Shields, *loc. cit*

[8] Ramsay and Shields, *Phil. Trans.*, 1896, 186, 657. See also Lucas, *Zeitsch. Elektrochem.*, 1905, 11, 182

[9] Joulin, *Compt. rend*, 1880, 90, 741.

[10] Expressed in calories. Adopting metric units, the conductivity is given by the expression

$$k = \text{calorie} \times \text{cm.}^{-1} \times \text{sec}^{-1} \times \text{temp. } (^\circ\text{ C.})^{-1}.$$

[11] Todd, *Proc. Roy. Soc.*, 1909, [A], 83, 19.

mean temperature of 55° C. is 0·0000593. According to the kinetic theory of gases the thermal conductivity, $k$, is given by the expression

$$k = f\eta C_v$$

where $\eta$ is the viscosity of the gas and $C_v$ the specific heat at constant volume. $f$ is a constant, apparently depending on the ratio of the specific heats,[1] and in the case of diatomic gases has the value 1·603.

The *viscosity* of oxygen at 23·00° C. and 760 mm. pressure is $2042{\cdot}35 \times 10^{-7}$.[2] The viscosity rises with the temperature. Its mean *specific heat* at constant pressure rises with temperature as indicated in the following table:[3]

## SPECIFIC HEAT OF OXYGEN.

| Temperature Interval, ° C. | Mean Specific Heat at Constant Pressure. |
|---|---|
| 20 to 440 | 0·2240 |
| 20 to 630 | 0·2300 |

The ratio of the specific heat at constant pressure to that at constant volume is

$$\gamma = Cp/Cv = 1{\cdot}399$$

—a value to be expected for a diatomic gas.[4]

The *molecular specific heat* at constant volume is given by the expression[5]

$$C_v = 4{\cdot}900 + 0{\cdot}00045t$$

and at constant pressure by[6]

$$C_p = 6{\cdot}50 + 0{\cdot}0010T$$

where $t$ and T are on the centigrade and absolute scales respectively. The molecular specific heat at constant pressure at 20° C. is calculated as 6·924 from the velocity of sound in oxygen by Kundt's method[7]

The *coefficient of expansion* per degree centigrade rise in temperature between 0° and 100° C., measured at constant pressure of one atmosphere, was determined by Jolly[8] as 0·0036743, and found to be constant for a temperature ranging up to 1600° C.

[1] Meyer, *Kinetische Theorie der Gase* (Breslau, 1877); Schleiermacher, *Wied. Annalen*, 1889, 36, 346.

[2] Yen, *Phil. Mag.*, 1919, [6], 38, 582. See also Schmitt, *Ann Physik*, 1909, 30, 398; von Obermeyer, *Sitzungsber. K. Akad. Wiss. Wien.*, 1875, 71, 281.

[3] Holborn and Austin, *Sitzungsber. K Akad. Wiss. Berlin*, 1905, p 175; earlier data are given by Regnault, *Mém. de l'Acad.*, 1862, 26, 1.

[4] Mercer, *Proc. Phys. Soc. London*, 1914, 26, 155, see for earlier data Cazin, *Ann. Chim. Phys.*, 1862, 26, 1; Müller, *Ber.*, 1883, 16, 214, *Wied. Annalen*, 1883, 18, 94; Lummer and Pringsheim, *ibid.*, 1898, 64, 555; Kuster, *Dissertation*, Marburg, 1911

[5] Pier, *Zeitsch. Elektrochem.*, 1909, 15, 536; 1910, 16, 879.

[6] Lewis and Randall, *J. Amer. Chem. Soc*, 1912, 34, 1128.

[7] Schweikert, *Ann. Physik*, 1915, 48, 593.

[8] Jolly, *Pogg. Annalen*, Jubelband, 1874, p. 82.

For a gas that obeys Boyle's Law the coefficient of expansion at constant pressure is numerically the same as the coefficient of increase of pressure with rise of temperature at constant volume. This has been determined for a temperature interval of 0° to 1067° C. and has the value 0·0036652 in the case of oxygen.[1]

The *refractive index* [2] of oxygen is 1·000272 at 0° C. and 760 mm. for the sodium D line ($\lambda=5893\times10^{-8}$ cm.); the indices for other wave-lengths not widely removed may be calculated from Cauchy's equation

$$\mu-1=A(1+B/\lambda^2)$$

where $\mu$ and $\lambda$ represent the refractive index and wave-length respectively, whilst A and B are constants; the latter constant, B, is the coefficient of dispersion. For oxygen gas, $A=26{\cdot}63\times10^{-5}$, and $B=5{\cdot}07\times10^{-11}$. According to Cuthbertson,[3] the refractive index, $n$, of oxygen for any incident light of frequency, $f$, is given by the expression

$$n-1=\frac{3{\cdot}397\times10^{27}}{12804\times10-f^2}.$$

Examination of long layers of the gas shows oxygen to exert a selective *absorption* for light in certain parts of the spectrum.[4]

The *emission spectra* obtained by an electric discharge through the gas under a reduced pressure and by the spark discharge are of a complex nature.[5]

Both the magnetic susceptibility [6] and the magnetic rotatory power [7] of gaseous oxygen have been subjected to investigation.

**Liquid oxygen** is a transparent liquid, possessed of a bluish tinge. Its critical constants have been variously determined as follows :

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[1] Jaquerod and Perrot, *Compt. rend*, 1905, 140, 1542.

[2] Rentschler, *Astrophys J*, 1908, 28, 345; see also Koch, *Ann. Physik*, 1905, 17, 658; Ramsay and Travers, *Proc. Roy. Soc*, 1897, 62, 225; Lorenz, *Wied. Annalen*, 1880, 11, 70; Craillebois, *Ann Chim. Phys.*, 1870, [4,] 20, 136. In the infra-red region, see Statescu, *Bull. Acad. Sci. Roumanie*, 1914–15, 3, 211.

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

[4] Egoroff, *Compt. rend*, 1885, 101, 1143; 1888, 106, 1118; Janssen studied the absorption under pressures ranging up to 27 atmospheres, *ibid*, 1885, 101, 111, 649; 1886, 102, 1352, 1888, 106, 1118; 1888, 107, 672. His results were supported by Liveing and Dewar, *Phil. Mag*, 1888, 26, 286. See also von Wartenberg, *Physikal. Zeitsch.*, 1910, 11, 1168; Bloch, *Compt rend.*, 1914, 158, 1161; Warburg, *Sitzungsber. Preuss. Akad. Wiss Berlin*, 1915, p 230; Duclaux and Jeantet, *Compt. rend*, 1921, 173, 581; Shaver, *Trans. Roy. Soc. Canada*, 1921, 15, [3], 7.

[5] See Schuster, *Proc Roy Soc*, 1878, 27, 383; *Phil. Trans.*, 1879, 170, 137; Vogel, *Ber.*, 1879, 12, 332; Smith, *Phil. Mag.*, 1882, 13, 330; Grunwald, *Chem. News*, 1887, 56, 201, 223, 232; Runge and Paschen, *Wied Annalen*, 1897, 61, 641; Steubing, *Ann. Physik*, 1910, 33, 553, 1912, 39, 1408; Stark, *Physikal. Zeitsch*, 1913, 14, 770, 779; Scharbach, *Zeitsch. wiss. Photochem.*, 1913, 12, 145; Croze, *Compt. rend.*, 1913, 157, 1061; 1912, 155, 1607; Paschen and Back, *Ann. Physik*, 1912, 39, 897; Yoshida, *Mem Coll. Sci. Kyoto*, 1919, 3 287; Bottcher and Tuczek, *Ann. Physik*, 1920, 61, 107; Runge, *Physica*, 1921, 1, 254. For a study of the spectrum in the extreme ultraviolet, see Hopfield, *Physical Review*, 1922, 20, 573.

[6] Onnes and Oosterhuis, *Proc K. Akad Wetensch. Amsterdam*, 1913, 15, 1404; Bauer Weiss, and Piccard, *Compt. rend.*, 1918, 167, 484; Weiss and Piccard, *ibid.*, 1912, 155, 1234; Piccard, *Arch. Sci. phys. nat*, 1913, 35, 458.

[7] Kundt and Rontgen, *Ann. Phys. Chem.*, 1899, 8, 278; 1880, 10, 257; Becquerel, *Compt. rend.*, 1880, 90, 1451.

## CRITICAL CONSTANTS OF OXYGEN.

| Critical Temperature, ° C. | Critical Pressure, Atm. | Critical Volume, c.c /gram | Critical Density, gram/c c. | Critical Volume expressed relatively to that of the Gas measured at N.T.P. | Authority. |
|---|---|---|---|---|---|
| −113 | 50 | . | .. | . | Wroblewski, *Compt. rend.*, 1883, 97, 309. |
| −118·8 | 50·8 | . | . | .. | Olszewski, *ibid.*, 1885, 100, 351. |
| −113 | 50 | .. | .. |  | Dewar, *Chem. News*, 1885, 51, 27. |
| −118 0 | .. | 2 269 | 0 4407 | .. | Dewar, *Proc. Roy. Soc.*, 1904, 73, 251. |
|  | .. | 2·326 | 0 4299 | 0·00426 | Mathias and Onnes, *Proc. K. Akad Wetensch. Amsterdam*, 1911, 13, 939. |
| −118 82 | 49 640 |  | .. | .. | Onnes, Dorsman, and Holst, *ibid*, 1915, 17, 950; 18, 409. |
| −118 0 | 49 3 |  | .. | . | Cardoso, *Arch Sci Phys. Nat.*, 1915, 39, 400, *J. Chim. phys.*, 1915, 13, 312. |

The boiling-point of liquid oxygen varies with the pressure, as indicated in the following table: [1]

## VARIATION OF THE BOILING-POINT OF OXYGEN WITH THE PRESSURE.[2]

| Pressure, mm. | Absolute Boiling-point. | |
|---|---|---|
| | Hydrogen Scale | Helium Scale. |
| 800 | 90·60 | 90·70 |
| **760** | **90·10** | **90·20** |
| 700 | 89·33 | 89·43 |
| 600 | 87·91 | 88·01 |
| 500 | 86·29 | 86·39 |
| 400 | 84·39 | 84·49 |
| 300 | 82·09 | 82·19 |
| 200 | 79·07 | 79·17 |

The vapour pressure rises from 9 096 atm. at −154·91° C. to 49·640 atm. at −118·70° C.[3]

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[1] Travers, Senter, and Jaquerod, *Proc. Roy. Soc.*, 1902, 70, 484.

[2] Earlier data are those of Wroblewski and Olszewski, *Compt. rend.*, 1883, 96, 1140; Wroblewski, *ibid.*, 1883, 97, 1553; 1884, 98, 984; 1885, 100, 351, 979; Estreicher, *Phil. Mag.*, 1895, 40, 458; Ladenburg and Krugel, *Ber.*, 1899, 32, 1818.

[3] Onnes, Dorsman, and Holst, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, 17, 950.

The vapour pressure of oxygen at any temperature between 57° and 90° abs. may be calculated from the expression

$$\log p = -419{\cdot}31/T + 5{\cdot}2365 - 0{\cdot}0648T$$

where the pressure $p$ is expressed in atmospheres, T being the absolute temperature.[1]

For $p=1$ atm., the value for T becomes 90·13°, which agrees very satisfactorily with the boiling-point under normal pressure as given in the preceding table.

## DENSITIES OF LIQUID OXYGEN AT VARIOUS TEMPERATURES.[2]

| Temperature, ° C | Density | Authority. |
|---|---|---|
| −183·6 | 1·1321 | Drugman and Ramsay, *Trans. Chem. Soc.*, 1900, **77**, 1228. |
| −183·3 | 1·1310 | |
| −182·5 | 1·1181 | Dewar, *Proc. Roy. Soc.*, 1904, **73**, 251. |
| −195·5 | 1·1700 | „ „ „ „ |
| −210·5 | 1·2386 | „ „ „ „ |
| −193·93 | 1·203 | Inglis and Coates, *Trans. Chem. Soc.*, 1906, **89**, 886. |
| −198·30 | 1·223 | |

When the values obtained by Dewar for the densities are plotted against the absolute temperatures, they are seen to lie very closely to a straight line, so that the densities at intermediate temperatures can readily be calculated. The expression is

$$\text{Density} = 1{\cdot}5154 - 0{\cdot}004420T$$

where T is the absolute temperature.

Using the data given by Ramsay and Drugman, the specific volume of oxygen at −183° C. is 0·8838, and the molecular volume 28·28.

Baly and Donnan [3] give the data (included in the Table on p. 48).

When exposed to the air, liquid oxygen absorbs appreciable quantities of nitrogen.[4]

Liquid oxygen is more compressible than water, its coefficient of compressibility (see p. 262) being 0·00195 between 10 and 20 atmospheres.[5]

The observed surface tension of the liquid is 13·074 dynes per cm — a value in fair agreement with that expected for a liquid of the same molecular weight as gaseous oxygen, although the possibility of slight association is not excluded.[6] From other data Inglis and Coates [7] conclude that the degree of association of liquid oxygen at about —195° C. is 1·09.

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[1] Cath, *Proc. K. Akad Wetensch. Amsterdam*, 1919, 21, 656.

[2] Earlier data are those of Cailletet and Hautefeuille, *Compt. rend*, 1881, 92, 1086; Olszewski, *Sitzungsber. K. Akad Wiss Wien*, 1884, p. 72, Wroblewski, *Compt. rend.*, 1886, 102, 1010; Dewar, *Chem. News*, 1896, 73, 40; Ladenburg and Krugel, *Ber.*, 1899, 32, 46, 1415.

[3] Baly and Donnan, *Trans Chem Soc*, 1902, 81, 907.

[4] Erdmann and Bedford, *Ber.*, 1904, 37, 1184 and 1432; see also Stock, *ibid.*, p. 1432.

[5] Eucken, *Ber. deut. physikal Ges*, 1916, 18, 4

[6] Baly and Donnan, *Trans Chem. Soc.*, 1902, 81, 907; Grunmach, *Sitzungsber. K. Akad. Wiss. Berlin*, 1906, p. 679.

[7] Inglis and Coates, *Trans. Chem. Soc.*, 1906, 89, 886.

## DENSITIES OF LIQUID OXYGEN.

(Baly and Donnan, 1902.)

| Temperature, ° Abs | Temperature, ° C | Density. |
|---|---|---|
| 68·0 | —205 | 1·2489 |
| 70·0 | —203 | 1·2393 |
| 74·0 | —199 | 1·2200 |
| 78·0 | —195 | 1·2008 |
| 80·0 | —193 | 1·1911 |
| 82·0 | —191 | 1·1815 |
| 86·0 | —187 | 1·1623 |
| 89·0 | —184 | 1·1479 |

These densities may be represented by the formula

$$d=1{\cdot}248874-0{\cdot}00481\ (T-68).$$

The specific heat of liquid oxygen between —200° and —183° C. is 0·347,[1] and the heat of evaporation is 51·3 calories per gram at 763 mm. pressure,[2] its molecular heat of vaporisation being 1599 calories [3] according to another computation. Its coefficient of expansion with rise of temperature is 0·00157 at —252·6° C. The refractive index for sodium light, $n_D$, is 1·2236, and the spectrum absorption similar to that of gaseous oxygen.[4]

Liquid oxygen is a non-conductor of electricity; but it is strongly attracted by a magnet.[5] It readily absorbs nitrogen from the atmosphere, and can be mixed with liquid fluorine without suffering chemical change. The magnetic rotatory power and dispersion have been determined.[6]

**Solid Oxygen.**—By rapid evaporation and consequent cooling, or by cooling in liquid hydrogen, liquid oxygen can be converted into a bluish-white solid of density [7] 1 4256 at —252·5° C. and melting at —219° C. under a vapour pressure of 0·9 mm.[8] The solid exhibits allotropy, $\alpha$, $\beta$, and $\gamma$ forms being recognised. The transition between the $\alpha$ and $\beta$ forms occurs at —249·5° C. and between the $\beta$ and $\gamma$ forms at —230·5° C.[9]

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[1] Scheel and Heuse, *Sitzungsber. K Akad. Wiss Berlin*, 1913, p 44, Alt, *Ann. Physik*, 1904, [4], 13, 1010; Barschall, *Zeitsch. Elektrochem.*, 1911, 17, 345.

[2] Alt, *Ann. Physik*, 1906, [4], 19, 739.

[3] Eucken, *Ber. deut. physikal. Ges*, 1916, 18, 4.

[4] Liveing and Dewar, *loc. cit* See also Shaver, *Trans. Roy. Soc. Canada*, 1921, 15, [3], 7.

[5] Tanzler, *Ann. Physik*, 1907, [4], 24, 931; Onnes and Perrier, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, 12, 799.

[6] Chaudier, *Compt. rend*, 1913, 156, 1008.

[7] Dewar, *Proc Roy. Soc.*, 1911, 85, [A], 589; 1904, 73, [A], 251

[8] Estreicher, *Zeitsch. physikal Chem.*, 1913, 25, 432. See also Onnes and Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 163.

[9] Wahl, *Proc. Roy. Soc.*, 1913, [A], 88, 61; Eucken, *Ber. deut. physikal. Ges.*, 1916, 18, 4.

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## CHAPTER IV.

## THE CHEMICAL PROPERTIES OF OXYGEN.

OXYGEN is capable of uniting to form simple compounds with all the elements save fluorine and the noble or inert gases. Such combination is termed **oxidation** and can in general be produced by the direct union of the two elements, as for example in the oxidation of mercury when heated in air, although certain of the non-metals, particularly the halogen elements, show little tendency to direct combination in this manner. Compounds also are capable of uniting with oxygen, sometimes yielding a stable oxidation product of higher molecular weight in consequence of addition of one or more atoms of oxygen ; or the molecule of the compound may be disrupted upon oxidation into two or more products. As an example of the former type of reaction, the oxidation of sodium sulphite in aqueous solution may be quoted, sodium sulphate resulting. Thus

$$2Na_2SO_3+O_2=2Na_2SO_4.$$

The latter type of reaction is illustrated by acetylene which, when ignited, burns in air to form water and carbon dioxide.

$$2C_2H_2+5O_2=4CO_2+2H_2O.$$

Oxidation both of elements and compounds may be effected in the absence of free oxygen through the action of substances containing oxygen. Thus, for example, iron is oxidised by steam and potassium by carbon dioxide at high temperatures. The present section, however, is concerned more particularly with oxidation through the direct action of free elementary oxygen.

Most cases of oxidation are exothermic, that is to say they are accompanied by the evolution of heat, although a few cases are known which are endothermic in character. Such, for example, are the oxidation of water to hydrogen peroxide :

$$2H_2O+(O_2)=2H_2O_2Aq.-23059 \text{ calories,}$$

and the production of ozone from oxygen,

$$3O_2=2O_3-2\times 34000 \text{ calories,}$$

both of which reactions are accompanied by an absorption of heat.

It does not necessarily follow, however, that reactions involving the exothermic oxidation of substances are accompanied by a sensible rise in temperature. The rate of oxidation may be so slow that the heat is dissipated almost as rapidly as it is liberated, so that the rise in temperature is infinitesimal. This is well illustrated by the oxidation of iron upon exposure to air, a reaction commonly known as rusting.

On the other hand, combination with oxygen is often accompanied by the rapid liberation of so much energy that heat and light are emitted. The term **combustion** is then applied.

The majority of substances require to be raised in temperature before they can combine with oxygen to any appreciable extent. Thus electrolytic gas—a mixture of two volumes of hydrogen with one of oxygen—is very stable at the ordinary temperature; combination, however, begins to be appreciable at temperatures slightly above 400° C., and at higher temperatures proceeds with explosive violence. On the other hand, some substances rapidly combine with oxygen when brought into contact with the gas at the ordinary temperature. Such bodies are said to be **spontaneously oxidisable,** and include the pyrophoric metals, phosphorus, coal dust, nitric oxide, ferrous and manganous hydroxides, liquid phosphine, silicon hydride, and many organic substances. Under suitable conditions most of these steadily rise in temperature as oxidation proceeds until rapid combustion, accompanied by light, ensues. This is termed **spontaneous combustion,** a familiar example on a large scale being afforded by the firing of hayricks. **Autoxidation** is a term frequently used to designate spontaneous oxidation.

The rate of oxidation of any particular substance is dependent upon various factors, to wit, its own physical condition as well as that of the oxygen; the presence of moisture or of a catalyser; and the application of light, heat, and pressure. Thus, liquid oxygen does not affect phosphorus or the alkali metals; neither does it combine with solid nitric oxide,[1] although a small jet of burning hydrogen will continue to burn below the surface of liquid oxygen, the water produced being removed as ice and a considerable amount of ozone being formed. Similarly graphite and diamond, when once ignited, will burn on the surface of liquid oxygen, the carbon dioxide produced being frozen and some ozone passing into solution. Oxidation is usually facilitated to a considerable extent by increasing the superficial area of the substance to be oxidised. Well-known illustrations are supplied by the pyrophoric forms of iron, lead, etc. When a solution of phosphorus in carbon disulphide is poured on to a sheet of filter paper, the solvent rapidly evaporates, leaving the phosphorus within the pores of the paper in an excessively fine state of subdivision, so that vigorous combustion ensues.

Moisture plays an important rôle in many cases of oxidation. Its presence is necessary, for example, to effect the spontaneous combustion of pyrophoric metals. At ordinary temperatures, also, the majority of metals are stable in dry oxygen, although readily attacked by the moist gas. Small quantities of many foreign substances are capable of catalytically assisting the rate of oxidation of certain substances. Thus a trace of platinum black introduced into electrolytic gas causes the gases to instantly unite with explosive violence; and the passage of a mixture of sulphur dioxide and oxygen over platinised asbestos effects their union to form sulphur trioxide.

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[1] Dewar, *Chem. News*, 1896, 73, 40, *Proc. Chem. Soc.*, 1895, 11, 221.

Light frequently exerts a considerable influence on the rate of oxidation;[1] thus phosphorus trichloride when illuminated undergoes more rapid conversion into the oxychloride[2] than in the dark; and iron likewise corrodes more rapidly in similar circumstances. Oxidation may be catalytically accelerated by radio-active substances. Thus thorium-X has been found[3] to assist the oxidation of adrenaline and morphine.

Many metals on being heated in dry air or oxygen yield an adhering coat of oxide which tends to protect the underlying metal from attack. The rate at which oxidation proceeds at any temperature is given by the expression[4]

$$\theta = ae^{by} - a,$$

where $a$ is a constant independent of the temperature; $b$ is a constant depending on the temperature and on the delay of film thickening during time $\theta$. $y$ is the thickness of the oxide layer.

The time required for a visible film of oxide to form on the surface of some of the more common metals at 15° C. has been calculated to be as follows:

| Metal. | Time in Years. | Initial Velocity of Oxidation. Thickness of layer $\mu\mu$ per second. |
|---|---|---|
| Lead | 90 | 219 |
| Zinc | $31 \times 10^2$ | 104 |
| Copper | $6 \times 10^8$ | 89 |
| Tin | $36 \times 10^8$ | 856 |
| Iron | $25 \times 10^{17}$ | 2712 |
| Nickel | $475 \times 10^{17}$ | 146 |

Oxidation processes are, as a general rule, greatly accelerated by a rise in temperature; the first effect of the application of heat may be merely to initiate a slow oxidation which soon ceases on the removal of the source of heat; but a higher temperature may cause so marked an increase in the rate of the chemical action that the heat produced suffices to maintain the temperature, and the oxidation or combustion will proceed unaided. This temperature at which the process of rapid combustion becomes independent of external supplies of heat is termed the **ignition temperature** of the substance (see p. 106). Phosphorus does not commence rapid combustion until a temperature of 60° C. is attained; hydrogen will combine, albeit excessively slowly, with oxygen already at 180° C., but the reaction is not very appreciable below 400° C., and continuous inflammation does not occur until near

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[1] See Schevezoff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 219.

[2] Besson, *Compt. rend.*, 1895, 121, 125.

[3] Lemay and Jaloustre, *Compt. rend.*, 1922, 174, 171; 1921, 173, 916.

[4] Tammann and Koster, *Zeitsch anorg. Chem.*, 1922, 123, 196. These results apply only to dry air, and are not comparable with those for the slow oxidation of metals in the presence of water. See p. 55.

530° C.; a red-hot glass rod will cause the ignition of carbon disulphide vapour, but not of ether vapour.

By **flame** is generally understood a mass of gas raised to incandescence. Flame is produced only in those cases of combustion in which gases or vapours are present, which become more or less luminous or incandescent on account of their high temperature. But a visible flame does not always accompany rapid gaseous combustion, a striking exception being afforded by the rapid oxidation of hydrogen or coal-gas mixed with air on a surface of platinised asbestos or porous firebrick. Such combustion is termed **surface combustion,** and is utilised commercially in a variety of ways.

Pressure exerts an important influence upon the rate of oxidation. Thus silicon, ethane, phosphorus, arsenic, and several other substances, are found to oxidise more readily at low oxygen pressures; on the other hand, the rates of the rusting of iron and the oxidation of ferrous sulphate solution are accelerated by increase of pressure.

**Active Oxygen.**—It is possible to prepare an active form of oxygen analogous to active nitrogen by subjecting the dry, ozone-free gas to the influence of an electric discharge. It yields a weak, bluish-green afterglow, which is less persistent than that of hydrogen. When mixed with active nitrogen, this active oxygen yields oxides of nitrogen. Both oxygen and ozone are unaffected by active nitrogen. Hence active oxygen is different from these, but is capable of existing for only a short time.[1]

## OXIDATION.

A few elements yield oxides only with difficulty, and such oxides are frequently unstable at high temperatures. For example, when platinum foil or sponge is heated in dry oxygen, the monoxide, PtO, is produced as a superficial blackening. At higher temperatures, however, this oxide dissociates to metallic platinum and free oxygen.[2] Gold cannot be oxidised directly by gaseous oxygen, although several oxides can be prepared by decomposition of compounds containing gold atoms in their molecules.[3]

Fluorine appears quite incapable of yielding an oxide under any conditions.[4]

**Types of Oxides.**—When oxygen combines with an element, the resulting product is termed an oxide.

The oxides of the various elements show marked differences in their chemical behaviour towards water and also towards acids. These differences form a convenient basis for the classification of the oxides.

1. *Basic Oxides.*—It is characteristic of the metallic elements that each forms at least one oxide which will react with acids producing salts, the valency of the metal remaining unaltered. Such oxides are termed *basic oxides* or sometimes merely *bases.* Some metals yield more than one oxide, and it is then generally observed that the oxide richer in oxygen possesses a more feebly basic character. In the case of the most electro-positive metals, for example the alkali metals, the oxides will combine with water, producing soluble hydroxides which are strongly

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[1] Koenig and Elod, *Ber.*, 1914, 47, 516.

[2] See this series, Vol. IX., Part I.

[3] See this series, Vol. II.

[4] Ruff and Zedner, *Ber.*, 1909, 42, 1037.

alkaline, and in fact constitute the typical *alkalies*; the less electropositive the metal, the smaller the tendency of the oxide to combine with water, and the greater the tendency of the hydroxide, which can then generally be obtained by precipitation methods, to eliminate water with formation of the oxide.

The suggestion has been made[1] that the hydrates of the metals of Groups I. and II. do not contain hydroxyl groups, but are true hydrates of the corresponding oxides. In other words, molecules of water are assumed to be associated with the metallic oxide in a similar manner to the so-called water of crystallisation of salts. Thus sodium hydroxide would be written $Na_2O.H_2O$, and not as $NaOH$. The constitutions of the hydroxides of Groups III. and IV. will depend, according to this theory, upon the electrochemical conditions under which they are produced. Thus $Al(OH)_3$ and $Al_2O_3.H_2O+2H_2O$ are both regarded as capable of existing. The hydroxides of the metalloids and non-metals—the acidic oxides (see 2 below)—are true hydroxides containing hydroxyl groups.

2. *Acidic oxides*, often termed acid *anhydrides*, are generally derived from the non-metals, but may also be higher oxides of certain of the metals. It is characteristic of such oxides that they combine with water, producing hydroxides, which are *acids*. Unlike the basic oxides, an acidic oxide rarely adds sufficient water to convert all its oxygen atoms into hydroxyl groups, *e.g.*

$$SO_3 \rightarrow SO_2(OH)_2, \quad N_2O_5 \rightarrow 2NO_2(OH), \quad Mn_2O_7 \rightarrow 2MnO_3(OH).$$

It is, however, sometimes possible to prepare organic derivatives of the completely hydroxylated (often termed "*ortho-*") acids; thus although the aqueous solution of carbon dioxide appears to contain no other acid than an unstable one of the formula $CO(OH)_2$, ethyl ortho-carbonate, $C(OEt)_4$, is known, corresponding with the hypothetical ortho-carbonic acid, $C(OH)_4$.

3. *Mixed Oxides.*—In some cases so-called *mixed* acidic oxides are known which combine with water, producing a mixture of two acids; nitrogen tetroxide is an example of this class, as also is chlorine dioxide—

$$N_2O_4+H_2O=HNO_2+HNO_3.$$

Some basic oxides behave as mixed oxides, yielding with acids two salts derived from the constituent oxides, *e.g.* magnetic oxide of iron yields a ferrous and a ferric salt. A few oxides may be regarded as a special class of "mixed" basic oxides or as salts derived from a basic and acidic oxide of the metal according to the point of view; thus red lead and lead sesquioxide behave as feeble compounds of lead monoxide and lead dioxide ($2PbO.PbO_2$; $PbO.PbO_2$), and chromium dioxide ($CrO_2$) as a compound of chromic oxide with chromic anhydride ($Cr_2O_3.CrO_3$).

4. There is yet a small class of oxides, the *neutral oxides*, which do not belong to any of the classes before named; they do not combine with water to form acids, nor do they neutralise acids. This class has tended steadily to decrease as chemical knowledge has extended. Carbon monoxide, nitrous oxide, and nitric oxide were once included in this class, but each of these can be obtained by the loss of the elements

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[1] Tiemann, *Chem. Zeit.*, 1921, 45, 1125.

of water from a corresponding acid, so that in a wide sense they might be classed with the acidic oxides. Hydrogen peroxide, on account of its relationship with the peroxides, can hardly in the strictest sense represent a neutral oxide, and the only common oxide which may be regarded as representing this class is water; this must be, in its total behaviour, a neutral oxide, because, as the formula H.OH indicates, any tendency to acidic properties must be accompanied by an equal tendency towards basic properties.

It is worthy of note that, although the behaviour is by no means general, many oxides give indications that they are polymerised, *i.e.* that their simple molecules have combined together in certain numbers to form more complex aggregates. Water is a well-recognised example. The high melting-points of certain other oxides, *e.g.* silica and stannic oxide, is also attributed by some to this cause.

5. *Amphoteric oxides* are capable of functioning either as acidic or as basic oxides. Thus tin dioxide, $SnO_2$, functions as a basic oxide in stannic sulphate, $Sn(SO_4)_2$, but as an acidic oxide in sodium $\alpha$ stannate, $Na_2SnO_3$. Lead dioxide yields the tetrachloride, $PbCl_4$, and sodium metaplumbate, $Na_2PbO_3$, respectively Similarly aluminium oxide, $Al_2O_3$, yields the trichloride, $AlCl_3$, and the aluminate $Na_2Al_2O_4$.

6. *Suboxides* are of frequent occurrence amongst the metals, but are less well known amongst non-metals. The element combined with the oxygen is admittedly unsaturated. Thus when lead is gently heated a little below its melting-point, the suboxide $Pb_2O$ is formed.[1] In the case of nickel,[2] three suboxides, $Ni_4O$, $Ni_3O$, $Ni_2O$, have been postulated. One of the best known non-metallic suboxides is that of carbon, $C_3O_2$.

7. *Dioxides* contain two atoms of oxygen combined with usually one atom of the metal. They usually yield up a portion of their combined oxygen with relative ease, but are distinguished from isomeric peroxides in that they do not yield hydrogen peroxide on treatment with dilute acids. Familiar examples are manganese dioxide, $MnO_2$; lead dioxide, $PbO_2$; and nickel dioxide, $NiO_2$—usually incorrectly referred to as $Ni_2O_3$ in the literature.

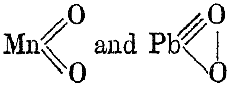
Marino [3] has directed attention to the fact that sulphur dioxide and manganese dioxide react, yielding the dithionate:

$$2SO_2+MnO_2=MnS_2O_6,$$

whilst lead dioxide yields a mixture of sulphite and sulphate:

$$SO_2+PbO_2=PbSO_3+O\,;$$
$$H_2O+SO_2+O=H_2SO_4\,;$$
$$PbSO_3+H_2SO_4=PbSO_4+H_2O+SO_2.$$

He therefore suggests that the structural formulæ of these oxides are



respectively.

8. *Peroxides* [4] are frequently isomeric with dioxides, but in acid

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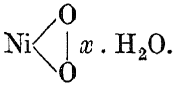
[1] See this series, Vol. V.

[2] See this series, Vol. IX., Part I.

[3] Marino, *Zeitsch. anorg. Chem.*, 1907, 56, 233.

[4] See Tanatar, *Ber.*, 1903, 36, 1893; 1914, 47, 87; Riesenfeld and Mau, *Ber.*, 1911, 44, 3589; Tubandt and Riedel, *ibid.*, p. 2565; Pellini and Meneghini, *Zeitsch. anorg. Chem.*, 1908, 60, 178; Antropoff, *J. prakt. Chem.*, 1908, 77, 273.

solution react like hydrogen peroxide. Sodium peroxide, $Na_2O_2$, is a typical example. The peroxides of divalent metals are usually regarded as having a cyclic structure. Thus nickel peroxide, obtained by the action of hydrogen peroxide upon the well-cooled hydroxide, $Ni(OH)_2$, is written as



Other peroxides are those of manganese and mercury, obtained in an analogous manner to the above. Sometimes these oxides are known as *peroxydates.*

## SLOW OXIDATION.

In 1858 Schönbein noticed that when many substances were exposed to atmospheric oxidation, the oxidisable material appeared to combine with half a molecule of oxygen, leaving the other half in the form of hydrogen peroxide or ozone. This is well exemplified by the corrosion of many non-ferrous metals, such as lead and zinc. When lead, mixed with mercury, is shaken with dilute sulphuric acid in the presence of air or oxygen, lead sulphate is formed, together with some hydrogen peroxide. The amount of the latter is readily ascertained by titration of a portion of the liquid with permanganate, and the quantity of sulphuric acid involved is estimated by titration with alkali. It is then found that the amount of peroxide formed is equivalent to that of the lead dissolved. Thus

$$\mathrm{Pb+H_2SO_4+O_2=PbO\,.\,SO_3+H_2O_2},$$

half of the oxygen molecule combining with the lead, and half with the liberated water.

Schonbein pointed out that this was capable of explanation on Brodie's assumption [1] that the oxygen molecule consists of a positive atom united to a negative atom—a revival of the Berzelian dualistic conception. The positive atom was termed *antozone*, and the negative *ozone*, so that upon oxidation the resulting oxides were termed antozonides and ozonides respectively—terms that at the present time would, if employed, be most confusing.

In contact with oxygen, therefore, metallic lead would tend to unite with the negative or ozone atom, and water with antozone. Thus

$$\mathrm{Pb}+\underset{-}{\mathrm{O}}:\underset{+}{\mathrm{O}}+\mathrm{H_2O}=\underset{\substack{\text{Lead}\\\text{ozonide.}}}{\mathrm{PbO}}+\underset{\substack{\text{Water}\\\text{antozonide.}}}{\mathrm{H_2O_2}}$$

Such a theory, however, could not long prevail, for there is no direct experimental evidence whatever in favour of the assumption that one atom of oxygen in the molecule is different from another. This was urged by Hoppe-Seyler,[2] who in 1878 suggested that during oxidation of a substance one atom from the oxygen molecule is liberated in the nascent condition, and is thus free to oxidise any second substance that may be present. This theory may be represented schematically as follows:

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[1] Brodie, *Phil. Trans*, 1850, 141, 759; 1862, 151, 837; 1863, 152, 407; *Proc. Roy. Soc*, 1858, 9, 361; 1861, 11, 442, *J. Chem. Soc.*, 1852, 9, 194; 1855, 7, 304; 1863, 16, 316; 1864, 17, 266, 281.

[2] Hoppe-Seyler, *Zeitsch. physiol. Chem*, 1878, 2, 22; *Ber.*, 1883, 16, 117.

$$Pb+O:O=PbO+\underset{\text{Nascent.}}{O:}$$

$$H_2O+:O=H_2O_2.$$

**Traube's theory** was a considerable advance on both of the foregoing views. As the result of a large number of experiments Traube[1] was led to the conclusion that *dry* oxygen does not combine with any substance at the ordinary temperature. Although this is a sweeping assertion to make, as is shown in the sequel (see p. 285), there is a considerable amount of evidence in favour of its being generally true. Such being the case, it seemed reasonable to suppose that the water and oxygen must act *simultaneously* in cases of oxidation, and not in series as Hoppe-Seyler's views would require.

Traube therefore concluded that it is the water molecule that yields its oxygen to the metal (or substance) undergoing oxidation, the hydrogen thus liberated being simultaneously oxidised by a whole molecule of atmospheric oxygen yielding the peroxide. Thus, in the case of the lead already referred to, oxidation proceeds as follows:

$$Pb+O\ H_2+O_2=PbO^*+H_2O_2.$$

The hydrogen peroxide does not accumulate unless the experimental conditions are specially arranged for its preservation, since

$$Pb+H_2O_2=PbO+H_2O.$$

It follows from this theory that hydrogen peroxide is to be regarded as a *reduction product* of the oxygen molecule, and not as an oxidation product of the water molecule. Such a conception, though fundamentally different, was not entirely new. Weltzien[2] had already in 1860 suggested the same idea, and it receives support, Traube points out, from the heat liberated when hydrogen peroxide is decomposed. For if hydrogen peroxide were produced by the oxidation of water, already formed, an *absorption* of heat would be expected upon decomposition.

A modification of Traube's theory was introduced simultaneously in 1897 by Bach[3] and by Engler and Wild,[4] who laid emphasis on Traube's idea that the oxygen molecule combines as a whole, but extended its powers of combination to other substances than nascent hydrogen. In support of this, it was pointed out that sodium will burn on an aluminium plate to the peroxide, $Na_2O_2$, whilst rubidium is almost quantitatively converted into the peroxide, $RbO_2$, in a similar manner.[5]

Probably all of these theories possess an element of truth; against each of them some objection may be raised; there is yet room for some comprehensive explanation which shall remove all difficulties.

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[1] Traube, *Ber.*, 1882, 15, 659, 2325, 2421, 2824, 1883, 16, 1201; 1885, 18, 1877, 1887.

* Actually $2PbO.H_2O$ is formed, but the water of hydration is omitted for simplification.

[2] Weltzien, *Annalen*, 1860, 115, 121, 1866, 138, 129.

[3] Bach, *Compt. rend.*, 1897, 124, 951.

[4] Engler and Wild, *Ber*, 1897, 30, 1669.

[5] Erdmann and Köthner, *Annalen*, 1897, 294, 66.

The solution of gold in potassium cyanide solution in the presence of air is believed by Bodlander to proceed as follows:[1]

$$2Au+4KCN+O_2+2H_2O=2KAu(CN)_2+2KOH+H_2O_2;$$
$$4KCN+H_2O_2+2Au=2KAu(CN)_2+2KOH.$$

**The Activation of Oxygen in Slow Oxidation.**—The spontaneous oxidation of a substance at ordinary temperatures is often termed *autoxidation* (see p. 50). It frequently happens that during autoxidation processes other substances, which may be present and which are themselves stable in air, become oxidised. This suggests that a part of the oxygen in the system has become specially reactive or *activated*, and the stable substance is said to have been oxidised by *induction*.[2] An interesting example is afforded in sodium sulphite which, in solution, is slowly oxidised to sulphate. An aqueous solution of sodium arsenite, $Na_3AsO_3$, on the other hand, is stable in air. If, however, the two solutions are mixed and shaken in air, *both* salts undergo oxidation. The oxygen is termed the **actor**; the sodium sulphite, which induces the oxidation of its companion, the **inductor**; and the arsenite, which accepts oxidation, is the **acceptor**. The ratio

$$\frac{\text{Amount of acceptor oxidised}}{\text{Amount of inductor oxidised}}=\text{Induction factor.}$$

The experiment may be varied by passing a current of air or oxygen through a suspension of nickel hydroxide to which small quantities of sodium sulphite solution are periodically added. This not only effects the oxidation of the sulphite, but also converts the nickel hydroxide into black nickelic oxide, a change which is not producible by oxygen only.[3]

Many other examples might be instanced.

Thus, if a piece of hydrogenised palladium is immersed in a solution coloured with indigo, and air or oxygen allowed to bubble through, the colouring matter is oxidised, the solution being bleached. In a similar manner iodine is liberated from potassium iodide and may undergo further oxidation to iodic acid; even nitrogen gradually undergoes conversion into ammonium nitrite[4]; whilst carbon monoxide is partially converted into the dioxide.[5] The last-named reaction is also induced by the slow oxidation of moist, yellow phosphorus.[6]

According to Traube's theory, the first-named reaction proceeds as follows:

$$Na_2SO_3+OH_2+O_2=Na_2SO_4+H_2O_2.$$

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[1] Bodlander, *Zeitsch. angew Chem*, 1896, p. 583. See also Watts, *Chem. Met. Eng.*, 1918. 19, 652, Crowe, *ibid.*, p. 283.

[2] Ostwald (*Zeitsch. physikal Chem*. 1900, 34, 248) suggested the term *coupled* reaction; Mellor (*Chemical Statics and Dynamics* (Longmans, 1904, p 333)) speaks of *sympathetic* reactions; the usual term of *induced* reaction is adopted in this work.

[3] Haber, *Zeitsch physikal. Chem.*, 1900, 35, 84

[4] Hoppe-Seyler, *Ber.*, 1879, 12, 1551, 1883, 16, 1917; 1889, 20, 2215; *Zeitsch. physiol. Chem*, 1886, 10, 35

[5] Baumann, *Zeitsch. physiol. Chem*, 1881, 5, 244.

[6] Leeds, *Chem. News*, 1883, 48, 25, Baumann, *Ber.*, 1883, 16, 2146; 1884, 17, 283; *Zeitsch. physiol. Chem*, 1881, 5, 250; W A Jones *Amer Chem. J.*, 1903, 30, 40; Russell, *Trans. Chem. Soc*, 1903, 83, 1263. It was disputed by Remsen and Keiser, *Ber.*, 1884, 17, 83; *Amer. Chem. J.*, 1883, 4, 454.

This is the *primary* action, followed immediately by the *secondary*, *induced*, or *sympathetic* reaction :

$$Na_3AsO_3+H_2O_2=Na_3AsO_4+H_2O.$$

The explanation offered by Bach and Engler's theory is clearly

$$Na_2SO_3+O_2=Na_2SO_5 ;$$
$$Na_2SO_5+Na_3AsO_3=Na_2SO_4+Na_3AsO_4.$$

From many points of view this latter explanation is the more acceptable. It is applicable in many cases of oxidation amongst organic compounds.

The commonest example in all probability is that of turpentine; this by slow oxidation, caused by a stream of air or of oxygen in the presence of moisture, is converted into a "peroxidised" product, which on account of its oxidising power possesses marked disinfectant properties and forms the basis of the Sanitas disinfectants. In some cases the primary peroxide product can be isolated in a pure condition; thus benzaldehyde, $C_6H_5 \cdot CHO$, readily undergoes atmospheric oxidation to benzoic acid, $C_6H_5 \cdot CO_2H$, the primary product probably being perbenzoic acid, $C_6H_5 \cdot CO_3H$, a relatively unstable substance which, on account of its tendency to decompose into benzoic acid, is capable of oxidising other substances which may be present. In the absence of any foreign substance, the perbenzoic acid oxidises a remaining molecule of benzaldehyde so that the autoxidation of benzaldehyde may be written

$$2C_6H_5 \cdot CHO \xrightarrow{O_2} C_6H_5 \cdot CO_3H + C_6H_5 \cdot CHO \rightarrow 2C_6H_5 \cdot CO_2H.$$

Perbenzoic acid has been isolated and its characteristics are in accord with the requirements of the above explanation.[1]

There has been discovered in the tissues of animals and plants a class of complex organic compounds, termed *ferments* or *enzymes*, which are capable of exerting marked catalytic influence on certain chemical reactions. Some of these substances are catalytically active towards oxidation processes by the atmosphere, and these bodies are frequently distinguished by the term *oxydases*. Oxydases are widely distributed, and the discoloration of the freshly-broken surface of some fruit is to be referred to atmospheric oxidation induced or aided by an oxydase. Alcoholic tincture of guaiacum resin in the presence of an oxydase undergoes oxidation by free oxygen with formation of a blue coloration, and so provides a convenient reagent for the identification of this type of substance.[2] Manganese, and also iron compounds, are frequently present in these oxydases, and it appears probable that in some cases one of these metals, if not both, actually plays an important part in the catalytic process.[3] In some cases, however, compounds of these metals are absent, so that in such oxydases the activating effect appears to be characteristic of the organic enzyme itself.[4]

These oxydases are not obtainable as pure substances, and it is quite possible that, at least in some cases, they consist of a mixture of two compounds, one capable of producing hydrogen peroxide or some other peroxide, and the other capable of imparting activity to the peroxide; the latter substance may therefore be more strictly termed a *peroxydase*.[1]

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[1] Baeyer and Villiger, *Ber.*, 1900, 33, 1569.

[2] Bertrand, *Bull. Soc chim.*, 1894, [3], 11, 717 ; 1895, 13, 361, 1095 ; 1896, 15, 793.

[3] Bertrand, *ibid.*, 1897, [3], 17, 619 ; Villiers, *ibid.*, [3], 17, 675 ; Dony-Hénault and others, *Bull. Acad roy. Belg.*, 1907, p. 537 ; 1908, p. 105, 1909, p. 342.

[4] Bach, *Ber.*, 1910, 43, 364, 366 ; *Arch. Sci. phys. nat.*, 1910, [4], 30, 162.

Oxygen also undergoes activation when exposed to ultraviolet radiation, the effect in this case being probably due to the formation of ozone, in which form the element attacks substances which are unattacked by ordinary oxygen (see p. 51). The radiations from radium [2] and radium emanation [3] also appear to effect an activation of oxygen towards such substances as hydrogen, although the observed activity may not be due entirely to the oxygen, inasmuch as hydrogen is itself activated by radium radiations yielding the unstable triatomic molecule, $H_3$.[4]

## SELECTIVE OXIDATION.

When a mixture of oxidisable substances is so treated that certain of the constituents only are oxidised to the more or less complete exclusion of the remainder, the process is known as **selective oxidation.** In cases of gaseous combustible mixtures, the passage over a catalyst frequently effects the selective combustion of one constituent. Thus, for example, when a mixture of oxygen, hydrogen, carbon monoxide, methane, and nitrogen is passed over spongy platinum at 177° C. the hydrogen and carbon monoxide are oxidised, but not the methane.[5] This is termed selective oxidation, and is the basis of Hempel's method [6] of analysing certain gaseous mixtures. The selective oxidation of carbon monoxide in excess of hydrogen by passage over catalysts at suitable temperatures has been studied by Rideal,[7] who shows that the oxide of copper (operative at 110° C.) and the oxides of iron and chromium (operative at 250° to 350° C.) are active in inducing the oxidation of the monoxide, although in no case is the selective oxidation complete. Thus, for example, when mixtures of carbon monoxide, hydrogen, and oxygen, in the proportions 9, 14, and 77 per cent. respectively, were passed through iron oxide catalyst at 220° C., the mean value for the ratio of monoxide to hydrogen burnt was

$$CO/H_2=4{\cdot}32,$$

despite the preponderating proportion of hydrogen in the original mixture.

The rates of oxidation of the two gases between 100° and 400° C. are connected with their partial pressures by the following expression:

$$-\frac{dC_1}{dt}\bigg/\frac{dC_2}{dt}=K\frac{(CO)}{(H_2)(O_2)^{\frac{1}{2}}}$$

where $C_1$ and $C_2$ are the concentrations of carbon monoxide and hydrogen respectively in the original mixture, K being a constant.

Elevation of temperature effects a decrease in the apparent selective character of the reaction, more hydrogen in proportion being oxidised.

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[1] Chodat and Bach, *Ber.*, 1903, 36, 606.

[2] Weigert, *ibid.*, 1913, 46, 815; Lind, *Amer. Chem. J.*, 1912, 47, 397; Davis and Edwards, *J. Soc. Chem. Ind.*, 1905, 24, 266; Jorissen and Ringer, *Ber.*, 1906, 39, 2093.

[3] Cameron and Ramsay, *Trans. Chem. Soc.*, 1908, 93, 971.

[4] Wendt and Landauer, *J. Amer. Chem. Soc.*, 1920, 42, 930.

[5] Henry, *Annals of Philosophy*, 1825, 25, 422.

[6] Hempel, *Ber.*, 1879, 2, 1006.

[7] Rideal, *Analyst*, 1919, 44, 89; *Trans. Chem. Soc.*, 1919, 115, 993.

Up to the present, reactions of this type have not been very thoroughly studied,[1] but would appear to offer a useful field for fruitful research.

An interesting case of selective oxidation in solution is given by Jones,[2] who has studied the absorption spectrum of a solution of uranous bromide in a mixture of water and methyl alcohol. Addition of potassium perchlorate effects an alteration in the absorption bands in such a manner as to show that the portion of the uranous salt combined with the methyl alcohol has undergone no change, whilst that united with the water has become oxidised.

## COMBUSTION.

Combustion has already been defined in a restricted sense as oxidation proceeding with such vigour and the liberation of so much energy, that heat and light are emitted. The term combustion is now applied broadly to any reactions in which heat and light are evolved, irrespective of whether or not oxygen is present. Thus it is correct to speak of the combustion of hydrogen in chlorine, of phosphorus in bromine, or of copper in sulphur vapour. But owing to the fact that our atmosphere contains large supplies of oxygen, it is evident that by far the greatest number of examples of combustion in ordinary occurrence are due to oxidation. Combustion implies chemical change; it does not include such purely physical phenomena as occur, for example, when electric discharges are passed through Geissler tubes.

If oxidation is accompanied by the evolution of a small amount of heat only, and no light, it is frequently termed **slow combustion.** The term is not altogether an appropriate one, for although in most cases the oxidations referred to may be really slow, this is not always the case. A familiar example is afforded by nitric oxide, which readily combines with oxygen to yield the peroxide. The reaction is rapid and exothermic, a marked rise in temperature being observable.

$$2(NO)+(O_2)=(N_2O_4)+40{,}500 \text{ calories.}$$

A pretty lecture experiment consists in admitting oxygen to a large glass bell jar filled with nitric oxide, and containing the bulb of an air thermoscope. As the brown fumes are formed, the thermoscope registers a sharp rise in temperature.

Accepting, however, the extended use of the word " slow " in this connection, the reaction may be described as a good example of slow combustion. The term slow combustion is usually limited to cases of oxidation. Thus, for example, the slaking of lime is accompanied by considerable heat evolution:

$$[CaO]+Aq.=CaO\,.\,Aq.+18{,}330 \text{ calories.}$$

Such a reaction, however, is not generally regarded as an example of slow combustion. Slow combustion is usually facilitated by the presence of a solid phase which may be the combustible substance itself—as in the case of phosphorus—or even an inert substance, such as porcelain, when the combustibles are gaseous only. This is well illustrated in the slow combustion of hydrogen, which is dealt with in the sequel. When slow combustion is accompanied by decided luminosity it is termed **phosphorescence.** The term **luminescence** includes all kinds of light emission whether purely physical, as in Geissler tubes, or chemical. But the term phosphorescence is conveniently restricted to chemical luminosity. It is not an exceptional phenomenon,[1] but an intermediate stage between typical slow and rapid combustion. The best known example, of course, is that of phosphorus; but under suitable conditions sulphur, arsenic, and many other substances may be observed to phosphoresce. The reason why it is so obvious in the case of phosphorus lies in the fact that its phosphorescent temperature interval ranges from 7° to 60° C., and thus includes ordinary atmospheric temperatures south of the Arctic Circle. At 60° C. phosphorus catches fire or **ignites**—in other words, phosphorescence has culminated in rapid combustion.

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[1] See also Richardt, *Zeitsch. anorg. Chem.*, 1904, 38, 65; Lamb, Scabone, and Edgar, *J. Amer. Chem. Soc.*, 1922, 44, 738.

[2] Jones and Strong, *Amer. Chem. J.*, 1911, 45, 36.

Had Europe possessed an Arctic climate with a maximum temperature below 7° C., it is possible that the discovery of the phosphorescence of phosphorus might have been long delayed. Upon ignition with a lighted taper the phosphorescent temperature interval would have been so rapidly passed that the phenomenon would not ordinarily be observed.

Phosphorescence, therefore, is a frequent accompaniment of slow oxidation. It does not necessarily imply incomplete combustion. In the case of sulphur, for example, sulphur dioxide is produced just as in rapid combustion, but ozone is produced if the temperature is of the order of 200° C.[2]

**The Slow Combustion of Hydrogen.**—Owing partly to its familiarity, and partly to the ease with which it can be obtained in a highly pure condition, electrolytic gas has been studied by many investigators from the point of view of slow combustion.

In 1803 Hooke [3] observed that if the gas is allowed to stand for some months in the presence of water, the dissolved hydrogen and oxygen enter into combination. This has been confirmed by Marcacci [4] in more recent years.

The presence of colloidal platinum in water in contact with electrolytic gas accelerates the reaction,[5] the rate of formation of water being proportional to the concentration of the platinum and the pressure (*i.e.* the rate of solution) of the gases.[6] Many other surfaces also accelerate the reaction.[7]

It has further been shown [8] that in the course of several months a mixture of hydrogen and oxygen when moist and exposed to daylight shows signs of chemical combination, although the action is inappreciable during the course of an ordinary experiment.

If the temperature is raised slightly in contact with certain metals, such as platinum, the rate of union of the gases is greatly accelerated. Thus, compact platinum acts at 50° C., the gases combining with measurable velocity.[1] Finely divided silver acts at 150° C., thin gold leaf at 260° C., and even fragments of non-metallic bodies such as charcoal, pumice, porcelain, quartz, and glass are active at temperatures below 350° C.[2] Angular pieces of glass are found to be more efficient than glass balls of equal superficial area.

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[1] See Smithells, *B.A. Reports*, 1907, 77, 469; Perkin, *Trans. Chem. Soc.*, 1882, 41, 363.

[2] Bloch, *Compt. rend.*, 1909, 148, 782.

[3] Hooke, *Nicholson's J.*, 1803, 5, 228.

[4] Marcacci, *Atti R. Accad. Lincei*, 1902, [5], 11, i., 324.

[5] See Paal and Schwarz, *J. prakt. Chem*, 1916, 93, 106.

[6] Ernst, *Zeitsch. physikal. Chem.*, 1901, 37, 448.

[7] Hofmann and Ebert, *Ber*, 1916, 49, 2369; Paal and Hartmann, *J. prakt. Chem.*, 1909, 80, 337.

[8] Baker, *Trans. Chem. Soc.*, 1902, 81, 400.

Such being the case, it is clear that the walls of a containing vessel may exert an enormous influence upon the slow combustion of its gaseous contents. This is evidenced by the very varying results obtained for the lowest temperatures at which hydrogen and oxygen have been observed to unite with measurable velocity when heated in glass vessels. Thus, Bone and Wheeler[3] kept electrolytic gas in seven different glass bulbs at 350° C. for several days, and found no combination had taken place in six of them after one week, although in the case of the seventh bulb, in which the glass had become devitrified at one end, the presence of water could be detected. At 400° C. no change was observable in three bulbs, but after a week one of the bulbs contained water, although the other two were apparently unchanged.

These results clearly indicate the influence of the glass, and it is interesting to compare them with those reached by Meyer and Raum,[4] who obtained evidence of combination at considerably lower temperatures than the above. Their results were as follow:

### COMBINATION OF ELECTROLYTIC GAS.

(Meyer and Raum, 1895.)

| Temperature, ° C. | Period (days). | Remarks. |
|---|---|---|
| 100 | 218 | No combination. |
| 300 | 65 | Water detected. |
| 350 | 5 | ,, ,, |
| 448 | .. | Slow combination. |

Clearly the temperature of 400° C. may be regarded as the border-line temperature of the slow combustion of electrolytic gas.

These data, however, are merely qualitative in character. In 1906 Bone and Wheeler[5] published the results of a very thorough quantitative investigation of the reaction at about 450° C. in the presence of several different types of catalysers. These were as follow:

(*a*) Refractory acidic oxide—porcelain.
(*b*) A basic refractory—magnesite.
(*c*) Easily reducible oxides—oxides of copper, iron, and nickel.
(*d*) Compact metals—gold, nickel, platinum, and silver.

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[1] Erman, *Abhandl. Akad Wiss Berlin*, 1818–1819, p. 368.

[2] Dulong and Thénard, *Ann. Chim Phys.*, 1823, 23, 440, 1823, 24, 380.

[3] Bone and Wheeler, *Trans. Chem. Soc*, 1902, 81, 535.

[4] Meyer and Raum, *Ber.*, 1895, 28, 2804. See also Briner, *J. Chim. phys.*, 1912, 10, 129.

[5] Bone and Wheeler, *Phil. Trans.*, 1906, [A], 206, 1.

The catalyst chosen was packed into a hard glass combustion tube, heated to the desired temperature, and the gases, measuring some 1500 c.c. *in toto*, were continuously circulated throughout the system. Any combination to form water was measured by observing the fall in pressure. The majority of the experiments were carried out with *porcelain* [1] as catalyst, and it was found that *the rate of combination of hydrogen and oxygen in electrolytic gas is directly proportional to the pressure of the dry gas.*

In other words, the reaction is monomolecular, although, from the equation

$$2H_2+O_2=2H_2O$$

a reaction of the third order is to be expected.[2] By increasing the proportion of either the oxygen or the hydrogen above that required for the foregoing equation it was found that the rate of the reaction was directly proportional to the pressure of the hydrogen. A result so opposed to that which might be expected indicates that the reaction is indirect and complicated; this conclusion receives support from the further observation that previous exposure to hydrogen appreciably enhances the catalytic activity of the porcelain, although chemical reduction of the porcelain by this preliminary treatment is out of the question. Indeed, if reduction did take place, a prolonged preliminary exposure to hydrogen might be expected to enhance the catalytic action. But experiment showed that such was not the case. Further, the hydrogen could easily be removed again by heating the porcelain to redness in a vacuum. A preliminary ignition in oxygen did not appear to influence the results. It may therefore be concluded that porous porcelain adsorbs both hydrogen and oxygen at rates which depend to some extent upon the physical condition and past history of the surface. In general, the adsorption of hydrogen is less rapid than that of oxygen, but the limit of saturation is higher. Combination between the adsorbed gases occurs at a rate either comparable with or somewhat more rapid than that with which the film of occluded oxygen is renewed, but at a rate considerably higher than that of the adsorption of hydrogen.

When *magnesite* — a typical basic refractory — was used as catalyst, the temperature being 430° C., closely similar results were obtained. *Ferric oxide* and *nickel oxide* showed no reduction during the process, but behaved in an analogous manner to the magnesite. *Copper oxide*,[3] however, exhibited unique behaviour. The rate of formation of water was not only slow, but was proportional to the partial pressure, not of the hydrogen, but of the oxygen when the proportions of the two gases did not correspond to that in electrolytic gas. The authors explain this by supposing that the surface of the oxide becomes coated with a film of "active" oxygen, which protects it from the reducing action of the hydrogen. At low pressures water-vapour is formed because the hydrogen succeeds in penetrating the attenuated film.

*Gold* was studied at 250° C., and from the fact that its surface remained apparently unchanged throughout, the conclusion was drawn that the metal acted through adsorption or occlusion, and not in a chemical manner. The surface of *silver* gauze, however, when employed as catalyst, was observed to become frosted over, and its catalytic activity greatly increased. It would appear, therefore, that some chemical action takes place, such as the formation and subsequent decomposition of a hydride. An oxide is ruled out since silver oxides are unstable above 350° C.[1]

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[1] Kaolin is also catalytically reactive. Its influence can be observed at 230° C. Joannis, *Compt rend.*, 1914, 158, 501.

[2] Bodenstein (*Zeitsch. physikal. Chem.*, 1899, 29, 665) believed his experiments proved this to be the case.

[3] The influence of copper oxide has been studied also by Joannis, *Compt. rend.*, 1914, 159, 64.

As is well known, the **noble metals** are very powerful catalysts, and their activities have been carefully studied.[2] Pre-treatment of platinum, palladium, or iridium with oxygen greatly enhances their effectiveness as regards the catalysis of mixtures of hydrogen and oxygen. Pre-treatment with hydrogen produces a similar effect but to a less marked extent.

**The Slow Combustion of Gaseous Hydrocarbons.**—The fact that some substances unite with oxygen more readily than others paved the way for what may be termed the **preferential theory** of combustion, which was widely accepted during the greater part of last century. According to this theory, when a mixture of combustible substances is ignited, there is competition between the different elements for the oxygen. The same applies even in the case of a pure compound, such as a hydrocarbon, for the two constituent elements will compete for the oxygen. If the supply of air is limited the "most favoured" element will burn first, the remainder oxidising as opportunity serves.

This theory afforded a very plausible explanation for the luminosity of hydrocarbon flames.[3] The hydrogen is to be regarded as the favoured element, and thus becomes preferentially oxidised, whilst the less favoured carbon is precipitated out into the flame in the white-hot condition, and either burns in excess of air at the outward fringe or escapes as smoke or soot in the uncombined condition.

Although, as has already been mentioned (see p. 59), preferential combustion may take place in the presence of certain catalysts, the theory as applied promiscuously to all cases of combustion leads to many difficulties. For example, when methane is exploded with its own volume of oxygen—that is, a volume insufficient for complete combustion—hydrogen and carbon monoxide are produced as well as water-vapour, in accordance with the equation

$$CH_4+O_2=CO+H_2O+H_2.$$

Similarly, ethylene yields carbon monoxide and hydrogen :

$$C_2H_4+O_2=2CO+2H_2.$$

These facts were known to Dalton,[4] and received support from the work of Kersten[5] in 1861, who assumed that when once the hydrocarbon has been decomposed by the heat of the flame into hydrogen and carbon, the latter is preferentially oxidised to carbon monoxide, after which any excess of oxygen distributes itself between this gas and the hydrogen. A similar view was apparently held by Misteli.[1]

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[1] Carnelley and Walker, *Trans Chem Soc.*, 1888, 53, 79.
[2] Hofmann and Zipfel, *Ber.*, 1920, 53, [B], 298.
[3] See Dixon, *Cantor Lectures*, 1884.
[4] Dalton, *A New System of Chemical Philosophy*, 1808, vol. i.
[5] Kersten, *J. prakt. Chem.*, 1861, 84, 310.

The question therefore arises as to what factors decide whether or not an element shall be more favoured than another. If in the ordinary rapid combustion of ethylene, for example, hydrogen is the more favoured element, why should carbon be preferentially oxidised in an explosion? To this, a satisfactory reply has not as yet been forthcoming.

Although the preferential theory has not been disproved, modern opinion inclines towards the **association theory** of Bone and his collaborators. According to this, the oxygen of the air first combines with the hydrocarbons, forming more or less unstable hydroxylated products which ultimately, in a sufficiency of air or oxygen, decompose to carbon dioxide and water.

This theory was arrived at as the result of a series of classical researches into the mode of combustion of hydrocarbon gases in oxygen in contact with suitable catalysts.

In the preliminary series of experiments [2] the gases were sealed in glass bulbs and maintained at definite temperatures ranging from 325° to 400° C. for several weeks. As only small volumes of gases (about 70 c.c.) could be dealt with in this manner, and as, moreover, the detection of transient intermediate products was very difficult, the final experiments were conducted by continuously circulating the gases (some 1200 c.c.) through a combustion tube packed with porcelain, and maintained at the desired temperature in a furnace.[3]

A. It was first of all established that the following three reactions are incapable of taking place below 400° C.:

$$\text{(i) } C+H_2O=CO+H_2;$$
$$\text{(ii) } CO_2+C=2CO;$$
$$\text{(iii) } 2C+O_2=2CO.$$

The reversible reaction

$$\text{(iv) } CO+H_2O \rightleftharpoons CO_2+H_2$$

gave no evidence of proceeding at 325° C. in the direction left to right even after a fortnight. At 350° C. some 1·7 per cent. of carbon dioxide was produced after ten days, and at 400° C. about the same quantity resulted after a week. On the other hand, mixtures of hydrogen and carbon dioxide gave no indication of change at 350° C. for a fortnight, or at 400° C. for a week.

Mixtures of fairly dry carbon monoxide and oxygen underwent no change between 300° and 400° C. although the moist gases very slowly interacted at 325° C. and upwards in the course of a week, yielding carbon dioxide. The reaction

$$\text{(v) } 2CO+O_2=2CO_2$$

could, therefore, like the preceding ones, have but little effect upon the course of the experiments.

$$\text{(vi) } 2H_2+O_2=2H_2O.$$

---

[1] Misteli, *Chem. Zentr.*, 1905, ii., 1075; from *J. Gasbeleuchtung*, 1905, 48, 802. Compare also Tanatar, *Zeitsch. physikal. Chem.*, 1900, 35, 340; 1901, 36, 225; Bone and Cain, *Trans. Chem. Soc.*, 1897, 71, 26; Lean and Bone, *ibid.*, 1892, 61, 873.

[2] Bone and Wheeler, *Trans. Chem. Soc.*, 1902, 81, 535.

[3] Bone and Wheeler, *ibid.*, 1903, 83, 1074.

This reaction has already been discussed (see p. 61). A temperature of 400° C. is on the border-line where the formation of water may be detected in the course of a week The fact was also established that the following pairs of gases have no appreciable mutual action at or below 400° C., namely:

$$CH_4+CO_2,\ CH_4+H_2O, \text{ and } CO+H_2.$$

The elimination of these secondary reactions from the slow combustion of methane greatly simplifies the problem.

B. Bone and Wheeler next ascertained that methane combines with oxygen between 300° and 400° C. with an enormously greater velocity than does hydrogen itself, and in no case were they ever able to detect the liberation of free hydrogen or free carbon as an intermediate or final product.

Since, if once formed, it would be impossible for them to be oxidised away in accordance with equations (ii), (iii), or (vi), their detection and isolation would be an easy matter, and hence it may be postulated that under normal conditions of slow combustion the methane is not first dissociated into its constituent elements. It is equally clear that the carbon monoxide and water which were always found when the supply of oxygen was insufficient to completely oxidise the methane, are two of the primary disintegration products of the partial oxidation of the methane molecule at these temperatures, for these are too low for reaction (vi) to take place.

C. An unexpectedly large proportion of carbon dioxide was invariably found in the gases at each stage, but especially towards the end of the oxidation. This cannot be explained on the supposition that the carbon monoxide first formed is oxidised to the dioxide, for reaction (v) takes place with extreme slowness at temperatures below 400° C. It would therefore result from the decomposition of some more complex oxygenated molecule.

D. The presence of formaldehyde could be detected as an unstable intermediate product during the slow combustion of methane at 450° to 500° C., and must be regarded as an oxidation product of methane, since it was not produced when mixtures of hydrogen and carbon monoxide were circulated through the apparatus under analogous conditions.[1] Formaldehyde readily decomposes when heated in the absence of air or oxygen yielding carbon monoxide and hydrogen; whilst in the presence of air, carbon dioxide and water result. Formaldehyde thus came to be regarded as the initial product of oxidation of methane, but upon the suggestion of Armstrong [2] the view was finally adopted that methyl alcohol is the first product; this, however, cannot be detected on account of the rapidity with which it oxidised, presumably by hydroxylation to the hypothetical dihydroxymethane, which immediately decomposes to formaldehyde and water. This is followed by the formation of formic acid, which is readily detected amongst the intermediate products. Further oxidation yields carbonic acid, which dissociates into water and carbon dioxide. Thus: [3]

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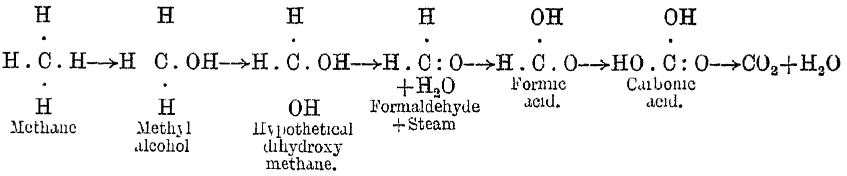
[1] Bone and Wheeler, *Trans. Chem. Soc.*, 1903, 83, 1074; Bone and Smith, *ibid.*, 1905, 87, 910.

[2] Armstrong, *ibid*, 1903, 83, 1088.

[3] Bone and Drugman, *ibid.*, 1906, 89, 679.

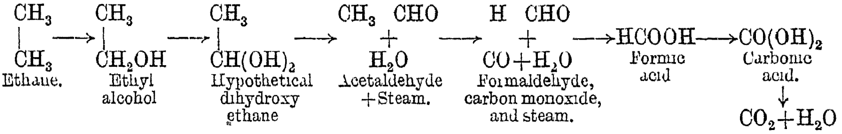


$$\begin{array}{c}H\\ \cdot\\ H.C.H\\ \cdot\\ H\end{array}\longrightarrow\begin{array}{c}H\\ \cdot\\ H\ C.OH\\ \cdot\\ H\end{array}\longrightarrow\begin{array}{c}H\\ \cdot\\ H.C.OH\\ \\ OH\end{array}\longrightarrow\begin{array}{c}H\\ \cdot\\ H.C:O\\ +H_2O\end{array}\longrightarrow\begin{array}{c}OH\\ \cdot\\ H.C.O\end{array}\longrightarrow\begin{array}{c}OH\\ \cdot\\ HO.C:O\end{array}\longrightarrow CO_2+H_2O$$

Methane
Methyl alcohol
Hypothetical dihydroxy methane.
Formaldehyde +Steam
Formic acid.
Carbonic acid.

One of the most interesting features of this scheme is the assumption that the first act of the oxygen atom is to associate itself with the methane; indeed, the oxygen atom appears to penetrate within the methane molecule, in much the same way as it is believed to enter the carbon network in the combustion of solid charcoal (see p. 74).

In the slow combustion of ethane, on the other hand, ethyl alcohol has actually been detected amongst the oxidation products,[1] and an analogous scheme is suggested [2] to that for methane. Thus:



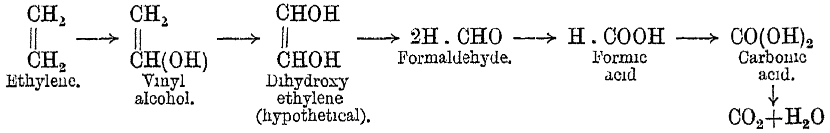
$$\begin{array}{c}CH_3\\ |\\ CH_3\end{array}\longrightarrow\begin{array}{c}CH_3\\ |\\ CH_2OH\end{array}\longrightarrow\begin{array}{c}CH_3\\ |\\ CH(OH)_2\end{array}\longrightarrow\begin{array}{c}CH_3\ CHO\\ +\\ H_2O\end{array}\longrightarrow\begin{array}{c}H\ CHO\\ +\\ CO+H_2O\end{array}\longrightarrow HCOOH\longrightarrow\begin{array}{c}CO(OH)_2\\ \downarrow\\ CO_2+H_2O\end{array}$$

Ethane.
Ethyl alcohol
Hypothetical dihydroxy ethane
Acetaldehyde +Steam.
Formaldehyde, carbon monoxide, and steam.
Formic acid
Carbonic acid.

Hydrogen, methane, and ethylene are also at times to be found amongst the products of oxidation, without, however, any carbon being liberated. Their appearance is believed to be due to the purely thermal decomposition of ethane, formaldehyde, and acetaldehyde.[3] Thus:

$$C_2H_6=C_2H_4+H_2$$
$$H.CHO=H_2+CO$$
$$CH_3.CHO=CH_4+CO$$

In the case of ethylene, $C_2H_4$, it was not to be expected that vinyl alcohol could be detected as a transient intermediate product;[4] but force of analogy leads to the assumption that the mechanism of the slow combustion is probably as follows:

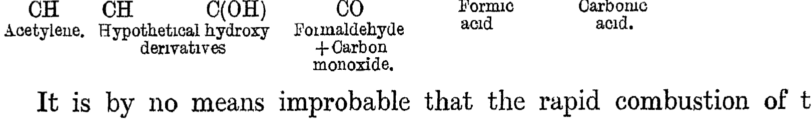


$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}\longrightarrow\begin{array}{c}CH_2\\ \|\\ CH(OH)\end{array}\longrightarrow\begin{array}{c}CHOH\\ \|\\ CHOH\end{array}\longrightarrow 2H.CHO\longrightarrow H.COOH\longrightarrow\begin{array}{c}CO(OH)_2\\ \downarrow\\ CO_2+H_2O\end{array}$$

Ethylene.
Vinyl alcohol.
Dihydroxy ethylene (hypothetical).
Formaldehyde.
Formic acid
Carbonic acid.

Vinyl alcohol could not, of course, be experimentally detected among the products.

For acetylene, the following scheme is suggested:[5]



$$\begin{array}{c}CH\\ |||\\ CH\end{array}\longrightarrow\begin{array}{c}C(OH)\\ |||\\ CH\end{array}\longrightarrow\begin{array}{c}C(OH)\\ \|\\ C(OH)\end{array}\longrightarrow\begin{array}{c}H.CHO\\ +\\ CO\end{array}\longrightarrow H.COOH\longrightarrow CO(OH)_2\longrightarrow CO_2+H_2O$$

Acetylene.
Hypothetical hydroxy derivatives
Formaldehyde +Carbon monoxide.
Formic acid
Carbonic acid.

It is by no means improbable that the rapid combustion of the hydrocarbon gases follows similar lines. Evidence on this point, however, is difficult to obtain.

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[1] Bone and Drugman, *Proc. Chem. Soc.*, 1904, 20, 127; Drugman, *Trans. Chem. Soc.*, 1906, 89, 939.

[2] Bone, *B.A. Reports*, 1910, p. 491; Bone and Stockings, *Trans. Chem. Soc.*, 1904, 85, 693.

[3] Bone and Smith, *Trans. Chem. Soc.*, 1905, 87, 910.

[4] Bone and Wheeler, *ibid.*, 1904, 85, 1637.

[5] Bone and Andrew, *ibid.*, 1905, 87, 1232.

**The slow combustion of phosphorus** in moist air is an apparent exception to the law of mass action, for the rate of oxidation *diminishes* with rise of pressure, becoming practically nil at 500 mm. of oxygen. This is really a case of false equilibrium akin to passivity in metals. The surface of yellow phosphorus is exceedingly sensitive to the action of traces of impurity. The moisture appears to be the primary cause of the irregularity referred to, although the *modus operandi* is not understood.[1] If, on the other hand, freshly distilled phosphorus is exposed to the action of air or oxygen dried by passage through sulphuric acid, and therefore having a moisture content of the order of 1 mg. per 400 litres,[2] the oxidation proceeds at all pressures and is monomolecular above 500 mm. It is accompanied by a very feeble glow and the formation of some unknown oxide.[1] Below 500 mm. the reaction is accelerated, the glowing is more intense and phosphorus pentoxide is formed.

On the other hand, if the oxygen is very dry [3] the oxidation proceeds exceedingly slowly, and probably if the system were entirely free from water no action would take place at all. Ozone and hydrogen peroxide, which are produced during the oxidation of moist phosphorus,[4] do not occur in the dry reactions. The slow oxidation of phosphorus in various oils has also been studied.[5]

**The slow combustion of coal** is, on account of its commercial importance, a subject of particular interest. Anthracite and anthracitic coals are but little affected by exposure to air, but the majority of bituminous coals undergo appreciable oxidation and deterioration. A photographic plate is affected by them in the dark in the presence of air or oxygen possibly owing to the production of traces of hydrogen peroxide.[6] The rate of oxidation increases with the surface area and with the temperature; if the resulting heat is unable to escape sufficiently rapidly the temperature may rise to such a height as to cause spontaneous combustion. In coal mines the conditions are peculiarly favourable to this, and the resulting fires are known as *gobfires*. The same difficulties present themselves in connection with the storage and transport of coals. It was at one time believed that the spontaneous heating of coal was due solely to the oxidation of included pyrites or marcasite. Thus:

$$FeS_2+H_2O+O_2=FeSO_4+H_2SO_4.$$

The researches of several investigators [7] have shown fairly conclusively that this cannot be the *main* cause. Indeed, it is not difficult to show, from thermochemical considerations, that if the coal contained as much as 2 per cent. of pyrites,[1] and the heat of the foregoing reaction were wholly accumulated in the mass of the coal, it would be totally inadequate to raise the temperature of the mass to ignition-point.[2] On the other hand, a straightforward chemical reaction of this type is not the only manner in which a substance, such as pyrites, may possibly assist in the oxidation of coal. It is well known that iron compounds, by virtue of their power of alternate reduction and oxidation, frequently exert a marked catalytic action upon reactions of the above-mentioned type; and evidence is not altogether wanting [3] that pyrites can and does exert a minor accelerating influence on the oxygen absorption of coal.

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[1] Russell, *Trans. Chem. Soc*, 1903, 83, 1271 See also this series, Vol VI.

[2] Morley, *Amer. J. Sci*, 1887, 34, 200.

[3] Dried with phosphorus pentoxide It then contains a maximum of only 1 mg. $H_2O$ per 40,000 litres.

[4] Schonbein, *Pogg. Annalen*, 1845, 65, 69, Schmidt, *J. prakt Chem.*, 1866, 98, 414; Russell, *loc. cit.*

[5] Centnerszwer, *Chem Zentr.*, 1910, ii., 1022.

[6] W. J. Russell, *Proc Roy. Soc.*, 1908, [B], 80, 376, Sinkinson, *Trans Chem. Soc.*, 1920, 117, 165.

[7] See particularly Richters, *Dingl Poly J.*, 1868, 190, 398; 1869, 193, 54, 264, 1870, 195, 315, 449; 1870, 196, 317, Fayol, *Bull. Soc Ind. Minerale*, 1879, 8, iii., 3487; Lawton, *Trans Inst Min. Eng*, 1904, 27, 112; Threlfall, *J Soc. Chem. Ind*, 1909, 28, 759; *Second Report of the Royal Commission on Coal Supplies*, 1904 (Cd. 1991), 2, 227; Lewes, *ibid.*, 232 Bulletin No. 116, *Engineering Experimental Station, University of Illinois.*

Apart from its thermochemical and catalytic activities, it seems very probable that pyrites can assist in the oxidation of coal in a purely mechanical manner as well, inasmuch as it tends to swell on oxidation and thus to increase the mechanical disintegration of the coal, thereby exposing larger surfaces to aerial attack.[4]

When air is passed over coal free from occluded gases oxygen is absorbed, water and oxides of carbon being produced. This reaction proceeds even at temperatures as low as 25° C.; [5] indeed, with freshly mined coal, oxidation proceeds at the ordinary temperature, although in this case it may not be attended with evolution of carbon dioxide.[6] Up to about 80° C., however, the reaction is relatively slow, and even when coal is exposed to oxygen under high pressure the oxidation is attended by only relatively small amounts of the oxides of carbon.[7] At about 80° C. the rate of oxidation undergoes a marked increase, and at 120° C. in oxygen and 135° C. in air oxidation proceeds freely.

Between 140° and 160° C in oxygen and 200° to 270° C. in air oxidation becomes *autogenous* or self-propellant, and as soon as this point is reached the temperature rises rapidly to the ignition-point.[8]

Moisture accelerates the oxidation of coal, but an excess of water retards it, partly because it enters the pores and thereby renders it less accessible to the atmosphere and partly also because its evaporation tends to keep down the temperature. Oxidation proceeds in the absence of bacteria.[9]

It has been suggested that, just as in the combustion of carbon and the slow combustion of hydrocarbon gases, the first step in the slow combustion of coal consists in the formation of an additive compound or complex, consisting of oxygen and one or more of the substances present in coal.[10]

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[1] Using the word pyrites in its broadest sense to cover any sulphide of iron.

[2] Bone, *Coal and its Scientific Uses* (Longmans, 1918), p. 150.

[3] Drakeley, *Trans. Chem. Soc*, 1916, 109, 723; 1917, 111, 853 See also Haldane and Meachem, *Trans. Inst. Min Eng.*, 1898, 16, 491, Jeffries, *ibid.*, 1905, 29, 532 Compare Harger, *ibid.*, 1913, 44, 318; Drescher, *Chem. Zeitung*, 1922, 46, 802

[4] Lewes, *J. Gaslighting*, 1890, 55, 145; 1906, 94, 33

[5] Mahler, *Compt. rend.*, 1910, 150, 1521, 1910, 151, 645.

[6] Parr and his Co-workers, *University of Illinois*, Bulletins Nos 17 (1908) and 46 (1911).

[7] Bone, *op. cit.*, p. 158.

[8] Parr, *loc. cit*; also Tideswell and Wheeler, *Trans. Chem. Soc.*, 1920, 117, 794.

[9] Godchot, *Compt rend.*, 1920, 171, 32.

[10] Wheeler, *Trans. Chem. Soc.*, 1918, 113, 945; Tideswell and Wheeler, *ibid.*, 1919, 115, 895 criticism by Partington, *Chem. News*, 1919, 118, 50.

**Surface Combustion.**—As has been seen, slow combustion of gases may be enormously accelerated by contact with catalysing surfaces. The rate may be so increased as to cause the evolution of light and intense heat, but without any visible flame. All such phenomena are grouped together under the term **surface combustion** (see p. 52).

Davy, in 1818,[1] called attention to the fact that a spiral of platinum wire, when plunged in a warm condition into a mixture of coal gas and air, becomes incandescent and may cause the gases to burst into flame. By holding a piece of platinised asbestos, after warming in the Bunsen flame, in a stream of coal gas and air, the surface of the asbestos glows brightly, but as a rule no flame appears. If, however, the asbestos is held over a jet of hydrogen, sufficient heat is generated to ignite the gas.

A pretty lecture experiment consists in suspending a spiral of platinum wire in a beaker over some methyl alcohol. The latter is ignited, and when the spiral has become warm a card, punctured with small holes, is laid over the top of the beaker. This extinguishes the flames, but sufficient air enters to allow some of the alcohol to burn on the surface of the platinum, which glows at red heat.

The reaction, when once started, is self-supporting, and may be represented as follows:

$$\text{(i)}\ \underset{\text{Methyl alcohol.}}{CH_3OH+O} = \underset{\text{Formaldehyde}}{HCHO}+H_2O;$$

$$\text{(ii)}\ HCHO+O=HCOOH;$$

$$\text{(iii)}\ HCOOH+O=H_2O+CO_2.$$

By suitably adjusting the apparatus formaldehyde may be made the most important product, and advantage has been taken of this to construct the well-known formaldehyde lamp,[2] in which a mixture of methyl alcohol vapour and air is passed over a warmed platinum wire.

Finely divided platinum, on account of its enormous surface area, is very reactive,[3] and a small quantity introduced into electrolytic gas may cause instant explosion.[4]

Surface combustion phenomena are not confined to platinum or the noble metals. A warmed iron wire may be raised to incandescence by surrounding it with an atmosphere of air and coal gas.[5]

It is now established that:

1. The property of accelerating gaseous combustion at temperatures below ignition point is shared by all substances irrespective of their chemical composition.

2. Whilst at lower temperatures there exist very marked differences in the catalysing powers of various solids, at high temperatures these disappear.

At bright incandescence all solids behave alike.

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[1] Davy, *Phil. Trans.*, 1817, 107, 77; *Quart. J Sci*, 1818, 5, 128.

[2] Tollens, *Ber*, 1895, 28, 261.

[3] Doebereiner, *Schweigger's J*, 1823, 34, 91; 1823, 38, 321; 1823, 39, 159; 1824, 42, 60; 1831, 63, 465.

[4] Hofmann, *Annalen*, 1868, 145, 357; *Ber.*, 1869, 2, 152, 1878, 11, 1686; Thomas, *J. Amer. Chem. Soc.*, 1920, 42, 867.

[5] Fletcher, *J. Gaslighting*, 1887, 1, 168. See also Meunier, *Compt. rend.*, 1908, 146, 539, 757.

Bone[1] has applied the phenomena to industrial problems, mixtures of coal gas and air being caused to burn on the surface of porous fire-brick, generating enormous heat, but with no visible flame.

**Combustion of Solid Carbon.**—Owing to their importance as fuel, carbonaceous materials have for centuries been the subject of scientific consideration. For some time prior to the discovery of oxygen, carbon or charcoal was regarded as composed mainly of the essence of combustibility, and Stahl (*c.* 1697) considered it to be almost pure phlogiston (see p. 11). On this theory, the fact that only a certain quantity of charcoal could burn in a limited supply of air was readily explained on the assumption that phlogiston could not leave a substance unless it had somewhere to go. The air could only absorb a definite amount, and when once fully phlogisticated behaved like a saturated body and refused to take up any more.

The discovery of oxygen by Priestley and independently by Scheele in the second half of the eighteenth century enabled Lavoisier to offer an entirely new explanation for the phenomena. The carbon was assumed to combine direct with oxygen to form the dioxide

$$\text{(i) } C+O_2=CO_2,$$

and the fact that carbon monoxide[2] was found to result in the presence of excess charcoal, was accounted for by reduction of the carbon dioxide

$$\text{(ii) } CO_2+C=2CO.$$

For more than half a century this theory was accepted almost without question,[3] but in 1872 Sir Lowthian Bell concluded that the theory was inadequate in so far as the combustion of coke in a blast furnace was concerned. He suggested that "carbon monoxide and not carbon dioxide is the chief, if not the exclusive and immediate, action of the hot blast on the fuel." If this view is accepted, carbon dioxide is to be regarded as an oxidation product of the monoxide rather than of carbon itself, and carbon monoxide as the primary oxidation product of carbon instead of a reduction product of the dioxide. Thus:

$$\text{(i) } 2C+O_2=2CO\ ;$$
$$\text{(ii) } 2CO+O_2=2CO_2.$$

Bell's theory received unexpected support from the work of C. J. Baker[4] some fifteen years later. This investigator studied the effect of admission of oxygen to charcoal that had previously been thoroughly exhausted of air and moisture by heating to redness in an evacuated tube containing phosphorus pentoxide. On admitting dry oxygen to the system, adsorption took place, and a temperature of 450° C. was required to expel it. It then escaped mainly as carbon monoxide. In the presence of moisture carbon dioxide was formed, but the more thoroughly free from moisture the substances were, the less the amount of carbon dioxide produced.[1] This, coupled with the fact, proved by Baker, that dried carbon dioxide is reduced by dry carbon only with difficulty to the monoxide, strongly supports the conclusion that under these conditions carbon burns directly to the monoxide.

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[1] Bone, *J. Roy. Soc. Arts*, 1914, 62, 787, 801, 818 ; *Coal and its Scientific Uses* (Longmans, 1918).

[2] A gas prepared by Lassone in 1776 and mistaken for hydrogen, but later recognised as a true oxide of carbon.

[3] As late as 1888 Lang (*Zeitsch. physikal. Chem.*, 1888, 2, 161) claimed to have proved that in the combustion of carbon the formation of dioxide precedes that of the monoxide. His conclusions, however, were disputed by Dixon (*Trans. Chem. Soc.*, 1899, 75, 630).

[4] C. J. Baker, *Trans. Chem. Soc.*, 1887, 51, 249.

Still further support was forthcoming the following year from the researches of H. B. Baker,[2] who found that no visible combustion occurred when thoroughly dry oxygen [3] was led over highly purified sugar charcoal at bright-red heat. That combination had taken place, however, was clear from the resulting gaseous mixture, namely:

| | |
|---|---|
| Oxygen . . . . | 58·1 per cent. |
| Carbon monoxide . . | 39·5 ,, |
| Carbon dioxide . . . | 2·2 ,, |

Johnson and M'Intosh [4] found from 6·2 to 8·9 per cent. of carbon monoxide in the gases evolved during the combustion of a mixture of carbon with excess of potassium chlorate, both in air and in a vacuum. As the temperature was only of the order of 1000° C., the authors argue that the monoxide could not have resulted from the thermal decomposition of the dioxide, so that the monoxide would appear to be the first product in the combustion of solid carbon.

In 1896 Dixon [5] showed that the rate of explosion of cyanogen in oxygen reaches a maximum when the gases are in molecular proportions. Thus:

$$C_2N_2+O_2=N_2+2CO.$$

Further, the pressure developed during the explosion is greater, and the reaction proceeds more rapidly, than when sufficient oxygen is present to convert the carbon into the dioxide.

It would appear, therefore, that in so far as gaseous carbon is concerned, carbon monoxide is the initial product.

For many years chemists appear to have been satisfied with one or other of these theories. In 1912 attention was again directed to the subject by Rhead and Wheeler,[6] who point out that if it could be shown that either the reaction

$$C+O_2=CO_2$$

or

$$CO_2+C=2CO$$

proceeds at a temperature at which either

$$2C+O_2=2CO$$

or

$$2CO+O_2=2CO_2$$

takes place with inappreciable velocity, a decision between the two foregoing theories could be arrived at. Although unable to arrive at a complete solution of the problem in this simple manner, Rhead and Wheeler succeeded in showing that—

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[1] In one experiment 98·91 per cent. of CO and only 1·08 per cent. of $CO_2$ were obtained, the substances having been dried for two months over phosphorus pentoxide.

[2] H. B. Baker, *Proc. Roy. Soc.*, 1888, 45, 1; *Phil. Trans.*, 1888, 179, [A], 571.

[3] Dried by prolonged exposure to phosphorus pentoxide.

[4] Johnson and M'Intosh, *Trans. Roy. Soc. Edin.*, 1913, 7, iii, 161.

[5] Dixon, Strange, and Graham, *Trans. Chem. Soc.*, 1896, 59, 759; Dixon, *Phil. Trans.*, 1893, 184, 97.

[6] Rhead and Wheeler, *Trans. Chem. Soc.*, 1912, 101, 846.

1. Some carbon monoxide is produced during the oxidation of carbon at low temperatures, under conditions that do not admit of the reduction of carbon dioxide by carbon.
2. Carbon dioxide is produced at low temperatures in quantities that cannot be entirely accounted for on the assumption that the monoxide is first formed and subsequently oxidised.

The conclusion appears inevitable that both the monoxide and the dioxide are produced *simultaneously*. In other words, neither gas is the primary product of oxidation in that it takes precedence over the other. The two previous theories are therefore to be regarded as correct, each as far as it goes. The question now arises as to the nature of the reaction between carbon and oxygen, and this was discussed by Rhead and Wheeler the following year.[1] It was found that charcoal that had been heated to 950° C. in an evacuated vessel and allowed to cool, readily adsorbs oxygen at all lower temperatures, the rate of adsorption being very rapid during the first few seconds, after which the velocity gradually slows down, but continues for several hours (see fig. 8). The total amount of occluded oxygen increases with fall of temperature, and is approximately constant for any given temperature for the particular specimen of charcoal under observation. This oxygen cannot be removed by exhaustion alone, but only by increasing the temperature of the carbon during exhaustion. When quickly released in this manner it appears, not as oxygen, but as carbon dioxide and carbon monoxide. The proportions in which it appears in these

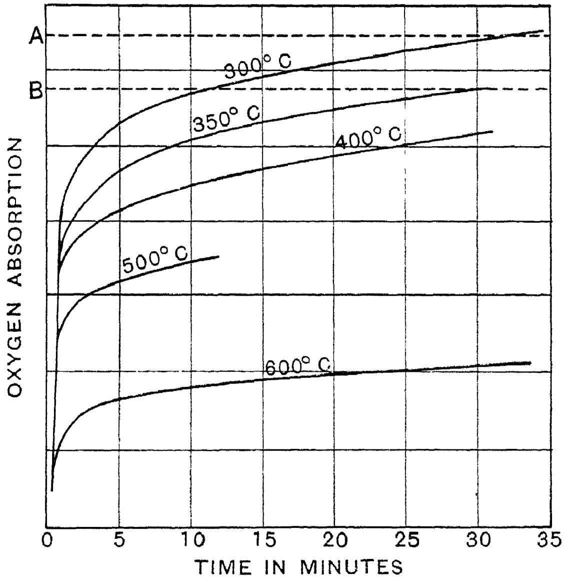

FIG 8.—Oxygen absorption by exhausted charcoal. (Rhead and Wheeler, 1913.)

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[1] Rhead and Wheeler, *Trans. Chem. Soc.*, 1913, 103, 461.

two oxides when completely removed depend on the temperature at which the carbon has been heated during oxygen-fixation.

If, for example, the temperature is raised, say from 300° to 350° C., oxygen is evolved in vacuo, corresponding to the amount AB in fig. 8, as a mixture of monoxide and dioxide until the saturation limit of the charcoal at this higher temperature has been reached, and then ceases.

The authors suggest that this is more than a purely physical "fixation" of oxygen, being in all probability the outcome of a physico-chemical attraction between oxygen and carbon. Physical, inasmuch as it seems hardly possible to assign any definite molecular formula to the complex formed, which, indeed, shows progressive variation in composition; chemical, in that no isolation of the complex can be effected by physical means.

It would appear, therefore, that the first product of combustion of carbon is a loosely formed physico-chemical complex, which can be regarded as an unstable compound of carbon and oxygen of an at present unknown composition, $C_xO_y$. It is probable that no definite formula can be assigned to this complex.

Stated mainly in the words of the authors themselves, the conception of what takes place during the combustion of carbon is, briefly, as follows: each oxygen molecule that comes into collision with the carbon becomes "fixed," in so far as it is rendered incapable of further progress by the attraction of several carbon molecules. There is as yet no absolute knowledge of the number of atoms contained in the carbon molecule. The formation of benzenehexacarboxylic acid (mellitic acid) by the oxidation of either amorphous carbon or graphite, warrants the assumption that the carbon molecule contains not fewer than twelve atoms,[1] and may be even more complex.[2] It is conceivable, therefore, the authors point out, that in the oxidation of carbon the oxygen molecule actually *enters* the carbon molecule, a rearrangement of atoms taking place. However, for the present it is sufficient to assume that several carbon molecules hold one oxygen molecule, in bond as it were, and do not allow it to escape in conjunction with one of their atoms. A considerable evolution of heat takes place during this attachment of oxygen molecules, so much so that some of them eventually acquire sufficient energy to seize hold of a carbon atom and depart with it as carbon dioxide. Some of them become torn apart in the process—become atomised—and leave the carbon molecule as carbon monoxide.

This formation of a complex, and partial decomposition as fresh oxygen molecules become attached, goes on until the carbon becomes "saturated," the products of combustion during this period (a comparatively short one) being $C_xO_y$, $CO_2$, and CO. After the carbon has become saturated there is an alternate formation and decomposition of the complex. Each oxygen molecule that impinges on the carbon is at once seized hold of to form the complex, but the energy set free when this occurs decomposes an equivalent proportion of the complex formed from previous oxygen molecules. So that, finally, when air is passed over saturated carbon maintained at a constant temperature by the application of an external source of heat, carbon dioxide and carbon monoxide appear in the products of combustion in volume sufficient to account for the total volume of oxygen in the air originally passed.

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[1] Dewar, *Chem. News*, 1908, 97, 16.

[2] Aschan, *Chem. Zeit*, 1909, 33, 561. See also Redgrove, *Chem. News*, 1908, 97, 36; Dunroth and Kerkovius, *Annalen*, 1913, 399, 120. Contrast, however, Hans Meyer, *Monatsh.*, 1914, 35, 163.

In the normal burning of carbon, therefore, the carbon dioxide and carbon monoxide found as the apparently primary products of combustion, arise from the decomposition, at the temperature of combustion, of a complex the formation of which is the first result of the encounters between oxygen and carbon molecules.

The idea of "oxygenation" of the combustible as a preliminary to definite chemical reaction is not without precedent.

Indeed, it receives strong support from the work of Bone on the combustion of hydrocarbon gases (see pp. 65–67). Although not definitely proved, this attractive theory is certainly a most suggestive one; it not only fits in well with known facts, but is in harmony with the various points urged in favour of each of the two earlier theories.

*Composition of the Complex.*—An attempt was made to determine the quantity of oxygen adsorbed by a sample of charcoal at 300° C. The result indicated an adsorption of 0·16 gram of oxygen by 12 grams of carbon, corresponding to a formula of $C_{100}O$. This, of course, only refers to the temperature chosen, namely, 300° C. The relative proportions of carbon dioxide and monoxide evolved on raising the temperature of saturated charcoal were found to vary with the initial temperature, so that it appears impossible to determine the values for $x$ and $y$ from the available data.

As mentioned above, however, Baker has shown that carbon dioxide, when thoroughly dried by prolonged contact with phosphorus pentoxide, is not reduced by carbon even at bright-red heat. On the other hand, Rhead and Wheeler have shown that the complex $C_xO_y$ is readily formed from its dry constituents. These two observations suggest a method by means of which the ratio $x/y$ might be discovered, if not exactly at any rate approximately. For by exposing thoroughly dry charcoal which has been exhausted at, say, 1100° C. to thoroughly dry oxygen at a lower temperature, the complex $C_xO_y$ should be obtained in an equally dry condition. On raising the temperature and pumping off the two oxides of carbon, these should be obtained in the proportions in which the atoms of oxygen and carbon are distributed in the complex, inasmuch as none of the carbon dioxide once produced in this way can be reduced to monoxide during the experiment, as undoubtedly occurs in the case of the moist gases.

Only two series of experiments have been carried out with this object in view, the results being inconclusive.[1]

## FLAME.

Flame has already been defined as a mass of gas raised to incandescence. It will be observed that this definition does not limit flame to such phenomena as are attendant upon combustion; it simply postulates the existence of vapour or gas. Whilst flames may and often do exist under conditions excluding all types of combustion, as for example during the electric discharges through rarefied gases, in the majority of cases flames are the result of rapid oxidation.

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[1] Rhead and Wheeler, *Trans. Chem. Soc.*, 1913, 103, 1210; H. H. Lowry and Hulett, *J. Amer. Chem. Soc*, 1920, 42, 1408.

**Cool Flames.**—It has long been known that certain flames are capable of existence at relatively low temperatures. Thus, a century ago, Davy observed that when a hot platinum wire was introduced into a mixture of ether-vapour and air, not only did the wire become red hot in consequence of active surface combustion, but a pale phosphorescent light could be detected above the wire, particularly when the latter ceased to glow, if the experiment were conducted in a dark room. Doebereiner observed the same phenomenon, and mentioned that when ether is dropped into a retort at 100° C. it may assume the spheroidal state accompanied by a pale blue flame, visible only in the dark, and too cool to set fire to other bodies. Perkin [1] suggests several ways by which this phenomenon may be exhibited at lectures. Of these, perhaps the best is to heat an iron or copper ball to dull redness, allow it to cool to such a temperature that it is just invisible in the dark, and, by means of a wire, suspend it over a dish containing several filter papers saturated with ether. "As the ball approaches the ether, a beautiful blue flame will form, passing over its heated surface upwards for several inches. The ball may be let right down into the ether without causing ordinary combustion."

The blue flame is characterised by its low temperature. The fingers may be placed in it without discomfort; paper is not charred by it, and even carbon disulphide is not ignited by it.

In studying the limits of flame propagation both in ether-air and in acetaldehyde-air mixtures, White [2] observed that, upon ignition with a hot platinum spiral at the bottom of a vertical glass tube, "a ray of glowing gas often seemed to extend upwards from the spiral for any distance up to 80 cm. The ray often remained in this position for many seconds before the top opened into a 'cool' flame travelling up the tube." The cool flame was found to readily yield the ordinary hot flame, particularly in the case of acetaldehyde. The author points out that the existence of this type of cool flame may serve to explain some of the hitherto inexplicable explosions with combustible vapours. On one occasion he was attempting to demonstrate in the usual way in daylight the flow of heavy ether vapour down an open wooden gutter 4 metres long, the vapour being obtained from a sponge saturated with liquid ether and held just above the top of the gutter. The inclination of the gutter was 1 in 4. After a time the attempt to ignite the ether-air mixture at the bottom of the gutter by means of a taper was apparently unsuccessful, although the characteristic odour of the so-called lampic acid was readily detectable. A few seconds later, however, the sponge burst into flame. It would appear, therefore, that a cool flame, practically invisible in the daylight and unobserved by the experimenters, had travelled up the gutter and given rise to ordinary combustion at the top.

## The Hydrogen Flame.

The hydrogen flame is a simple one to study, for no solids are present either in the pure gas, in pure air, or in any of the products of combustion.

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[1] Perkin, *Trans. Chem. Soc.*, 1882, 41, 363. See also Leighton, *J. Physical Chem.*, 1914, 18, 619.

[2] White, *Trans Chem Soc*, 1922, 121, 1254

When first ignited, a jet of hydrogen issuing from a glass tube yields a colourless and almost invisible flame; but as the glass becomes warm the flame acquires a yellow tint in consequence of sodium present in the glass. By employing a platinum nozzle the flame is rendered colourless and practically invisible. It consists of two portions, namely, an inner zone initially of pure gas, which rises in temperature and gradually becomes admixed with air as it passes towards the outer zone where combustion is complete.

It would appear [1] that the combustion of hydrogen between 600° and 1000° C. proceeds in such a manner that hydrogen peroxide is formed in considerable quantity, but rapidly decomposes into water and nascent oxygen. Some of the oxygen atoms unite to form ozone, which decomposes less rapidly than the peroxide. For this reason, under suitable conditions, both hydrogen peroxide and ozone may be detected in the products. The temperature of the oxyhydrogen flame has been determined as lying between 2200° and 2300° C. according to the proportion of oxygen.[2]

## The Candle Flame.[3]

The so-called "wax" of a candle is a solid fuel, with carbon and hydrogen as combustible constituents. When once the candle has been lighted, and equilibrium has established itself, the wax at the foot of the wick melts by the heat radiated from the flame, and ascends the wick by capillary attraction. Arrived in the flame, it vaporises with partial decomposition, yielding a combustible gaseous mass, apparent to the outside observer as a *non-luminous inner zone.*[4] By inserting a short, narrow glass tube into that portion of the flame, the supply may be tapped, and the vapours ignited at the free end of the tube. As the vapours ascend the cone, slow combustion begins and admixture with a little air takes place.[5] At the apex of this cone combustion begins to be vigorous, for air has now diffused towards it, and the temperature rises towards 1000° C. Above this apex, and forming also a thin mantle all round the lower portions of the cone, is a brightly *luminous mantle.* In this region partial combustion is taking place and the temperature ranges from 1000° to 1300° C. As the gases flow towards the outer surface of this mantle they meet fresh supplies of air to enable complete combustion to ensue. This takes place in what is termed the *non-luminous outer mantle*, and it is in this region that the flame is hottest. Here, too, the bent wick, already charred, projects its end, which becomes completely

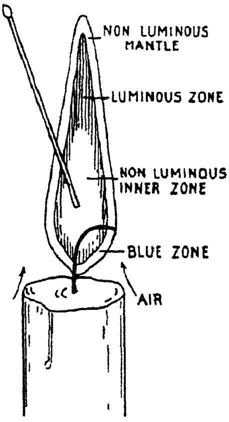

FIG. 9.—The candle flame.

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[1] von Wartenberg and Sieg, *Ber.*, 1920, 53, [B], 2192.

[2] Bauer, *Compt. rend.*, 1909, 148, 1756.

[3] See summary by Smithells, *Trans. Chem. Soc.*, 1892, 61, 217.

[4] Francis Bacon was aware "that flame burneth more violently towards the sides than in the midst," *Sylva Sylvarum, or a Naturall History in Ten Centuries*, Bacon, 1615, 6th ed., p. 9). Quoted by Smithells, *loc. cit.*

[5] Hilgard, *Annalen*, 1854, 92, 129; Landolt, *Pogg. Annalen*, 1856, 99, 389.

oxidised so that the services of snuffing-tongs are no longer in demand. Just beneath the wick lies a small *blue zone* which can easily be distinguished but is of relative unimportance. Air rising up the outside of the candle keeps the walls of wax cool and thus prevents guttering.

**Cause of Luminosity.**—In 1815 Davy [1] suggested that the luminosity of a candle flame is due to the presence of minute particles of carbon at white heat. These particles were believed to be produced by incomplete combustion of the hydrocarbon vapours in the restricted supplies of air available within the flame, the hydrogen of the vapours being "preferentially" oxidised (see p. 64), leaving the carbon to shift for itself. This theory was generally accepted for many years, and it was not until 1867 that a rival theory was projected by Frankland,[2] according to which the luminosity of the flame "is due to radiations from dense but transparent hydrocarbon vapours."

The relative merits and demerits of these theories may most advantageously be considered by reviewing a few of the more important physico-chemical phenomena of flame.

1. The deposition of soot upon a cold object introduced into a candle flame is a familiar obstacle to the adoption of this otherwise convenient method of heating small bodies. The deposition occurs only when the object is heated in the luminous zone, the outer non-luminous mantle in general yielding no soot. This was advanced as an argument in favour of the existence of carbon particles in the flame. Whilst this is exactly what might be expected in such circumstances, it would also result upon the decomposition of dense hydrocarbons under like treatment. Hence this experiment alone is in harmony with both theories, and does not enable a distinction to be made.

2. The preferential theory of combustion is not now regarded as correct, having given place to the more satisfactory association theory of Bone (see p. 65) But whilst Davy's theory of luminosity thus loses a certain amount of support, it receives support from other directions. Thus it is well known that the higher hydrocarbons are apt to undergo decomposition at high temperatures. In technical practice this is termed "cracking," and it is quite conceivable that analogous reactions might occur in a candle flame.

3. When an intense beam of light is projected on to a candle flame the beam is both bent from its original direction and polarised.[3] In other words, the flame behaves as though it were a turbid medium, that is, one containing minute particles, termed the disperse phase, floating about in a continuous phase.

If the diameters of the disperse particles, supposed spherical, lie between the limits of 1 and 100 $\mu\mu$ ($\mu\mu = 10^{-6}$ mm.) the particles are of colloid dimensions, and the flame is colloidal. It is termed a *stationary*, but not a *stable* dispersoid system by von Weimarn.[4] In a stable system the particles would not change, whereas in a flame they constantly disappear and are as frequently renewed.

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[1] See Davy, *Phil. Trans*, 1817, p. 77.

[2] See Frankland, *Proc. Roy. Soc*, 1868, 16, 419, *Sketches from the Life of Sir Edward Frankland* (Spottiswoode, 1902), pp. 234–256, *Experimental Researches*, Frankland (London, 1877), p. 906.

[3] Senftleben and Benedict, *Kolloid Zeitsch.*, 1920, 26, 97; Stokes, *Chem. News*, 1891, 64, 167.

[4] von Weimarn, *Ann. école mines Oural*, 1919, i., part 2, 5.

Whilst, however, this result clearly indicates the diphasic character of the luminous zone, it does not indicate the nature of the disperse phase Hence it does not enable a decision to be made between Davy's theory and that of Frankland.

4. Similarly, indecisive results are obtained by the spectroscopic study of the luminous zone. A continuous band of colour is observed, and this would result whether the luminous particles were solids or dense hydrocarbon vapours. As is mentioned later (see p. 84), even the flame of hydrogen burning in oxygen under high pressures yields a continuous spectrum, and in this case the possibility of solid particles being present is entirely ruled out.

5. The luminosity of a flame can be greatly increased by the introduction of solid particles which become incandescent,[1] and the rapid combustion of such substances as give non-volatile solid oxidation products is usually accompanied by brilliant luminosity. A familiar example is the combustion of metallic magnesium. But hydrogen burns in oxygen under pressure with high luminosity, so that solids are not essential to the phenomenon.

From the foregoing it will be evident that a decision between the theories of Davy and Frankland cannot be easily arrived at. Indeed, it is by no means impossible that both theories are correct in so far as they go. The only really certain feature is that the luminous zone is diphasic.[2]

## Coal-gas Flame.

The coal-gas flame is practically a replica of the candle flame, for it may be divided into three analogous zones, and the phenomena attendant upon its luminosity are closely similar to those already detailed.[3]

Examination of the spectrum of illuminating gas leads to the conclusion that two superimposed effects must be considered.[4] Firstly, there is the continuous temperature spectrum, caused by the incandescent particles floating in the flame, and secondly, a band spectrum caused possibly by the luminous particles in the act of burning in the outer mantle of the flame, or perhaps by their products of combustion.

If air is admitted into the heart of the flame in sufficient quantity, the luminosity[5] suddenly disappears almost entirely, and a flame resembling that of pure hydrogen results. Owing to the rapid combustion of the hydrocarbons, no luminous particles are separated, and the flame, being intensely hot, is a convenient one to employ for heating purposes, since it yields no soot when made to impinge upon a cold object. This is the principle of the Bunsen burner, the flame of which consists of two parts only, both of which are non-luminous. The inner zone is essentially a mixture of unburned gas with air.[1] It is warmed by radiation from the outer zone, and ranges in temperature from about 300° C. a little above the nozzle, to 1000° C. at the apex, where rapid combustion commences. The outer zone is a hot mantle of burning gas, the temperature of which may rise to about 1550° C.,[2] or even as high as 1760°±50° C.[3] Combustion is here fairly complete.

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[1] A practical application of this effect is seen in the ordinary incandescent mantle composed of oxides of thorium and cerium. For an account of the history of the incandescent mantle, see Fischer, *Der Auerstrumf*, *Sammlung Ahrens*, 1906.

[2] See Heumann, *Annalen*, 1876, 181, 129, 1876, 182, 1; *Phil Mag.*, 1877, 3, 1, 89, 366; Soret, *ibid*, 1875, 49, 50; Burch, *Nature*, 1884, 31, 272, Stokes, *ibid.*, 1892, 45, 133 On the temperatures of the luminous particles, see Ladenburg, *Chem. Zentr.*, 1906, ii., 1707.

[3] For analyses of the products of combustion from the inner cone, see Bubnov, *Zeitsch. physikal Chem.*, 1914, 88, 641.

[4] Amerio, *Atti R. Accad. Sci. Torino*, 1907, 42, 673

[5] See p. 81 for a discussion of the luminosity of the Bunsen flame.

Carbon monoxide may appear amongst the products of combustion, principally as the result of sudden cooling of the flame.[4] It appears that an incandescent mantle tends to act in this way, and cause appreciable amounts of carbon monoxide to escape. The amount depends upon the type of burner, and is independent of the amount of carbon monoxide in the original combustible gas between the limits of 0 and 60 per cent.

**Smithells Separator.**—When a mixture of a combustible gas with air or oxygen is burning at the mouth of a tube, there is a constant tendency for the flame to "strike back," this explosive tendency being counteracted by the velocity with which the gaseous mixture passes along the tube. By adjusting the relation between the proportion of oxygen in the gas and the rate of flow, it is possible to effect the separation of a flame into its component parts, because when the rate of flow of the gas is just insufficient to maintain the combustion at the end of the tube, the inner portion of the flame recedes towards the origin of the supply of the gaseous mixture, whilst the outer mantle of the flame, although enfeebled, remains in the original position. By providing a constriction inside the tube, a local increase is caused in the rate of flow of the gas, and the receding portion of the flame can be arrested at this point. This is the principle of the Smithells Separator,[5] which may be conveniently made by fixing, with the aid of a piece of rubber tubing, a short glass tube some 6 inches in length, on to the nozzle of a Bunsen burner. A second, wider tube is slipped over and fixed in position by means of a cork. The tops of the two glass tubes are protected with metal foil to prevent cracking at A and B. The gas is turned on full and ignited at the top, yielding the ordinary Bunsen flame. By turning down the gas and regulating the air supply, the flame becomes unstable and the inner portion recedes down the tube taking up a fixed position at A. At this point partial combustion only ensues, the products being CO, $CO_2$, $H_2$, and $H_2O$. In the upper flame combustion is rendered complete.

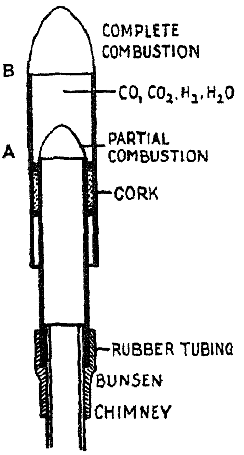

Fig. 10.—The Smithells separator.

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[1] On the chemical changes taking place in the inner cone, see Ubbelohde and Dommer, *Chem. Zentr.*, 1914, ii., 1379 On the variation of internal friction and connection with the composition of the gaseous mixture in the flame, see Becker, *Ann. Physik*, 1907, 24, 823.

[2] Féry, *Compt rend.*, 1903, 137, 909, Ladenburg, *Chem. Zentr.*, 1906, ii., 1707; Allner, *Chem. Zentr.*, 1906, i., 309; Lewes, *J. Soc Chem Ind*, 1892, 11, 231.

[3] Bauer, *Compt rend*, 1909, 148, 908, 1908, 147, 1397

[4] Kling and Florentin, *Compt. rend*, 1919, 169, 1404

[5] Smithells and Ingle, *Trans. Chem. Soc.*, 1892, 61, 204, Smithells and Dent, *ibid*, 1894, 65, 603.

The effect is very beautiful if carried out in a darkened room.

A curious experiment has been described by Price[1] in which a flame is obtained very similar to the inner flame of the Smithells separator. The experiment consists in fixing a glass chimney over the base of a Bunsen burner, and a horizontal wire an inch or two above its upper end (fig. 11). If the height of A above the burner and the rate of flow of gas are correctly adjusted, upon applying a light at C the gas burns with a pale blue flame, and bears a resemblance to the "gas cap" of a miner's lamp.

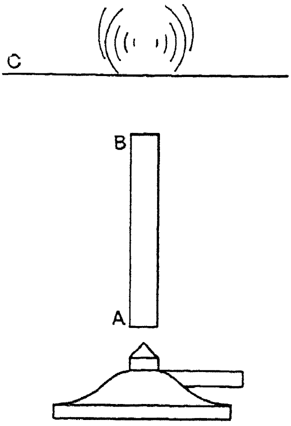

FIG. 11.—Price's experiment (1920)

When sodium chloride is sprinkled on a glowing coal fire a characteristic blue flame results, which is attributable to the presence of salts of copper originating in the pyrites in the coal. This was demonstrated by Salet[2] who, in 1890, not only identified the flame spectrum as that of copper chloride, but succeeded in separating metallic copper from the fuel ash. The colour is not due to carbon monoxide, the two flames being quite distinct.[3]

**Microphonic Flames.**—It has recently been observed by de Forest[4] that flames can be employed for direct production of telephonic currents by sound-waves.

**Luminosity of the Bunsen Flame.**[5]—Mention has already been made of the fact that the introduction of air into the heart of the flame enables rapid combustion to take place without the separation of luminous particles, so that the Bunsen flame tends to lose the luminosity characteristic of coal gas. This, however, is not the entire cause[6]; there are several contributory factors. For example, the air introduced into the flame is cold and thus tends to cool the whole. Again, the formation of intermediate luminous bodies is retarded by the nitrogen which serves as a pure diluent and elevates the temperature necessary to effect the partial decomposition of the hydrocarbons.

## Influence of Temperature upon Luminosity.

The higher the temperature of a flame, the greater will become its luminosity, the change being due to a general shortening of the wave-length of the radiation. This can be readily demonstrated by a comparison of the flames produced by the combustion of cold and heated coal gas respectively; by burning phosphorus or carbon disulphide in air and in oxygen respectively, an atmosphere of the latter gas causing a hotter and brighter flame.

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[1] Price, *Chem. News*, 1920, 120, 149. Spiral flames are described by Meunier, *Compt. rend.*, 1912, 154, 698

[2] Salet, *Compt. rend.*, 1890, 110, 282; earlier discussions by Gladstone, *Phil. Mag.*, 1862, 24, 417; Muller, *Nature*, 1876, 13, 448.

[3] Smithells, *Nature*, 1922, 109, 744 See also W. Hughes, *ibid.*, p. 683; Merton, *ibid.*, p 683; Bancroft and Weiser, *J. Physical Chem.*, 1915, 19, 310.

[4] de Forest, *Nature*, 1923, 111, 739

[5] On the luminosity of the Bunsen flame, see Haber and Richardt, *Zeitsch. anorg. Chem.*, 1904, 38, 5; Lacy, *Zeitsch. physikal. Chem.*, 1908, 64, 633.

[6] Lewes, *J. Soc. Chem. Ind.*, 1902, 11, 231.

**The calculation of the flame temperature** for a combustible gas like hydrogen, carbon monoxide, or methane at first sight appears to be a simple problem since the apparently necessary data are only the heat of combustion and the specific heats of the products. Such calculations always yield very high results much above those recorded by direct experimental measurements. The discrepancy is probably due to a combination of several causes. On account of the temperature of the flame the products are partially dissociated,[1] so that combustion is not complete in the flame. The specific heat of gases increases with rise in temperature, so that the value obtained at the ordinary temperature for the specific heat is too low. In addition to these two causes, another contributory factor is the loss of heat by radiation, which may be very considerable even in non-luminous flames, whilst the general presence of an excess of the "supporter of combustion" and the non-instantaneous character of the combustion also detract from the accuracy of the calculation.[2]

A convenient method of determining the temperature of a luminous flame consists[3] in inserting a thin wire of incorrodible metal, such as gold or platinum, into the flame and estimating the temperature with a pyrometer. The loss of heat occasioned by insertion of the wire is compensated for by raising the wire to the temperature of the flame by an electric current. When the wire has reached the same temperature as the flame there is no deposition of carbon. The wires should not exceed 1 mm. in diameter.

### Influence of Pressure on the Luminosity of Flames.

Frankland[4] burned six stearin candles in Chamounix, and the same six afterwards in a tent on the top of Mt. Blanc. The average losses in weight were:

| | |
|---|---|
| At Chamounix . . . | 9·4 grams per hour. |
| Summit of Mt. Blanc . . | 9·2 " " |

Attributing the small difference to variation in temperature, Frankland concluded that

*the rate of combustion of a candle is entirely independent of the density of the air.*

He explained the result as follows: In the combustion of a candle, the radiant heat from the flame first melts the wax, and this, by the capillary action of the wick, rises into the flame. It is thus evident that the rate of consumption of the wax is entirely dependent upon the capillarity of the wick, provided the heat radiated from the flame is sufficient to maintain the supply of liquid fuel and to volatilise it on its arrival near the apex of the cotton. Since capillary action is not affected by variations in atmospheric pressure, and as the temperature is almost independent of the same influence, it is clear that neither factor will vary, and the above constancy in rate of combustion is to be anticipated.

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[1] Compare Haber and others, *Zeitsch. physikal. Chem.*, 1909, 66, 181; 67, 343.

[2] *Brit. Assoc. Reports*, 1908, pp. 313, 335; 1909, p. 249; 1910, pp. 199, 469.

[3] Senftleben and Benedict, *Physikal. Zeitsch.*, 1918, 19, 180.

[4] Frankland, *Experimental Researches* (London, 1877), p. 876.

During his experiments on Mt. Blanc, Frankland was impressed with the small amount of light emitted by the candles. The inner blue zone was extended, and the size of the luminous zone proportionately reduced. Upon returning to England he carried out a series of photometric measurements with coal-gas flame, and deduced the law that

> *the diminution in illuminating power is directly proportional to the diminution in atmospheric pressure,*

down to a minimum of about 14 inches of mercury. For every inch fall in pressure of the atmosphere, the luminosity fell, under the particular conditions of the experiments, by 5·1 per cent. Thus, a quantity of coal gas which in London would yield a light equal to 100 candles would, if burned in Munich, give an illuminating effect equal to little more than 91 candles; whilst in Mexico its luminosity would be reduced to 61·5 candles—these numbers being independent of the change of volume of the coal gas by the reduced pressure.

Experiments were next carried out on the influence of compression. This was a difficult task to execute satisfactorily, for it was soon found that any considerable increase of pressure caused both candle and oil flames to smoke. Frankland therefore decided to employ flames that were but feebly luminous at ordinary pressure. In the experiments between atmospheric and two atmospheres' pressure, a lamp fed with amyl alcohol was used. As this smoked at somewhat higher pressures, a mixture of 5 parts ethyl alcohol with 1 of amyl was employed. This had no appreciable illuminating power at ordinary pressure.

It was found that the same law held as for diminution of pressure, an upper limit being reached at about three atmospheres, after which the observed luminosity rapidly increased.

The results obtained may be grouped as follows:

## THE INFLUENCE OF PRESSURE UPON LUMINOSITY.

(Frankland, 1877.)

| Pressure in atmospheres. | Combustible. | Observed Luminosity. | Calculated Luminosity. |
|---|---|---|---|
| 1 | Coal gas . . . | 100 | 100 |
| 2 | Amyl alcohol . . | 262·5[1] | 253 |
| 3 | 5 parts ethyl alcohol with 1 part amyl alcohol . | 406 | 406 |
| 4 | do. | 959 | 559 |

Analyses of escaping gases from two candles burning under different pressures yielded similar results, and showed that there was no escape of unconsumed combustible vapour. Consequently

> *the diminution of light in rarefied atmospheres is not due to imperfect combustion.*

On the other hand, compression tends to render the combustion less complete. Neither is the reduced luminosity due to a fall in temperature, for although a slight fall does take place, it is not sufficient to account for the whole change.[1] It appears to depend "chiefly, if not entirely, upon the ready access of atmospheric oxygen to, or its comparative exclusion from, the interior of the flame."

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[1] Mean of two series.

Frankland also investigated the influence of pressure upon the combustion of hydrogen in oxygen. At 10 atmospheres the light is very bright, and the spectrum continuous from red to violet. Carbon monoxide, which normally burns with a feebly luminous flame, becomes even more luminous at high pressures than a flame of hydrogen of the same dimensions.[2]

## The Cyanogen Flame.

The phenomena attendant upon the combustion of cyanogen in a Smithells separator are distinctly beautiful.[3] The flame of cyanogen burning at the nozzle consists of two parts, namely, an inner cone of bright peach-blossom tint, and an outer cone shading off from bright blue to greenish grey. On introducing air into the system, the inner cone diminishes in size and descends the outer tube (fig. 10). Whilst this process of detachment, however, is in progress, the inner cone is seen to be surrounded by a rosy halo, which still adheres to it after the descent, but disappears upon entry of more air, being almost immediately replaced by a blue halo. The whole of this time the outer cone remains unaltered. Further addition of air causes the outer cone to disappear, whilst the inner one now becomes more blue, and its halo acquires a greener tint.[4]

Dixon[5] has shown that the rate of explosion of cyanogen with oxygen reaches a maximum when the two gases are present in molecular proportions. Further addition of oxygen reduces the velocity, the extra oxygen acting as a diluent, just like a neutral gas, such as nitrogen, might be expected to do. It appears, therefore, that the first product of combustion is carbon monoxide, with liberation of nitrogen.

$$(CN)_2+O_2=2CO+N_2.$$

This is the main reaction in the inner cone of peach-blossom tint. It is followed, in the outer cone, by the combustion of carbon monoxide, and the greenish fringe alluded to above is attributed to the presence of small quantities of oxides of nitrogen.

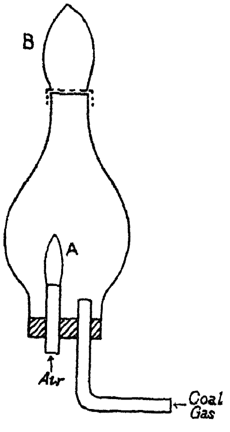

Fig. 12.—Reciprocal combustion

## Reciprocal Combustion.

From the foregoing it is clear that a flame resulting from chemical action must be regarded as a meeting ground between combustible gases—a region where chemical combination is proceeding with great activity. For the sake of convenience air is regarded as a supporter of combination, and coal gas as the combustible body.

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[1] See also Ubbelohde and Andwandter, *J. Gasbeleucht.*, 1917, 60, 225, 242, 268.

[2] Frankland, *loc cit.*, p 907.

[3] See Smithells and Dent, *Trans. Chem. Soc*, 1894, 65, 603.

[4] For a thorough study of the cyanogen-air and cyanogen-oxygen flames, see Reis, *Zeitsch. physikal. Chem.*, 1914, 88, 513.

[5] Dixon, *Phil. Trans.*, 1893, 184, 122.

But this is simply a convention, and if a glass globe be filled with coal gas, as in fig. 12, and ignited at B to prevent its free escape into the room—a lighted taper may be made to ascend A and ignite the air drawn by suction up the tube. This is air burning in an atmosphere of coal gas.[1]

## Combustion of Carbon Monoxide.

From the time of Lavoisier until 1880, the combustion of carbon monoxide was regarded as a simple oxidation process completely represented by the equation

$$2CO+O_2=2CO_2.$$

In the latter year, however, Dixon,[2] in his address to the Chemical Section of the British Association, made the startling announcement that when an electric spark is passed through a thoroughly dried mixture of two volumes of carbon monoxide and one volume of oxygen, no explosion is caused. The introduction of a small quantity of water-vapour suffices to determine the explosion, which gains in intensity up to a certain point with increasing amounts of water. Gases like $H_2S$, $C_2H_4$, $NH_3$, $HCl$, and ether-vapour act like water, but $SO_2$, $CO_2$, $CS_2$, $C_2N_2$, $CCl_4$ do not, if perfectly dry. It seems clear, therefore, that such substances as will form steam under the conditions of the experiment are capable of determining the explosion.

In order to explain these results, Dixon [3] suggested that "the carbon monoxide is oxidised by the steam in the path of the spark, and that the hydrogen set free unites with oxygen to form steam at a high temperature." The steam thus acts as an oxygen carrier itself, undergoing successive oxidation and reduction as follows:

$$\text{(i) } 2CO+2OH_2=2CO_2+2H_2;$$
$$\text{(ii) } 2H_2+O_2=2H_2O.$$

Moritz Traube [4] rejected this explanation on the ground that carbon monoxide does not decompose steam at the temperature of the electric spark, for reaction (i) is reversible and under these conditions proceeds in the direction right to left.

This objection, however, is not valid, for, whatever the temperature, the law of mass action requires that definite, even if small, amounts of carbon dioxide and hydrogen shall exist in equilibrium with the other gases in the system. Hence, if for any reason the partial pressure of the carbon dioxide or hydrogen falls below that required for equilibrium, it is always possible for reaction (i) to proceed, even at high temperatures, in the direction of left to right. Traube explained the reaction, however, on the assumption that the function of the steam is to unite with one atom of the oxygen molecule, the second atom being occupied in the oxidation of the carbon monoxide. Thus

$$CO+O:O+OH_2=CO_2+H_2O_2.$$

---

[1] A variation of this experiment is given by Thomsen, *Chem. News*, 1871, **23**, 283.

[2] Dixon, *B A. Reports*, 1880, p. 503; *Chem. News*, 1882, **46**, 151; *Phil. Trans.*, 1884, **175**, 630; *Trans Chem Soc*, 1886, **49**, 95.

[3] Dixon, *Trans Chem Soc.*, 1886, **49**, 95.

[4] Traube, *Ber.*, 1882, **15**, 666.

The hydrogen peroxide is then reduced to steam by more carbon monoxide

$$CO + H_2O_2 = CO_2 + H_2O.$$

This is reminiscent of the Brodie-Schonbein theory of slow oxidation (see p. 55), and in support of it may be mentioned the fact that hydrogen peroxide can be detected when moist carbon monoxide is allowed to burn in air, the flame being made to impinge upon a cold surface of water.

The suggestion has also been made that percarbonic acid, $H_2C_2O_6$, may be formed intermediately, since by allowing a flame of the moist monoxide to impinge on a cold, dilute solution of cobalt chloride and potassium hydroxide, a precipitate is obtained closely resembling that yielded on adding potassium percarbonate to a solution of cobalt chloride.[1] The combustion would thus presumably proceed as follows :

$$4CO + 3O_2 + 2H_2O = 2H_2C_2O_6 ;$$
$$CO + H_2C_2O_6 = H_2O + 3CO_2.$$

The evidence is not conclusive, however, as the same precipitate is obtained with hydrogen peroxide in the presence of an alkaline cobalt salt solution. So the above test might well be cited as a further argument in favour of Traube's theory.

The mere fact that hydrogen peroxide can be detected in the above manner is no proof that it plays such an important part in flame kinetics as Traube suggests. Armstrong [2] agrees with Dixon that water is the inter-agent, but whilst Dixon considers that its oxygen becomes affixed to the carbon monoxide molecule, liberating free hydrogen, Armstrong suggests that the oxidation of the carbon monoxide by the oxygen of the water is dependent upon the *simultaneous* oxidation of the hydrogen of the water by the free oxygen. Thus the states before and after the explosion may be represented by the schemes :

$$\begin{array}{ccc} \begin{array}{l} O\ H_2O\ CO \\ | \\ O\ H_2O\ CO \\ \text{(before)} \end{array} & \text{and} & \begin{array}{l} OH_2\ OCO \\ \\ OH_2\ OCO. \\ \text{(after)} \end{array} \end{array}$$

Von Wartenberg and Sieg [3] strongly support Dixon's theory, and suggest the following scheme :

(1) The formation of formic acid—

$$CO + H_2O = H . COOH.$$

The production of this acid as an intermediate product during the combustion of carbon monoxide was demonstrated by Wieland [4] in 1912. The flame of the burning gas was allowed to impinge upon ice, and formic acid was found in solution in the water.

(2) The thermal decomposition of formic acid into carbon dioxide and hydrogen, both of which gases can be detected:

$$H . COOH = CO_2 + H_2.$$

---

[1] Constam and von Hansen, *Zeitsch. Elektrochem.*, 1896, 3, 137, 445, Bach, *Compt. rend*, 1897, 124, 2, 951 ; *Monit. Scient*, 1897, 11, ii., 479.

[2] Armstrong, *Trans. Chem. Soc*, 1886, 49, 112.

[3] von Wartenberg and Sieg, *Ber.*, 1920, 53, [B], 2192.

[4] Wieland, *ibid.*, 1912, 45, 679.

This is followed by—

(3) The production of hydrogen peroxide:

$$H_2+O_2=H_2O_2,$$

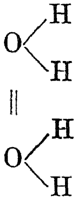
and (4) Decomposition into water and oxygen:

$$H_2O_2=H_2O+O.$$

Bone[1] has still further developed Dixon's theory. He points out that the flame of hydrogen burning in air is smaller and "sharper" than a flame of carbon monoxide, burning at the same orifice and under the same pressure. The lambent character of the latter flame suggests a slower burning gas than hydrogen. Again, hydrogen-air mixtures have lower ignition temperatures than CO-air mixtures (see p. 110), whilst the maximum flame speed of the former is more than eight times that of the latter (see p. 125). Finally, Bone and Haward have shown that when corresponding $H_2$-air and CO-air mixtures are exploded in closed vessels, the pressure rapidly rises to a maximum in the case of hydrogen, but much more slowly with carbon monoxide. The addition of only 1 per cent. of hydrogen to the CO-air mixture very greatly accelerates the attainment of maximum pressure. All of these points indicate that carbon monoxide is not capable of being oxidised so readily as hydrogen under these conditions.

Bone therefore suggests that oxygen in flames is capable of functioning in two distinct ways, namely (i) as the undissociated molecule $O_2$, and (ii) as dissociated atomic O.

An undissociated molecule, on being raised to a sufficiently high temperature, is presumed capable of exerting its latent valencies, and of combining with two hydrogen molecules without itself becoming disrupted. Thus the unstable complex $H_4O_2$ or



is momentarily formed. This, however, instantly breaks down, yielding in part its constituent elements, in the form of hydrogen molecules and atomic oxygen; and in part as nascent or activated steam molecules. Thus

$$100H_4O_2=2nH_2O:+2(100-n)(O:+H_2).$$

The magnitude of the ratio $n/(100-n)$ will obviously depend upon the conditions prevailing at the moment. The higher the temperature and the smaller the hydrogen concentration, the lower is the value for $n$.

Oxygen and carbon monoxide, however, are regarded as incapable of associating in the above manner, their molecules being mutually inert in flames. Before the carbon monoxide can undergo oxidation, the oxygen must either have dissociated, or be in the form of some activated or nascent compound such as the activated steam indicated above. Thus, whilst the reaction

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[1] Bone and Haward, *Proc. Roy. Soc.*, 1921, [A], **100**, 67. See also Bone and co-workers, *Phil. Trans.*, 1915, [A], **215**, 275.

$$2CO+O_2=2CO_2$$

is impossible, carbon dioxide can readily be obtained in either of the following ways:

$$\underset{\text{atomic}}{CO+:O}=CO_2$$

$$\underset{\text{activated.}}{CO+:OH_2}=CO_2+H_2.$$

The foregoing theory receives indirect support from several earlier researches. For example, Russell[1] caused nascent carbon monoxide and nascent oxygen to come into contact. This was effected by exploding—either with a spark or by heating in an air bath—a mixture of chlorine peroxide and carbonyl sulphide. It was found that the explosion exerted very considerable influence in bringing about the combination of carbon monoxide and oxygen. Russell was unable to decide whether the effect was direct or "due to the heightening of the action of the 'third substance.'" But if Bone's theory is correct, a very plausible explanation is clearly to hand for these observations. More recently Langmuir[2] has directed attention to the fact that oxygen when brought into contact with carbon monoxide adsorbed on platinum rapidly oxidises it to carbon dioxide. Conversely, free carbon monoxide immediately reacts with adsorbed oxygen. All of these results are suggestive of acceleration of oxidation involving an "activated" condition.

## The Equilibrium $2CO \rightleftharpoons CO_2+C$.

The reversibility of this reaction was discovered by Deville[3] in 1864, and its study receives renewed interest in view of recent developments in the theory of the combustion of carbon in oxygen to which reference has already been made (see p. 71). By circulating carbon dioxide continuously over purified wood charcoal packed in a porcelain tube heated to a high temperature, and subsequently analysing the gas when equilibrium had been reached, Rhead and Wheeler[4] obtained the following results:

| Temperature, Absolute | Temperature, ° C | 100 $C_1$, *i e* CO per cent. by Volume. | 100 $C_2$, *i e.* $CO_2$ per cent. by Volume. | K |
|---|---|---|---|---|
| 1073 | 800 | 86·15 | 13·85 | 18·76 |
| 1123 | 850 | 93·13 | 6·87 | 18·75 |
| 1173 | 900 | 96·63 | 3·37 | 18 74 |
| 1223 | 950 | 98·33 | 1·67 | 18·74 |
| 1273 | 1000 | 99·15 | 0·85 | 18·74 |
| 1323 | 1050 | 99·55 | 0·45 | 18·74 |
| 1373 | 1100 | 99·75 | 0·25 | 18·75 |

---

[1] Russell, *Trans. Chem. Soc*, 1900, 77, 361.

[2] Langmuir, *J. Amer. Chem. Soc.*, 1918, 40, 1361.

[3] Deville, *Compt rend.*, 1864, 59, 873; 1865, 60, 317.

[4] Rhead and Wheeler, *Trans. Chem. Soc.*, 1911, 99, 1140.

These results refer to atmospheric pressure, and K is calculated from a modification of Le Chatelier's formula, namely:

$$\frac{38\cdot055+2\cdot02T-0\cdot0031T^2}{2T}+\log_e P+\log_e\frac{C_1^2}{C_2}=K.$$

where T is the absolute temperature, and $C_1$ and $C_2$ are as defined in the table. P in this case is unity so that $\log_e P$ disappears.

No matter how high the temperature, theory demands the existence of a small but definite quantity of carbon dioxide in equilibrium with the monoxide.

A study of the velocity of reduction of carbon dioxide by carbon at 850° C. shows that the reaction is monomolecular, and the same is true for the reverse reaction, namely the decomposition of carbon monoxide, which, however, proceeds 166 times more slowly. Undoubtedly, therefore, the reactions are essentially surface phenomena, the rates varying directly with the partial pressure of the gas in either case. Since the decomposition of carbon monoxide is accompanied by a reduction in volume, increase of pressure should facilitate the reaction at constant temperature, and shift the equilibrium

$$2CO \rightleftharpoons CO_2+C$$

in the direction left to right. That such is the case is shown by the following data:[1]

| Temperature, ° C. | Pressure in Atmospheres. | $CO_2$ per cent. | CO per cent. |
|---|---|---|---|
| 800 | 1·23 | 16·12 | 83·88 |
| | 2·10 | 22 85 | 77·15 |
| | 3·05 | 28·40 | 71·60 |
| 900 | 0·65 | 2·17 | 97·80 |
| | 2·90 | 9·05 | 90·95 |
| 1000 | 0·66 | 0·65 | 99·35 |
| | 0·93 | 0·72 | 99·28 |
| | 2·02 | 1·63 | 98·37 |
| | 3·08 | 2·77 | 97·23 |
| | 3·78 | 3·17 | 96·83 |
| 1100 | 1·33 | 0·35 | 99·65 |
| | 3·64 | 0 92 | 99·08 |

## The Equilibrium $CO+H_2O \rightleftharpoons CO_2+H_2$.

When hydrocarbon gases are fired with oxygen in certain proportions the cooled products consist of hydrogen, water, and the oxides of carbon in various proportions. The relation between the amounts of the different constituents is given by the equation

---

[1] Rhead and Wheeler, *loc. cit.* For a study of the equilibrium between oxygen and the oxides of carbon, see Haber and Le Rossignol, *Zeitsch. physikal. Chem.*, 1909, 66, 181; Haber and Hodsman, *ibid*, 1909, 67, 343.

$$K_t=\frac{C_{CO}\times C_{H_2O}}{C_{CO_2}\times C_{H_2}}$$

where $K_t$ is the equilibrium constant at temperature $t°$ C. In 1884 Dixon[1] obtained the value $K_t=4$ in his experiments on the inflammation of mixtures containing carbon monoxide, hydrogen, and oxygen. This was supported by the results of Smithells and Ingle [2] on the composition of the interconal gases of hydrocarbon flames, and has recently been confirmed by Andrew,[3] who studied the combustion of hydrocarbon gases in oxygen and obtained values for $K_t$ ranging from 3·47 to 4·12, the mean value for several series of experiments being approximately 4.

Owing to experimental difficulties a high degree of concordance is not to be expected, and the above results may be regarded as showing reasonable agreement. From Andrew's results it would appear that the value of $K_t$ is largely independent of the initial nature of the hydrocarbon-oxygen mixture and of the pressure of the gas before ignition. It is apparently, therefore, also largely independent of the maximum flame temperature, since this would vary with the pressure and composition of the mixture to be ignited. Theoretically, however, some change with temperature is to be expected, and Hahn [4] calculates, from thermodynamical principles, that this change is given by the equation

$$\log K_t=-2232/T-0{\cdot}08463\log T-0{\cdot}0002203T+2{\cdot}5084$$

where T is the absolute temperature. The following values for $K_t$ have been derived from this equation :

| Temp. °C. . . . | 1005 | 1205 | 1405 | 1600 |
|---|---|---|---|---|
| $K_t$ . . . . . | 1·65 | 2·54 | 3·43 | 4·24 |

and these agree with reasonable approximation with the results of Haber and others.[5] Possibly in Andrew's experiments the differences in temperature were not sufficient to produce variations in $K_t$ large enough to exceed the experimental error. Andrew did not attempt to calculate his flame temperature, but believes that in all cases it would be higher than 1600° C. On the other hand, a more likely explanation and one favoured by Andrew is that $K_t$, as determined experimentally, " does not correspond with the maximum flame temperature, but is characteristic of some hypothetical temperature, the equilibrium condition at which corresponds with the integration of the chemical changes which occur in a rapidly cooling mixture from higher to atmospheric temperatures. This purely hypothetical temperature, which may be referred to as the *temperature of final reaction* (since it may be supposed that the gases are in equilibrium, and cease to further react at this temperature), is identified both on thermodynamic and experimental grounds between the limits 1500° and 1600° C."[1]

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[1] Dixon, *Phil. Trans*, 1884, 175, 617

[2] Smithells and Ingle, *Trans. Chem. Soc*, 1892, 61, 204.

[3] Andrew, *Trans Chem. Soc*, 1914, 105, 444.

[4] Hahn, *Zeitsch physikal Chem.*, 1903, 44, 510 ; 1904, 48, 735.

[5] Hiller (*Zeitsch physikal. Chem.*, 1913, 81, 591) obtained the value 2·8 for the ether flame, and for coal gas, diluted with carbon dioxide, and hence at a lower temperature than normal, a value less than 3·4 See Haber and co-workers, *ibid*, 1909, 68, 726 ; *Zeitsch. anorg. Chem.*, 1904, 38, 5 ; Lacy, *ibid.*, 1908, 64, 633 ; Tufts, *Physical Review*, 1906, 22, 193 ; Allner, *Chem. Zentr.*, 1906, i, 309.

If this is accepted the results indicate that the equilibrium

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

sets in with very great rapidity.

### LIMITS OF INFLAMMATION.

It is a matter of common knowledge that a room may smell quite strongly of coal gas without its being dangerous to strike a match within it. When this observation is pushed to its logical conclusion it is evident that a certain minimum quantity of the coal gas must be present for its inflammation to be self-supporting. This minimum quantity is termed the **lower limit of inflammation** of the combustible gas, and is influenced by two factors :[2]

1. The initial source of heat should be of sufficient volume, intensity, and duration to raise the layer of gases in its immediate vicinity to a temperature at least as high as the ignition temperature of the mixture.
2. The heat contained in the products of combustion of this first layer must be sufficient to raise the adjacent layer to its ignition temperature—and so on.

If too low a proportion of combustible gas is present, only a small quantity of heat per unit volume of mixture is liberated when the layer surrounding the initial source of heat is inflamed, and the products of combustion have to impart heat to a considerable volume of "inert" gases. The number of collisions between molecules of combustible gas and of oxygen that are chemically fruitful is therefore small. Such collisions, resulting in combination, will occur only in the neighbourhood of the initial source of heat, around which an aureole or "cap" will form of a size dependent on the nature and quantity of the combustible gas present.

Upon increasing the proportion of combustible gas, not only is a greater quantity of heat evolved per unit of mixture, but there is a smaller volume of inert gases present to absorb it; ultimately, therefore, a point may be reached when the amount of heat contained in the products of combustion of any given layer is just sufficient to raise the adjacent layer to its ignition-temperature. Flame is then propagated from layer to layer throughout the mixture without any necessity for the continued presence of the source of heat which started the inflammation, and the mixture either inflames or explodes according to the rapidity of the propagation.

Consideration will show that there must also be a **higher limit of inflammation** of the combustible gas, for if its proportion over that of the oxygen be largely increased, the excess will function as a diluent, absorb heat, and tend to retard flame propagation.

Since gaseous combustion is a reciprocal phenomenon, it follows that the amount of oxygen present in this latter case is the minimum quantity supporting combustion, and may be termed the **lower oxygen limit of inflammation.**

It may happen that the lower oxygen limit is above that which can be realised when the combustible gas is mixed with air In that case the gas will not normally burn in air, but may do so in an atmosphere enriched with oxygen. Ammonia[1] vapour is a typical example. If a lighted taper is applied to a jet from which this gas is escaping, the characteristic livid flame appears side by side with the flame of the taper; but it at once dies away upon removal of the latter. If, however, the jet is surrounded by air enriched with oxygen the flame of ammonia gas becomes self-supporting, and continues to burn even when the taper has been withdrawn.

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[1] Andrew, *loc cit*, p. 453.

[2] Burgess and Wheeler, *Trans. Chem. Soc.*, 1911, 99, 2013.

## The Gaseous Hydrocarbons.[2]

Amongst the earliest experiments carried out with a view to the quantitative determination of the limits of inflammability of combustible gases were those of Davy with fire damp, which is mainly methane, $CH_4$. Owing to the importance of this gas in connection with gob fires and explosions in coal mines, several other workers have also investigated it. The value of the results, however, is restricted by the fact that firedamp, like most natural products, is subject to very considerable variation in composition.[3] Even Davy recognised that it was not pure methane; indeed, perfectly pure methane is not easy to prepare in quantity. The gas, as obtained from sodium acetate, may contain as much as 8 per cent. of hydrogen, as well as ethylene.[4] No doubt this variation in composition is one contributory cause of the very varied results listed in the table on p. 93.

Of these results the most reliable are those of Burgess and Wheeler, and of Coward and his co-workers, which may now be briefly considered.

### *Experiments of Burgess and Wheeler.*[5]

Several methods of attacking the problem were devised, namely, central ignition in a large glass globe by means of an electric spark;

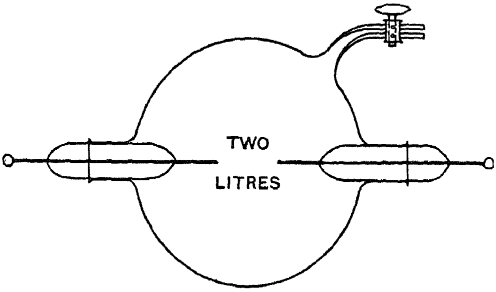

FIG 13—Apparatus used by Burgess and Wheeler (1911).

employment of vertical tube, closed at both ends, and ignited either at the bottom or at the top; and a horizontal tube, closed at both ends, ignited at one end.

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[1] For a thorough study of the ammonia-oxygen flame, see Reis, *Zeitsch. physikal. Chem.*, 1914, 88, 513.

[2] The limits of inflammation of organic substances, such as ether, alcohol, and acetone, in air have been determined by White and Price, *Trans Chem Soc.*, 1919, 115, 1462.

[3] See analyses by Gray, *Trans Inst. Mining Eng.*, 1910, 39, 286.

[4] Kolbe, *Ausfuhrl Lehrbuch Organisch. Chem*, 1854, i., 275.

[5] Burgess and Wheeler, *Trans. Chem Soc*, 1911, 99, 2013; 1914, 105, 2592. This method was also used by Parker, *ibid*, 1914, 105, 1002.

## LIMITS OF INFLAMMATION OF MIXTURES OF AIR AND FIREDAMP OR METHANE.

| Lower Limit of Inflammable Gas. Per cent by Volume. | Upper Limit of Inflammable Gas. Per cent. by Volume | Authority. |
|---|---|---|
| 6·2 to 6·7 | 20 to 25<br>14·3 to 16·7 | Davy, *Collected Works*, 1816, vol. vi., p. 24; *Phil. Trans.*, 1816, p. 1. |
| 7·7 | 14·5 | Mallard, *Ann Mines*, 1875, [7], **7**, 355. |
| 5·9 to 6·25 | 12·5 to 14·3 | Wagner, *Bayerisches Industrie und Gewerbeblatt*, 1876, **8**, 186. |
| 5·9 to 6·2 | 12·5 to 14·3 | Coquillon, *Compt. rend.*, 1876, **83**, 709. |
| 5·6 | 16·7 | Mallard and Le Chatelier, *Ann. Mines*, 1883, [8], **4**, 347. |
| 5·9 | 12·5 to 14·3 | Wullner and Lehmann, *Ber. Preuss. Schlagwetter-kommission*, 1886, **B**, **3**, 193. |
| 5·5 | 13·5 | Broockmann, *J. Gasbeleuchtung*, 1889, **32**, 189. |
| 6·1 | . . | Le Chatelier, *Ann. Mines*, 1891, [8], **19**, 388. |
| 5·8 to 6·1<br>5·7 to 6·0 | 12·4 to 12·8<br>13·0 to 13·2 | Roszkowski, *Zeitsch. physikal. Chem.*, 1891, **7**, 485. |
| 5<br>6 | 13<br>11 | Clowes, *Detection of Inflammable Gas and Air*, 1896. |
| 5·5 | 17 | Bunte, *Ber.*, 1898, **31**, 19. |
| 5·5 | 12·0 to 12·25 | Couriot and Meunier, *Compt. rend.*, 1898, **126**, 750. |
| 6 | . . | Le Chatelier and Boudouard, *Compt. rend.*, 1898, **126**, 1344. |
| 6·0 to 6·2 | 12·7 to 12·9 | Eitner, *Habilitations-schrift, Munchen*, 1902. |
| 3·20 to 3·67 | . . | Teclu, *J. prakt. Chem.*, 1907, [2], **75**, 212. |
| 2·5 | . . | Perman, *Nature*, 1911, **87**, 416. |
| 5·6 | 14·8 | Burgess and Wheeler, *Trans. Chem. Soc.*, 1911, **99**, 2013; 1914, **105**, 259. |
| 5·77 | . . | Parker, *ibid.*, 1914, **105**, 1002. |
| 5·3 (perfectly tranquil)<br>5·6 (under slight shock) | . . | Coward and Brinsley, *ibid.*, 1914, **105**, 1859. |
| . . | 15·4 | Coward, Carpenter, and Payman, *ibid.*, 1919, **115**, 27. |

1. Central Ignition in a Large Globe.—The apparatus consisted of a glass globe, of capacity about 2 litres, fitted with platinum electrodes having looped ends. The electrodes passed along a diameter of the globe through ground stoppers. The gases could be admitted and withdrawn through the tap. In all but a few special experiments a little distilled water was placed in the globe to saturate the gaseous mixture with water-vapour at the room temperature. The methane was obtained in a state of high purity by the action of an aluminium-mercury couple on a well-cooled mixture of methyl alcohol and iodide. The product was freed from traces of hydrogen by passage through "oxidised" palladium sponge heated to 98° C. and by subsequent liquefaction with liquid air.

The manner of determining the lower-limit mixtures was that of "trial and error"; for example, a mixture of methane and air containing 6·1 per cent. of methane having been tried and found to propagate inflammation on the passage of an electric spark, a second mixture was prepared containing 5·9 per cent. of methane. This also propagated flame. The percentage of methane was therefore further reduced by 0·10 in a new mixture, and so on, until two mixtures were obtained, differing in their content of methane by 0 20 per cent., one of which enabled flame to be propagated, whilst the other did not. The lower-limit mixture was taken to be that containing the mean percentage of methane contained in these two mixtures.

The lower-limit mixture could be distinguished with certainty from that just containing sufficient combustible gas; for the momentary passage of the electric spark sufficed to promote the inflammation of all the gas contained in the globe in the former case, and on further sparking no signs of combustion could be observed. Whilst in the latter case, although the flame of the burning gas might appear to travel nearly through the whole mixture on the first passage of the spark, and some doubt might exist as to whether it had not, in fact, travelled throughout, on causing the spark to pass a second time, a "cap" appeared above it, showing that the mixture still contained combustible gas. This cap remained whilst passage of the spark was continued, growing gradually smaller in size, until all the gas had been burnt.

All the experiments were made in a darkened room, so as to enable the appearance of the flames to be readily observed.

The appearance is beautifully shown in Plate I.

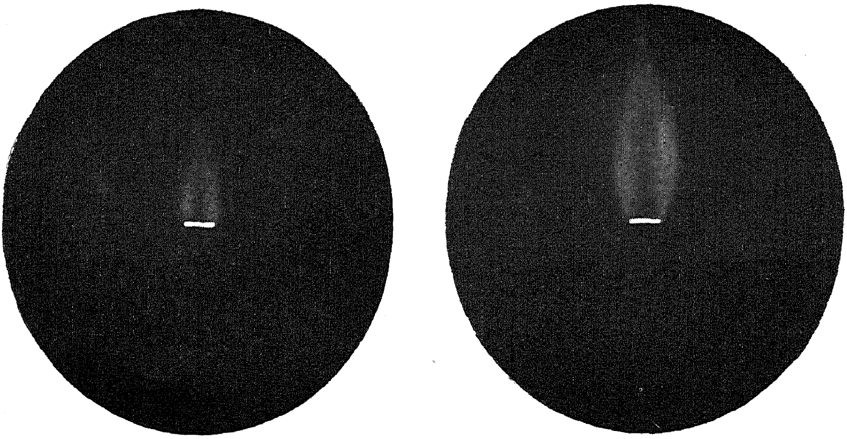
The following results were obtained:

## LOWER-LIMIT MIXTURES.

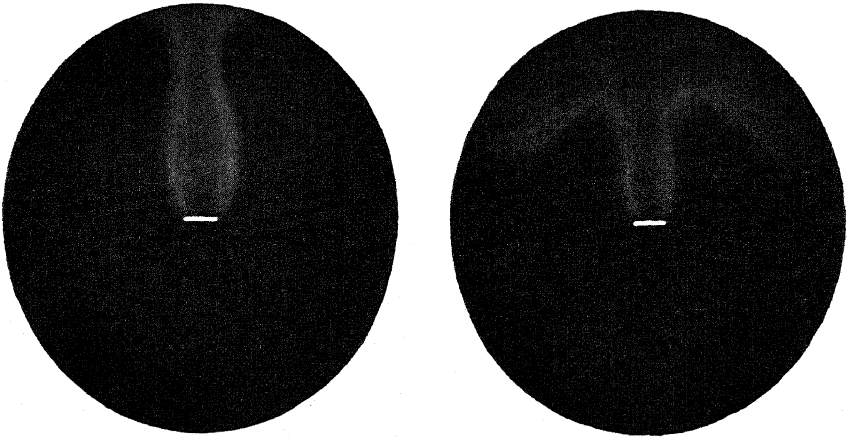
(Burgess and Wheeler.)

| Gas or Vapour. | Lower Limit Mixture in Air Per cent. by Volume |
|---|---|
| Methane . . . | 5·50 to 5 70 |
| Ethane . . . | 3·00 to 3·20 |
| Propane . . . | 2·15 to 2·30 |
| Normal-Butane . | 1·60 to 1 70 |
| Normal-Pentane . | 1·35 to 1·40 |
| iso-Pentane . . | 1·30 to 1·35 |

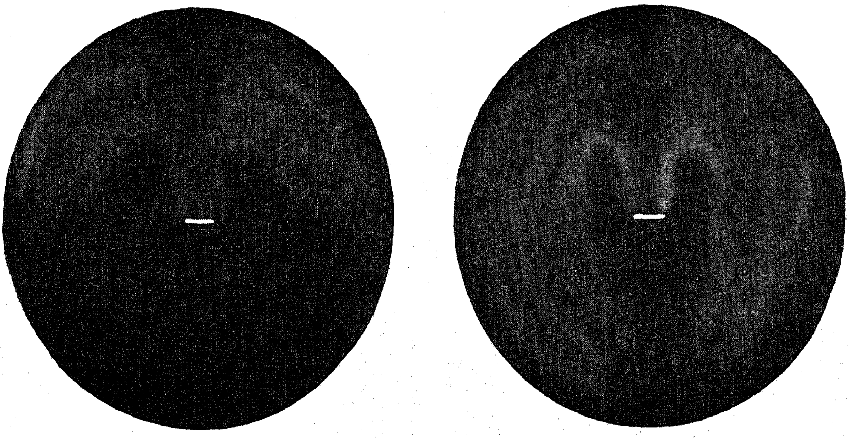
PLATE I.



Methane 4·30 per cent. 4·5 per cent.



4·65 per cent. 4·85 per cent.



5·00 per cent. 5·50 per cent.

LOWER LIMIT OF INFLAMMATION OF METHANE IN AIR.
(Burgess and Wheeler, 1911.)

The value for methane agrees quite well with that obtained both by Coquillon and Le Chatelier ;[1] for firedamp there are at least five factors concerned in the magnitude of the lower-limit mixture. These are :

(1) The heat of combustion of the gas ;
(2) The relative volumes and specific heats of the diluent gases ;
(3) The ignition temperature of the mixture ;
(4) The initial pressure ; and
(5) The initial temperature.

As Burgess and Wheeler point out, the first factor must undoubtedly exercise the preponderating influence. The last two factors can easily be kept constant.

As a first approximation, therefore, it would appear probable that the lower limit of inflammation should vary inversely as the calorific value of the gas ; that is to say, if L is the proportion of the combustible gas necessary to form a lower-limit mixture, and C its calorific value,

$$L=f(1/C) \text{ or } L=k/C$$

where $k$ is a constant.

The value obtained for the lower limit of inflammation of methane when mixed with air is 5·6. The calorific value of methane is 189·1. Substituting in the above equation a value of 1059 is obtained for $k$, and the relative values for L for other gases can then be calculated.

### LOWER-LIMIT MIXTURES.

(Burgess and Wheeler.)

| Gas or Vapour. | Heat of Combustion.[2] | L observed. | L calculated. |
|---|---|---|---|
| Methane . . . | 189·1 | 5·60 | standard |
| Ethane . . . . | 336·6 | 3·10 | 3·15 |
| Propane . . . | 484·2 | 2·17 | 2·19 |
| *n*-Butane . . . | 631·7 | 1·65 | 1·68 |
| *n*-Pentane . . . | 779·2 | 1·37 | 1·36 |
| *iso*-Pentane . . . | 779·2 | 1·32 | 1·36 |

The agreement between the observed and calculated values of L is very striking, and seems to point to a definite and dominating relationship between the calorific values of the combustibles named in the table —the paraffin hydrocarbons—and their lower limits of inflammation when mixed with air.

But when this method of calculation is applied to other combustible gases, the agreement is not so close. This, however, is scarcely surprising, for there is no reason why L should be actually in direct proportion to C, and this is the basic assumption of the calculations.

2. Vertical Tube closed at Both Ends.—In these experiments glass cylinders 6 cm. in diameter and some 2 metres in length are employed, and the combustible mixture is fired by sparking between platinum terminals at either the upper or the lower end. Bottom ignition tends to give a low value for the low limit and a high value for the higher

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[1] It is difficult to understand the low values obtained by Teclu and by Perman (see p. 93).

[2] These are the data used by Burgess and Wheeler.

limit of inflammation, in consequence of convection currents. Top ignition behaves in an exactly opposite manner. This is evident from the results in the table below.

The quantitative values for the higher and lower limits are greatly affected by the diameters of the tubes[1] unless these exceed 5 cm. Narrow tubes raise the lower limit and depress the higher limit, thereby reducing the total range of inflammability. This is illustrated in the case of mixtures of acetone and air in the accompanying table.[2] If the diameters are very small indeed, no combustion will take place.

### INFLUENCE OF DIAMETER OF TUBE UPON THE LIMITS OF INFLAMMABILITY.

(Wheeler and Whitaker, 1917.)

| Diameter, cm. | Lower Acetone Limit. | | | Higher Acetone Limit | | |
|---|---|---|---|---|---|---|
| | Upward. | Downward | Horizontal | Upward | Downward | Horizontal. |
| 2·5 | 2·30 | 2·75 | 2·40 | 7·5 | 6·5 | 6·7 |
| 5·0 | 2·20 | 2·40 | 2·25 | 9·5 | 8·3 | 9·3 |
| 10·0 | 2·15 | 2·35 | 2·20 | 9·7 | 8·5 | 9·5 |

3. Horizontal Tube, closed at Both Ends.[3]—The ignition is effected at one end as already indicated, and the flame creeps along the upper portion of the tube in a similar manner to a small air bubble in a spirit-level.

The diameter of the tubes, if less than about 5 cm., exerts an analogous influence upon the results, as was found to be the case with vertical tubes. This is shown by the data in the above table.

*Experiments of Coward and his Co-workers.*

In carrying out some of these a bottle of capacity 11 litres was chosen, and fitted with a rubber stopper conveying gas and water tubes and insulated leads for the sparking wires. The gases were admitted by displacement of water, the air being first added in nearly sufficient amount, followed by a measured volume of inflammable gas. Finally, the total volume was brought to 10 litres by the addition of sufficient air. The water remaining in the vessel, amounting to about 1 litre, enabled the gases to be thoroughly admixed by shaking. This procedure necessitated the experiments being confined to gases saturated with moisture. In the case of gases of but slight solubility mixtures could be made accurately to one part per thousand. For upward ignition, the bottle was supported upside down on a tripod stand and the sparking gap extended about 2 cm. above the surface of the water. When downward ignition was required, the bottle stood on its base. As the beautiful vortex rings of flame rising through the mixture were soon extinguished owing to the limited capacity of the bottle it was impossible to decide whether such rings were capable of travelling indefinitely, or if they would tend to break up and produce a general inflammation, or eventually become extinguished. A long, rectangular tube was therefore constructed, two sides of which were of wood and two of plate glass. Square in cross-section, and of total length 1·8 metres, its capacity was 170 litres. Its top was of wood, and its bottom open, but water-sealed during experimentation by immersion in a tank. The gases were admitted by displacing water, and ignited electrically. An analysis of the gaseous mixture was made, as a check on the accuracy of mixing, just prior to the test of its inflammability. The methane was prepared from aluminium carbide and water, with subsequent removal of acetylene and liquefaction to separate hydrogen.

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[1] Burgess and Wheeler, *Trans. Chem. Soc*, 1914, 105, 2592; Leprince-Ringuet, *Compt. rend.*, 1914, 158, 1793, 1999.

[2] Wheeler and Whitaker, *Trans. Chem. Soc.*, 1917, 111, 267.

[3] Burgess and Wheeler, *loc cit.*

## LIMITS OF INFLAMMATION OF METHANE-AIR AND ETHYLENE-AIR MIXTURES.

| | Methane per cent. by Volume. | | Ethylene per cent. by Volume. | |
|---|---|---|---|---|
| | Lower Limit. | Upper Limit. | Lower Limit. | Upper Limit. |
| Central ignition in large globe . . . | 5·6 [1] | 14·8 [1] | .. | .. |
| Vertical tube closed at both ends : | | | | |
| *a.* Bottom ignition . | not $<$5·4 [1] | not $>$ 14·8 [1] | 3·3 [4] | 25·6 [4] |
| *b.* Ignition at top . | 6·0 [1] | 13·4 [1] | 3·6 [4] | 13·7 [4] |
| Horizontal tube closed both ends . . | 5·4 [1] flame travels only along top of tube . . | 14·3 [1] | 3·4 [4] | 14·1 [4] |
| Ignition one end . | 5·6[1] all $CH_4$ burned | .. | .. | .. |
| Under slight shock . | 5·6 [2] | .. | .. | .. |
| Perfectly tranquil . | 5·3 [2] | .. | .. | .. |
| Do. | .. | 15·4 [3] | .. | .. |

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With a 5·1 per cent. methane mixture in this large box, a ring of flame was formed which travelled about 30 cm., broke quickly, and formed a tongue of flame which travelled another 30 cm. before extinction. With 5·3 per cent. methane a stout ring of flame travelled a few cms. and resolved itself into a steady flame nearly as wide as the box, travelling right to the top with a swaying motion. This experiment could not be satisfactorily repeated, and even a 5·5 per cent. mixture failed to yield a flame sufficiently strong to traverse the whole box; but with 5·6 per cent. of methane, a steady flame with a convex front passed throughout the whole mixture. The authors therefore conclude that the flames of mixtures containing 5·3 to 5·6 per cent. of methane are very sensitive to extinction by shock, and that a 5·6 per cent. mixture will invariably propagate flame when the shocks are no greater than those occasioned by the somewhat violent bubbling of gas through water. When, however, circumstances are such that a tranquil passage is assured, 5·3 per cent. is the lower limit of inflammability.

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[1] Burgess and Wheeler, *Trans. Chem Soc.*, 1914, 105, 259.
[2] Coward and Brinsley, *ibid.*, p. 1859.
[3] Coward, Carpenter, and Payman, *ibid.*, 1919, 115, 27.
[4] Chapman, *ibid.*, 1921, 119, 1677.

The foregoing data, in so far as methane and ethylene are concerned, may be summarised as shown on p. 97.

### Hydrogen.

Widely differing results have been obtained for the limits of inflammability of hydrogen-air mixtures, as is evident from the following table:

## LIMITS OF INFLAMMABILITY OF HYDROGEN-AIR MIXTURES.

| Lower Limit of Hydrogen. Per cent by Volume. | Higher Limit of Hydrogen. Per cent. by Volume. | Authority. |
|---|---|---|
| 7·7 to 8·3 | 50 to 60 | Wagner, *Bayerisches Industrie und Gewerbeblatt*, 1876, **8**, 186. |
| 6 | 80 | Mallard and Le Chatelier, *Ann. Mines*, 1883, [8], **4**, 347. |
| 7 | 75 | Broockmann, *J. Gasbeleuchtung*, 1889, **32**, 189. |
| 9·2 to 9·5 | 64·7 to 65·0 | Roszkowski, *ibid.*, 1890, **33**, 491, 524, 535, 553; *Zeitsch. physikal. Chem.*, 1891, **7**, 485. |
| 5 | 72 | Clowes, *Detection of Inflammable Gas and Air*, 1896. |
| 10 | .. | Le Chatelier and Boudouard, *Compt. rend.*, 1898, **126**, 1510. |
| 6·3 | 80 | Bunte, *Ber.*, 1898, **31**, 19. |
| | | Eitner, *Habilitations-schrift*, *Munchen*, 1902. |
| 8·7 | 75·5 | In sphere of one litre. |
| 8·5 | .. | Downward ignition in cylinder. |
| 4·5 | .. | Upward ignition in cylinder. |
| 9·73 to 9·96 | 62·75 to 63·58 | Teclu, *J. prakt. Chem.*, 1907, [2], **75**, 212. |
| 4·1 | .. | Coward and Brinsley, *Trans. Chem. Soc.*, 1914, **105**, 1859. |
| .. | 74·2 | Coward, Carpenter, and Payman, *ibid.*, 1919, **115**, 27. |

These divergences are due partly to the different methods adopted, as witness Eitner's results—which may be useful compared with those found by Burgess and Wheeler, under analogous conditions for methane-air mixtures[1]—and partly owing to lack of appreciation of the influence of minor factors upon the results. Of these results undoubtedly the most reliable are those of Coward and his co-workers, obtained by methods already described.

A similar want of accord is manifest in the results given for the limit-mixtures of hydrogen and oxygen.

## LIMITS OF INFLAMMABILITY OF HYDROGEN-OXYGEN MIXTURES.

| Lower Limit of Hydrogen. Per cent by Volume. | Upper Limit of Hydrogen. Per cent by Volume. | Authority. |
|---|---|---|
| 9·5 to 10 0 | . . | Humboldt and Gay Lussac, *J. Phys.*, 1805, **60**, 129. |
| 6 7 to 8 3 | 95·2 to 96·3 | Davy, *Phil. Trans.*, 1817, p. 45. |
| 4 4 to 5 1 | 95·8 to 96·7 | Turner, *Phil. J. Edin.*, 1824, **11**, 311. |
| 10·0 to 11·1 | 91·2 to 92·5 | Regnault and Reiset, *Annalen*, 1850, **73**, 129. |
| 5·7 to 6 7 | 92·4 to 93·2 | Bunsen, *Gasometrische Methoden*, 1857. |
| 13 to 14 | 91 to 92 | Wagner, *Bayerisches Industrie und Gewerbeblatt*, 1876, **8**, 186. |
| 5·8 to 6 4 | . . | Bunsen, 1877. |
| 9·4 to 9·7 | 90·8 to 91·0 | Roszkowski, *Zeitsch. physikal. Chem.*, 1891, **7**, 485. |
| 9·1 to 9·3 | . . | Eitner, *Habilitations-schrift*, *München*, 1902. |
| 5·45 | 94·7 | Fischer and Wolf, *Ber.*, 1911, **44**, 2956. |

### Carbon Monoxide.

The following results have been obtained by different investigators (see p. 100) for the lower and upper limits of inflammability of mixtures of carbon monoxide and air. The wide divergence which characterises the published data for hydrogen is not so evident, for the results agree much more closely. Undoubtedly the most reliable are those of Coward and his co-workers.

### Organic Vapours.

The limits for the propagation of flame by twelve organic vapours when mixed with air in glass tubes 5·0 cm. in diameter, determined, unless otherwise stated, at approximately 18° C., are given on p. 100.[2]

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[1] See Table, p. 93.

[2] White, *Trans. Chem. Soc*, 1922, 121, 1257.

## LIMITS OF INFLAMMABILITY OF CARBON MONOXIDE-AIR MIXTURES.

| Lower Limit of Carbon Monoxide. Per cent. by Volume. | Upper Limit of Carbon Monoxide. Per cent. by Volume. | Authority. |
|---|---|---|
| 14·3 to 16·7 | 75 to 80 | Wagner (1876), *loc. cit* |
| 14·1 to 14·3 | 74·6 to 74·8 | Roszkowski (1891), *loc. cit.* |
| 13 | 75 | Clowes (1896), *loc. cit.* |
| 15·8 to 16·0 | 72·5 to 76·5 | Le Chatelier and Boudouard, *Compt. rend.*, 1898, **126**, 1344. |
| 16·4 to 16·6 | 74·8 to 75·1 | Eitner (1902), *loc. cit.* |
| 12·5 | . . | Coward and Brinsley, *Trans. Chem. Soc.*, 1914, **105**, 1859. |
| . . | 74·2 | Coward, Carpenter, and Payman, *ibid.*, 1919, **115**, 27. |

## LIMITS OF INFLAMMABILITY OF VAPOUR-AIR MIXTURES.

(White, 1922.)

| Vapour. | Upward. | Downward. | Horizontal. |
|---|---|---|---|
| Ethyl ether | 1·84 to 48·0 | 1·90 to 6·25 | 1·88 to 33 |
| Acetone | 2·90 to 12·6 | 2·99 to 8·40 | 2·96 to 9·9 |
| Methyl ethyl ketone | 2·05 to 9·9 | 2·10 to 7·4 | 2·05 to 8·5 |
| Benzene | 1·45 to 7·45[1] | 1·48 to 5·55[1] | 1·46 to 6·65[1] |
| Toluene | 1·31 to 6·75[1] | 1·32 to 4·60[1] | 1·30 to 5·80[1] |
| Methyl alcohol | 7·10 to 36·5[1] | 7·65 to 26·5[1] | 7·35 to 30·5[1] |
| Ethyl alcohol | 3·69 to 18·0[1] | 3·78 to 11·5[1] | 3·75 to 13·8[1] |
| Ethyl acetate | 2·32 to 11·4[1] | 2·37 to 7·1[1] | 2·35 to 9·8[1] |
| Acetaldehyde | 4·21 to 57 | 4·36 to 12·8 | 4·32 to 16·0<br>and<br>25 to 45[3] |
| Ethyl nitrite | 3·51 to >50 | 3·91 to 14·4 | 3·63 to >45 |
| Pyridine | 1·81[1] to 12·4[2] | 1·88[1] to 7·2[1] | 1·84[1] to 9·8[2] |
| Carbon disulphide | 1·41 to 50·0[1] | 2·03 to 34·0 | 1·83 to 49·0[1] |

The two ranges for acetaldehyde with horizontal propagation are noteworthy, due to the possible existence of two kinds of flame, namely the normal hot flame, and a "cool" flame (see p. 76) respectively.

**Influence of Temperature.**—Rise of temperature effects an appreciable reduction in the lower limit of inflammation as is to be anticipated from theoretical considerations. This is evident from the following data, which pertain to methane in air :[1]

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[1] Determined at 60° C. [2] Determined at 70° C [3] "Cool" flame limits.

| | | | | | | |
|---|---|---|---|---|---|---|
| Initial temperature ° C. . | 20 | 175 | 237 | 312 | 555 | 690 |
| Lower methane limit . . | 5 80 | 5·25 | 4·75 | 4 30 | 3·40 | 3·00 |

Similarly, the upper limit rises with the temperature :[2]

| | | | | | | |
|---|---|---|---|---|---|---|
| Initial temperature ° C. . | 20 | 150 | 250 | 400 | 600 | 800 |
| Upper methane limit . . . . | 13·40 | 13·60 | 14·00 | 14 70 | 16 40 | 29·00 |

Thus the total influence of the temperature is to widen the limits of inflammability.

**Influence of Pressure.**—Both the lower and the upper limits of inflammation are raised by increase of pressure. Hence the total effect upon the limits of inflammability is the algebraic sum of these two. In the case of methane the data[3] are as follow :

## INFLUENCE OF PRESSURE UPON THE LIMITS OF INFLAMMATION.

(Mason and Wheeler, 1918.)

| Initial Pressure. mm. Mercury | Lower Limit. Methane, per cent. | Upper Limit. Methane, per cent. |
|---|---|---|
| 760 | 6·00 | 13·00 |
| 1250 | 6·05 | 13·15 |
| 2100 | . . | 13·35 |
| 2900 | 6·20 | 13·60 |
| 3350 | 6·25 | . . |
| 3750 | . . | 13·80 |
| 4650 | 6·40 | 14·05 |

The lowest ignition-pressure of electrolytic gas observed[4] is 5 mm.

**Influence of Oxygen.**—In a series of experiments carried out with a Bunte burette (19 mm. in diameter and 115 to 120 c.c. capacity), top ignition being adopted, Terres[5] has found that whilst the lower limit of a combustible gas in air is but slightly different from that in oxygen, the upper limit is considerably higher in pure oxygen. His results are shown on p. 102.

Parker,[6] using a glass globe with central ignition similar to that figured on p. 92, determined the lower limits of inflammation of methane with mixtures of oxygen and nitrogen, the oxygen ranging from 100 to 13·25 per cent. by volume. His results are shown diagrammatically in fig. 14.

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[1] Taffanel, *Compt. rend.*, 1913, 157, 593. See also Burrell and Robertson, U.S Bureau of Mines, Technical Paper No. 121, 1916. Taffanel's results are in close accord with the later work of Mason and Wheeler (*Trans. Chem. Soc.*, 1918, 113, 45), and of Burrell and Robertson, *J. Ind. Eng. Chem*, 1915, 7, 417.

[2] Mason and Wheeler, *loc. cit.* The data refer to downward propagation of the flame in a vertical tube.

[3] Mason and Wheeler (*loc. cit.*), who confirm and extend the earlier work of Terres and Plenz, *J. Gasbeleuchtung*, 1914, 57, 990, 1001, 1016, 1025. See also Burrell and Robertson, *loc. cit.* ; Leprince-Ringuet, *Compt. rend.*, 1914, 158, 1793, 1999.

[4] Coward, Cooper, and Warburton, *Trans. Chem. Soc.*, 1912, 101, 2278.

[5] Terres, *J. Gasbeleucht.*, 1920, 63, 785, 805, 820, 836.

[6] Parker, *Trans. Chem. Soc.*, 1914, 105, 1002.

## LIMITS OF INFLAMMATION IN AIR AND OXYGEN

(Terres, 1920.)

| Gas or Vapour. | Limits of Inflammability. | |
|---|---|---|
| | In Air (per cent.). | In Oxygen (per cent.). |
| Carbon monoxide . . | 15·6 to 70·9 | 16·7 to 93·5 |
| Hydrogen . . | 9·5 to 65·2 | 9·2 to 91·5 |
| Methane . . | 6·3 to 11·9 | 6·5 to 51·9 |
| Ethane . . . | 4·2 to 9·5 | 4·1 to 45·8 |
| Ethylene . . | 4·0 to 14·0 | 4·1 to 61·8 |
| Acetylene . . . | 3·5 to 52·3 | 3·5 to 89·4 |
| Benzene . . | 2·8 to 6·8 | 2·8 to 29·9 |
| Water gas . . | 12·4 to 66·1 | 12·6 to 92·0 |
| Coal gas . . . | 9·8 to 24·8 | 10·0 to 73·6 |
| Light petroleum vapour . | 2·1 to 5·0 | 2·1 to 28·4 |

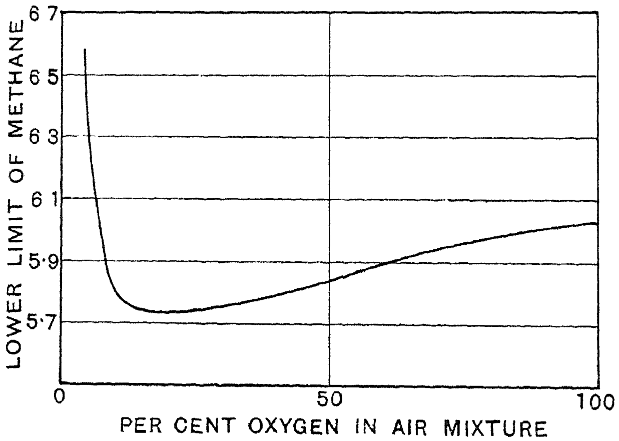

Fig. 14.—Lower limits of methane (Parker, 1914).

"The lower limit of methane reaches a minimum of 5·76 in a mixture containing 25 per cent. of oxygen and 75 per cent. of nitrogen. Increase in the oxygen content causes a gradual rise in the lower limit, whilst decrease effects a rapid rise. This latter rise may be explained by the decreased rate of combustion and the consequent greater loss of heat to the surroundings." [1] For air the lower limit is found as 5·77 per cent. methane.

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[1] Parker, *loc. cit.*, p. 1009.

The fact that the lower limit of methane is greater in the case of pure oxygen than with air is probably connected with the fact that the specific heat of oxygen is higher than that of air.

**Residual and Extinctive Atmospheres.**—Closely connected with the foregoing study is that of the composition of the residual atmosphere in which a substance has been burning, and of one which just extinguishes a flame—the so-called extinctive atmosphere. Their composition is not determined solely by the percentage of oxygen ; the nature of the inert or diluent gases also exerts an important influence. Thus, for example, nitrogen has a less powerful extinctive effect than carbon dioxide.[1] Theoretically extinctive and residual atmospheres are the same, but. owing to the difficulty caused by the products of combustion raising the temperature of the contents of the containing vessel, the flame is apt to continue burning for a longer time than if the surrounding air remained at the original temperature. The percentage of oxygen in the residual air is thus slightly lower than that in an extinctive atmosphere. Under theoretically ideal conditions the results would be the same for both residual and extinctive atmospheres under identical conditions. The following results are interesting :

| Combustible | Residual Atmospheres (Volume per cent.). |
|---|---|
| Candle flame [2] . . . | 15–16 oxygen.<br>80–81 nitrogen.<br>3 $CO_2$. |
| Do. [3] . . . | 13–15 oxygen.<br>4–6 ,,<br>4–6 $CO_2$ |
| Alcohol, burning on cotton wool [3] | 11 oxygen.<br>82·5 nitrogen.<br>6·5 $CO_2$. |
| Wood charcoal glowing to extinction [3] . . . . | 9 oxygen.<br>83 nitrogen.<br>8 $CO_2$. |
| Sulphur burning [3] . . . | 13·5 oxygen. |
| Glowing wood [4] . . . | 16 oxygen. |

It will be observed that the residual atmosphere for a candle closely resembles that exhaled by human beings (see p. 185). It may be inhaled by most people for a considerable time without producing any noticeable ill effects.

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[1] Dollwig, Kolls, and Loevenhart, *J. Biol. Chem.*, 1915, 20, xxxii. Compare Jorissen, *Rec. trav. chim.*, 1920, 39, 715.

[2] Clowes, *Proc. Roy. Soc.*, 1894, 56, 2 ; 1895, 57, 353.

[3] Müller, *Chem. Zentr.*, 1917, i, 991.

[4] Jorissen, *Chem. Weekblad*, 1913, 10, 1057

It is interesting to note that decrease of pressure raises the oxygen limit of the residual atmosphere as shown in the following table : [1]

## RESIDUAL ATMOSPHERES.

| Combustible. | Total Pressure, mm | Oxygen per cent. by Volume in Residual Atmosphere. |
|---|---|---|
| Candle . . . . | 736·7<br>91 | 16·1<br>19·9 |
| Ethyl alcohol burning from asbestos wick . . | 736·7<br>129 | 15·1<br>19·0 |

The oxygen in residual atmospheres from jets of various combustible gases has been determined by Rhead [2] as follows :

| Combustible. | Oxygen per cent. |
|---|---|
| Methane . . . . . | 15·6 |
| Propane . . . . . | 15·9 |
| Butane . . . . . | 16·0 |
| Pentane . . . . . | 16·4 |
| Cyanogen . . . . . | 15·3 |
| Hydrogen . . . . . | 5·7 |
| Carbon monoxide . . . | 10·2 |

The slight increase in oxygen noticeable on ascending the methane series of hydrocarbons is probably due to the highly extinctive effect of the increasing proportion of carbon dioxide, to which reference has already been made. The low oxygen content in the case of hydrogen is noteworthy.

In the case of burning gases, the composition of the extinctive atmosphere is affected by several factors, notably the speed at which either the combustible gas or the atmosphere surrounding it is allowed to move. Rhead found that for a constant speed of combustible gas issuing from a jet, and fed at constant speed by air passing into an encircling container, the extinctive atmospheres of the four lower hydrocarbon gases were identical, and contained approximately 16·6 per cent. of oxygen. This suggests a similar primary reaction in each case. With increased speed the oxygen content falls to a minimum. This is probably due to the fact that with a slow speed of atmosphere the oxygen is consumed too quickly, but upon increasing the speed the combustible mixture is formed sufficiently rapidly to maintain flame. The limiting speed will be reached when the rate of inflammation of the mixture is balanced by the upward movement. This is a point of considerable practical import, inasmuch as an atmosphere, too poor in oxygen to maintain a flame under ordinary conditions or when fed to it at a slow speed, may be able to maintain that flame at a higher speed.

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[1] Dollwig, Kolls, and Loevenhart, *J. Amer. Chem. Soc.*, 1917, 39, 2224; *J. Biol. Chem.*, 1915, 20, xxxii.–xxxiii.

[2] Rhead, *J. Soc. Chem. Ind.*, 1918, 37, 274 T.

Coal gas, on the other hand, was found to behave quite differently. The oxygen content of the extinctive atmosphere was almost independent of the speed of the atmosphere itself, but fell with increasing speed of the gas stream. This is undoubtedly due to the fact that coal gas is a mixture consisting mainly of hydrogen and methane, the extinctive atmospheres of which possess widely different oxygen contents. Hence, upon occasion, the atmosphere might contain sufficient oxygen to support a hydrogen flame, but not one of methane. With slow gas streams the hydrogen would be burned too quickly. By increasing the speed of the gas and hence of the hydrogen, the combustible mixture of oxygen and hydrogen is produced with sufficient rapidity to maintain a flame. The data in the following will serve to illustrate the foregoing conclusions :

## EXTINCTIVE ATMOSPHERES.

(Rhead, 1918.)

| Combustible. | Diameter of Jet, mm. | Speed of Gas. cm./min. | Speed of Atmosphere. cm./min. | Oxygen in Extinctive Atmosphere. Per cent. |
|---|---|---|---|---|
| Methane . . | 4 | 288 | 684 | 16·6 |
| Propane . . | 4 | 288 | 715 | 16·6 |
| Propane . . | 4 | 288 | 715 | 16·6 |
| ,, . . | 4 | 288 | 937 | 15·0 |
| Coal gas . . | 3 | 514 | 500 | 13·2 |
| ,, . . | 3 | 514 | 291 | 13·1 |
| ,, . . | 3 | 514 | 253 | 13·5 |
| Coal gas . . | 3 | 514 | 500 | 13·2 |
| ,, . . | 3 | 1028 | 500 | 12·3 |

Closely allied to this is the very important problem of the inflammability of hydrogen gas as used for the inflation of balloons and airships. The only non-inflammable gas that could be used economically for the purpose is helium, but, as this gas is twice as dense as hydrogen, its lifting power is somewhat reduced. It follows, therefore, that if a mixture of the two gases could be found which is non-inflammable, the result would be more efficient quite apart from financial aspects of the subject. It appears that, under favourable conditions, a jet of helium containing more than 14 per cent. of hydrogen can be ignited in air ; but in the case of a gas issuing from an orifice under conditions prevailing in balloon practice, a mixture containing even 18 to 20 per cent. of hydrogen will not burn with a persistent flame, and might, therefore be employed for military purposes with safety. Mixtures containing upwards of 20 per cent. of hydrogen would be dangerous.[1]

## IGNITION TEMPERATURES.

The temperature at which rapid combustion becomes independent of external supplies of heat is termed the **ignition temperature.** Wheeler [2] defines it as "the lowest temperature to which a mixture of a combustible gas with air or oxygen must be raised in order that the chemical action between the gas and the oxygen can become so rapid as to produce flame." A clear conception of this phenomenon [3] may be obtained by supposing a combustible mixture of gases, such as that of air and the vapour of carbon disulphide, to issue through an orifice into an indifferent atmosphere. If the orifice is surrounded by a ring of platinum wire, which is gradually heated up by a current of electricity, a flame will gradually make its appearance. If, as soon as this is observed, the heating of the wire by the current be discontinued, the flame will disappear; it is, in fact, not self-supporting, but depends on the accessory supply of heat through the electrically heated wire. If now the ring is raised to a higher temperature a brighter flame results, owing to an increased rate of chemical action, and at last we shall reach a point where it is possible to cut off the electric current without causing at the same time the extinction of the flame. This is the true temperature of ignition, the temperature at which the reaction proceeds at a rate just sufficient to overbalance the loss of heat by radiation, conduction, and convection from the burning layer of gases, so that the next layer is put in the same state, and steady combustion proceeds.

The minimum temperature at which the reaction in a combustible mixture of gases becomes self-supporting is termed[4] the *sub-ignition* temperature. This may not correspond to ordinary ignition. In many cases an ordinary flame, causing more or less complete and rapid combustion, cannot be obtained by heating a gas to its sub-ignition temperature, and in those cases in which such a flame appears it is only produced through the intermediary of a cool flame (p. 76).

In the case of a few substances the ignition temperature lies at or below that of the atmosphere. Liquid phosphoretted hydrogen, $P_2H_4$, and certain metallic alkyl derivatives are cases in point. These are spontaneously inflammable (see p. 50). Pure gaseous hydrogen phosphide, $PH_3$, may be ignited by a tube of boiling water, and carbon bisulphide vapour by a gently heated glass rod, the ignition temperature in this latter case being about 120° C. An interesting case of ignition is afforded by ordinary ethyl ether.[5] Its vapour ignites when mixed with air and allowed to rush into a partly exhausted tube. The conversion of the translational energy of the mixture into heat as the gases enter the tube effecting a rise in temperature sufficient to attain to the ignition point.

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[1] Ledig, *J. Ind. Eng. Chem.*, 1920, 12, 1098 Different results were obtained by Satterly and Burton (*Trans. Roy Soc Canada*, 1919, 13, [3], 211), who found that, in their particular experiments, the percentage of hydrogen might be raised to 26 before the mixture became inflammable. With more than 28 per cent of hydrogen the mixture burned.

[2] Wheeler, *Trans. Inst Mining Eng.*, 1922, 63, 14.

[3] Borrowing Smithells' illustration, *B A. Reports*, 1907, 77, 469.

[4] White and Price, *Trans. Chem. Soc.*, 1919, 115, 1462.

[5] M'Clelland and Gill, *Sci. Proc. Roy. Dublin Soc.*, 1920, 16, 109.

In 1816 Davy[1] gave the results of the first systematic attempts to determine the ignition temperatures of the more common combustible gases. He found as follows:

| | Ignition Temperature. |
|---|---|
| Hydrogen | "Lowest visible heat of iron" (*i.e* approx 500° C.). |
| Ethylene<br>Carbon monoxide | Red heat (*i e.* approx. 700° C ). |
| Firedamp (methane) | Iron in brilliant combustion. |

The importance of the subject, particularly in connection with hydrocarbons, will be evident when its bearing upon explosions in coal mines is remembered.[2] Of modern methods of determining ignition temperatures, the following deserve consideration:

I. A stream of the combustible gases mixed with air is passed through a tube, the temperature of which is raised until the gases inflame.[3]

In the experiments of Meyer and Münch the mixture of combustible gases and air (or oxygen) was passed through a capillary tube to the base of a small glass vessel, in which the ignition was destined to take place, and which was inserted in the bulb of an air thermometer. When the mixture inflamed, the temperature of the gases was calculated from the volume of the gas in the air thermometer.

This method is simple and possesses the advantage of yielding results at atmospheric pressures. But the results are liable to be influenced by the catalytic activity of the walls of the tube. Some of the results obtained in this manner are given in the table on p. 108.

It is important to remember that these results refer to the ignition temperatures of the gases when in motion. These are not quite the same as when the gases are at rest. Thus, it has been observed[4] that the ignition temperature of detonating gas at 150 mm. pressure falls as the velocity rises to a maximum, after which further increase in the velocity has but little influence. This is well shown by the following data:

| | | | | | |
|---|---|---|---|---|---|
| Velocity[5] | 37 | 93 | 130 | 187 | 280 |
| Ignition temperature, ° C. | 601 | 594 | 593 | 592 | 592 |

The ignition temperature rises with the pressure (*vide infra*). The diameter of the tube is without influence between the range 3·6 to 11 mm. With tubes of diameter less than 0·5 mm. no definite ignition temperature has been observed.[4]

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[1] Davy, *Phil. Trans.*, 1816, 106, 7.

[2] A useful summary on the ignition of firedamp is given by Wheeler, *Trans. Inst. Mining Eng.*, 1922, 43, 14. For researches on the inflammation temperatures of mixtures of organic vapours—alcohol, acetone, ether—in air or oxygen, see White and Price, *Trans. Chem. Soc.*, 1919, 115, 1462; Alilaire, *Compt rend.*, 1919, 168, 729; Moore, *J. Soc. Chem. Ind.*, 1917, 36, 109; Holm, *Zeitsch. angew. Chem*, 1913, 26, [1], 273.

[3] Mallard and Le Chatelier, *Compt. rend.*, 1880, 91, 825; Meyer and Freyer, *Ber.*, 1892, 25, 622; *Zeitsch. physikal. Chem.*, 1893, 11, 28: Meyer and Münch, *Ber.*, 1893, 26, 2421; Gautier and Hélier, *Compt. rend.*, 1896, 122, 566; Hélier, *Ann. Chim. Phys.*, 1897 [7], 10, 521; Bodenstein, *Zeitsch. physikal. Chem.*, 1899, 29, 665.

[4] A. Mitscherlich, *Zeitsch. anorg. Chem.*, 1921, 121, 53; 1916, 98, 145.

[5] The velocity is expressed as the number of c.c. passing a cross-section of 1 sq. cm. per minute.

## IGNITION TEMPERATURES AS OBTAINED BY METHOD I.

| Gaseous Mixture. | Ignition Temperature. ° C | Authority. |
|---|---|---|
| Hydrogen-oxygen | 650–730 | Meyer and Freyer, *Ber.*, 1892, **25**, 662. |
| | 620–680 | Meyer and Munch, *Ber.*, 1893, **26**, 2421. |
| | 550 | Mallard and Le Chatelier, *Compt. rend.*, 1880, **91**, 825. |
| | 653–710 | Bodenstein, *Zeitsch. physikal. Chem.*, 1899, **29**, 665. |
| | 674 | Mitscherlich, *Ber.*, 1893, **26**, 163. |
| | 840 | Gautier and Hélier, *Compt. rend.*, 1896, **122**, 566. |
| | 845 | Hélier, *Ann. Chim. Phys.*, 1897, **10**, 521. |
| Methane-oxygen . | 650–730 | Meyer and Freyer, *Zeitsch. physikal. Chem.*, 1893, **11**, 28. |
| Ethane-oxygen . | 606–650 | ,, ,, ,, ,, |
| | 605–622 | Meyer and Münch. |
| Propane-oxygen . | 545–548 | ,, ,, |
| Ethylene-oxygen | 577–590 | ,, ,, |
| | 606–650 | Meyer and Freyer (1893). |
| Acetylene-oxygen | 509–515 | Meyer and Münch. |
| Propylene-oxygen | 497–511 | ,, ,, |
| Isobutane-oxygen | 545–550 | ,, ,, |
| Isobutylene-oxygen | 537–548 | ,, ,, |
| Coal gas-oxygen . | 647–649 | ,, ,, |
| Carbon monoxide-oxygen . . | 650–730 | Meyer and Freyer (1893). |
| Hydrogen sulphide-oxygen . . | 315–320 | ,, ,, ,, |

II. A method devised by Dixon in 1903 and employed by Dixon and Coward [1] possesses many advantages over the preceding. The essential features are shown in fig. 15. Air (or oxygen) passed slowly through B and up the porcelain tube, the temperature of which was gradually raised by means of an electric current traversing a spiral of platinum wire wound round the outside of the tube. The combustible gas entering at A ascended the narrow tube and issued at the orifice C just above the thermo-junction T. The temperature was noted at which the escaping combustible gas yielded a visible flame at C.[2] The flowing current not only ensured a constant supply of fresh hot gas, but also the removal of the products of slow combustion. It was found that constant results could be obtained provided the rate of flow of the combustible gas through the orifice C and the diameter of the outer tube D exceeded certain minimum values. Thus, for example, in the case of hydrogen and oxygen, with an outer tube 45 mm. in diameter and an orifice of 1 mm. diameter, a constant ignition temperature was obtained provided the volume of hydrogen escaping through C exceeded 9 c.c. per minute. With a wider tube a more rapid flow of hydrogen was essential. Catalytic action of the walls of the tubes is clearly reduced to a minimum. It will be observed that the temperature of ignition yielded in this apparatus is not quite the same as that obtained by Method I. It is that to which the gases must be heated separately in order to inflame immediately upon contact.

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[1] Dixon and Coward, *Trans. Chem. Soc.*, 1909, 95, 514.

[2] The temperature was allowed to rise at the rate of 5° C. per minute.

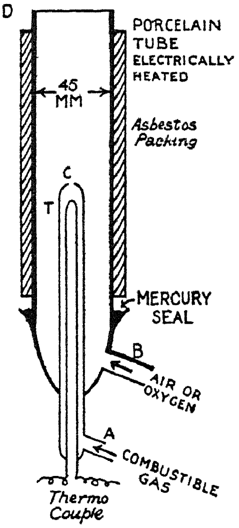

FIG. 15.—Dixon's apparatus (1903).

Experiments carried out with hydrogen and oxygen at pressures ranging from 428 mm. to 1460 mm. yielded interesting results, some of which were as follow :

## IGNITION TEMPERATURES OF HYDROGEN AND OXYGEN AT VARIOUS PRESSURES.

(Dixon and Coward, 1909.)

| Pressure, mm. | Ignition Temperature, ° C. | Remarks. |
|---|---|---|
| 427 | 597 | Mean of three. |
| 548 | 598 | Mean of two. |
| 760 | 592 | Mean of four. |
| 880 | 586 | . . |
| 960 | 580 | . . |
| 1030 | 577 | . . |
| 1133 | 570 | Mean of three. |
| 1456 | 564 | ,, ,, |

The ignition temperature is seen to rise but slowly as the pressure falls to almost half an atmosphere ; but increase of pressure above one atmosphere effects a considerable depression of the ignition temperature. The rate of depression, whilst well marked up to one and a half atmospheres is much slower afterwards, and at high pressures the ignition temperature would probably become fairly constant at about 550° to 560° C.

The main results obtained at atmospheric pressure were as follow :

## IGNITION TEMPERATURES.

(Dixon and Coward, 1909.)

| Combustible Mixture. | Ignition Temperature, ° C. | Combustible Mixture. | Ignition Temperature, ° C |
|---|---|---|---|
| Hydrogen-oxygen | 582–594 | Carbon monoxide-oxygen (dried over sulphuric acid) | 689–695 |
| Hydrogen-air | 582–594 | Carbon monoxide-air (moist) | 644–658 |
| Methane-oxygen | 550–700 | Cyanogen-oxygen | 803–818 |
| Methane-air | 650–750 | Cyanogen-air | 850–862 |
| Ethane-oxygen | 560–630 | Hydrogen sulphide-oxygen | 220–235 |
| Ethane-air | 560–630 | Hydrogen sulphide-air | 346–379 |
| Propane-oxygen | 490–570 | Ammonia-oxygen | 700–860 |
| Ethylene-oxygen | 500–519 | | |
| Ethylene-air | 542–547 | | |
| Acetylene-oxygen | 416–440 | | |
| Acetylene-air | 406–440 | | |
| Carbon monoxide-oxygen (moist) | 637–660 | | |

It is interesting to note that the ignition temperature of hydrogen in oxygen was found the same as for hydrogen in air. The same is true generally for carbon monoxide and ethane; but not for methane or ethylene. Cyanogen and hydrogen sulphide ignite at temperatures in oxygen considerably lower than in air. In the latter case, indeed, there is a difference of 140° C.

III. Adiabatic Compression.—It is a matter of common knowledge that when a gas is rapidly compressed, a rise in temperature takes place, the relationship between the initial and final temperatures being given by the expression

$$\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

when T is the absolute temperature and $\gamma$ the ratio of the gaseous specific heats at constant pressure and volume.

It is clear that if a mixture of a combustible gas and air were employed and the compression were sufficiently great, the temperature might rise to the ignition-point and rapid combustion ensue. This was suggested many years ago by Nernst, and carried into effect by Falk[1] in 1906 and by Dixon[2] eight years later. Falk's method, which may be regarded as of a pioneering character, is open to criticism[3] and has led to untrustworthy results.

The apparatus employed by Dixon and Crofts[2] is shown in fig. 16, and consisted of a steel cylinder, 56 cm. in length, bored with a central cavity, which at the base was enlarged abruptly so that it could be closed with a steel plate, kept in place by means of a powerful screw. An annular washer of lead served to keep the joint gastight, the lead being squeezed well into place with the aid of the screw. A hole was pierced through the side wall A near the bottom of the narrow bore, and fitted with a steel plunger, so that the cavity could be closed during compression or opened in connection with a gas-holder or the outside air when filling or emptying. A cylindrical piston fitted loosely into the explosion chamber, its lower extremity being fitted with a leather washer and a bronze cap, which made a close sliding fit with the cylindrical walls.

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[1] Falk, *J. Amer. Chem. Soc*, 1906, 28, 1517; 1907, 29, 1536.

[2] Dixon and Crofts, *Trans. Chem. Soc*, 1914, 105, 2036. See also Tizard and Pye *Phil. Mag.*, 1922, 44, 79.

[3] Dixon, Bradshaw, and Campbell, *Trans. Chem. Soc.*, 1914, 105, 2027.

The descent of the cylinder was centred by the steel collar, and hard chrome steel plates, cut with a slot, could be placed on this collar to stop the piston-head at any point in its descent. The cylinder was held by an iron frame, which rested upon a large concrete bed. It was surrounded by a brass water-jacket, not shown in the figure, for regulating the temperature. The compression was effected by allowing a mass of iron, weighing 76 kilograms (2·5 cwt.), to fall from a given height, usually 1·5 metres (5 feet) on to H. Lanoline was employed as lubricant.

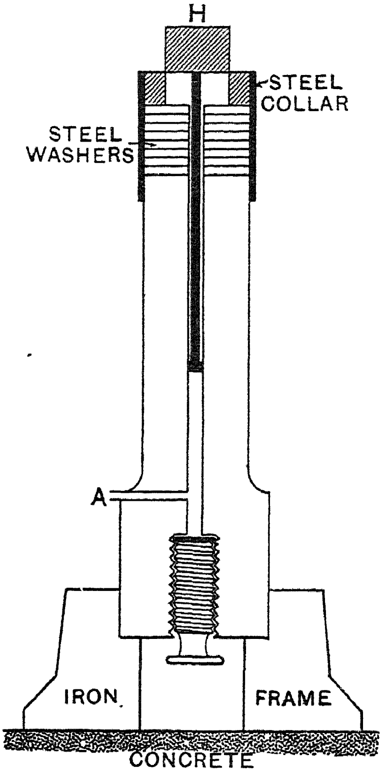

Fig. 16.—Dixon and Crofts' apparatus (1914).

The value for $\gamma$ was taken as 1·40, and the assumption made that there was no loss of heat during the compression of the gases in the cylinder. Actually that was not quite the case, but experiment showed that the compression lasted only about 0·06 second in the case of electrolytic gas, so that the loss of heat would be small. The effect would be to raise the calculated temperature of ignition. The experiments were carried out by the method of trial and error, by regulating the number of steel collars until an explosion just took place. The initial and final volumes were thus known, and these data, coupled with the initial temperature, enabled the ignition temperature to be calculated from the equation given above. The main results obtained are given in the table on p. 112.

A study was made of the influence of the initial temperature upon the ignition,[1] but variation between the normal temperature of the room and 100° C. made no appreciable difference. Increase of pressure likewise appeared without effect, although reduction to half an atmosphere raised the ignition temperature from 526° to 549° C. Addition of excess of oxygen beyond that required for complete combustion

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[1] Dixon and Crofts, *loc. cit.*

## THE IGNITION TEMPERATURES OF HYDROGEN AND OXYGEN AS DETERMINED BY ADIABATIC COMPRESSION. (Dixon and Crofts, 1914.)

| Relative Volumes of the Gases | Initial Temperature, ° C | Initial Pressure (Atm.) | Ignition Temperature, ° C |
|---|---|---|---|
| $2H_2+O_2$ | Room | 1·0 | 526 |
| | | 1·0 | 520* |
| | 100 | 1·0 | 527 |
| $2H_2+O_2$ | Room | 0·5 | 549 |
| | | 1·0 | 526 |
| | | 1·5 | 526 |
| | | 2·0 | 527 |
| $2H_2+O_2$ | Room | 1·0 | 526 |
| $2H_2+O_2+O_2$ | | | 511 |
| $2H_2+O_2+7O$ | | | 478 |
| $2H_2+O_2+15O_2$ | | | 472 |
| $2H_2+O_2+31O_2$ | | | .. |
| $2H_2+O_2$ | Room | 1·0 | 526 |
| $2H_2+O_2+H_2$ | | | 544 |
| $2H_2+O_2+2H_2$ | | | 561 |
| $2H_2+O_2+4H_2$ | | | 602 |
| $2H_2+O_2+8H_2$ | | | 676 |
| $2H_2+O_2+13H_2$† | | | 762 |
| $2H_2+O_2$ | Room | 1·0 | 526 |
| $2H_2+O_2+N_2$ | | | 537 |
| $2H_2+O_2+2N_2$ | | | 549 |
| $2H_2+O_2+4N_2$ | | | 571 |
| $2H_2+O_2+8N_2$ | | | 615 |
| $2H_2+O_2+14N_2$ | | | 712 |

## IGNITION TEMPERATURES OF MIXTURES OF ELECTROLYTIC GAS AND ARGON.[1]

(Crofts, 1915.)

| Gaseous Mixture. | Temperature, ° C. |
|---|---|
| $2H_2+O_2$ | 520 |
| $+A$ | 532 |
| $+2A$ | 545 |
| $+3A$ | 557 |
| $+4A$ | 570 |
| $+8A$ | 622 |
| $+12A$ | 674 |

---

* Crofts, *Trans. Chem. Soc.*, 1914, 105, 2036.

† It is interesting to note that this mixture will not explode with a spark under normal conditions (Roszkowski, *Zeitsch. physikal. Chem.*, 1891, 7, 485).

[1] Crofts, *Trans. Chem. Soc.*, 1915, 107, 299.

resulted in a gradual depression of the ignition temperature[1] until, when the gases were in the proportions $2H_2+32O_2$, no explosion would take place.

Addition of excess of hydrogen, on the other hand, served to raise the ignition temperature[2] steadily, with practically linear precision, so that the temperature of ignition in the presence of $x$ molecules of hydrogen, within the limits $x=0$ and 13, could be calculated from the expression

$$(2H_2+O_2+xH_2) \text{ explodes at } (526+18x)\,^{\circ}\text{C}.$$

Nitrogen behaved similarly,[2] the corresponding expression between the limits $x=0$ and 14 being

$$(2H_2+O_2+xN_2) \text{ explodes at } (526+11x)\,^{\circ}\text{C}.$$

IV. A fourth method, employed by Fiesel,[3] consists in raising the combustible gases separately to a given temperature, allowing them to mix, and noting by means of a delicate membrane or a manometer whether or not a difference in pressure occurs. Variation in pressure indicates chemical change.

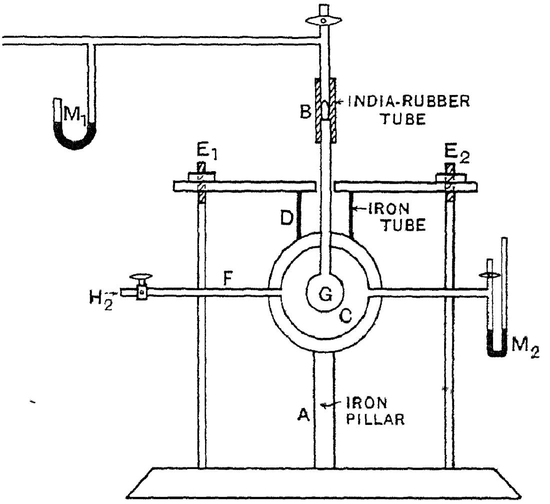

Fig 17.—Fiesel's apparatus (1921).

The apparatus consisted of an iron globe C (fig. 17), in which combustion took place. Into this was fixed a thin-walled glass bulb G, attached to a manometer M, and to the oxygen supply. A small piece of metal is hung in the rubber-pressure tubing at B, and can be released at will. C rests on an iron pillar A, and is kept in position by the iron tube D, which is pressed on to it by screwing up nuts $E_1$, $E_2$.

The apparatus was placed in an electric furnace and G filled with oxygen. The temperature was now raised, and hydrogen introduced into C. A steady temperature being attained, as registered by two thermo-couples in C (not shown in the figure), the pressure of the oxygen in G was slightly increased, and the metal piece in B allowed to fall and break G, thus causing the oxygen to pour into the hydrogen. If combustion took place, a variation in pressure occurred which was registered either by the manometer or by a delicate membrane attached thereto.

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[1] First observed by Mallard and Le Chatelier, *Compt. rend.*, 1880, 91, 825. See also Hélier, *Ann. Chim. Phys.*, 1897, 10, 521; Bodenstein, *Zeitsch. physikal. Chem.*, 1899, 29, 665; Emich, *Monatsh.*, 1900, 21, 1061; Falk, *J. Amer. Chem. Soc*, 1906, 28, 1517; 1907, 29, 1536.

[2] Dixon and Crofts, *loc. cit.*

[3] Fiesel, *Zeitsch. physikal. Chem.*, 1921, 97, 158.

The following results were obtained :

## IGNITION TEMPERATURES OF MIXTURES OF OXYGEN AND HYDROGEN.

(Fiesel, 1921.)

| Gaseous Mixture. | Dry Gases. | Moist Gases. |
|---|---|---|
| | ° C. | ° C. |
| $H_2+O_2$ . . | 407 | 407 to 417 |
| $3H_2+2O_2$ . | 397·5 | 398 to 420 |
| $2H_2+O_2$ . | 401 | 401 to 425 |
| $3H_2+O_2$ . | 412 | 436 |
| $4H_2+O_2$ . | 433 | 479 |

The minimum ignition temperature was found to occur with 3 volumes of hydrogen to 2 of oxygen, both in the dry and when moist. Further addition of hydrogen raised the ignition temperature, as was observed by Dixon and Crofts, but the results obtained by the latter investigators were very much higher (see p. 112).

With the moist gases the rate of combination suggested a bimolecular reaction, which might proceed through the formation of hydrogen peroxide. For the dry gases the reaction was found to be trimolecular, as is to be expected from the equation :

$$2H_2+O_2=2H_2O.$$

The results for acetylene were not altogether satisfactory, the ignition temperature of a mixture of acetylene and air appeared to be about 390° C.

V. Hot-wire Ignition.—Attention has already been directed to the influence exerted by hot, solid surfaces upon gaseous combustion (see p. 70). Mallard and Le Chatelier examined the effect of heated wire gauze upon the combustion of firedamp, and several later investigators have studied the problem of gaseous ignition in contact with hot wires.[1] These researches have been mainly concerned with methane and firedamp. More extensive experiments were carried out by Thornton [2] in 1919, who admitted various combustible mixtures to a small glass vessel A (fig. 18) of capacity 50 c.c. Thin wire B, soldered to thick copper leads C D, was then rapidly heated by an electric current. It was observed that there was for each diameter and metal a particular current which just caused ignition, provided the temperature rose suddenly and not gradually. The lowest current required for igniting the gases under these conditions was noted, and from this it was easy to calculate the temperature of inflammation. It was found that the phenomena of surface combustion played an important part, and temperatures of ignition were very much lower than those obtained by the methods previously described. Thus, for example, the ignition of hydrogen in air began when the temperature of the wire did not exceed 213° C., nearly 400 degrees lower than the value found by Dixon and Coward, namely, 582° to 594° C. The influence of variation of pressure between 20 and 600 cm. of mercury was negligible, and the proportion of combustible gas exerted in general but little effect upon the igniting current. Clearly, therefore, these results are more comparable with those connected with surface combustion than with the ignition data determined by the methods previously described.

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[1] See Denoël, *Ann. Min. Belg.*, 1907, 12, 1088 ; Couriot and Meunier, *Compt. rend.*, 1907, 145, 1161 ; 1898, 127, 559 ; Hauser, *Leçons sur le Grison* (Madrid, 1908).

[2] Thornton, *Phil. Mag.*, 1919, 38, 613.

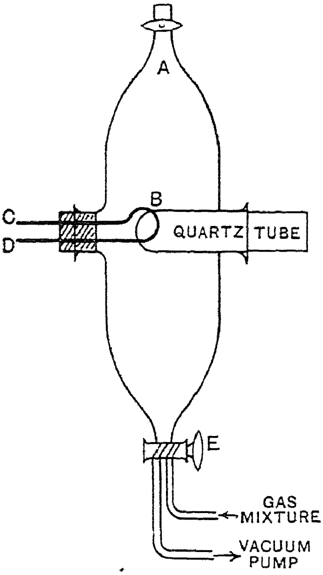

FIG. 18.—Thornton's apparatus (1919).

In 1917 McDavid[1] suggested that ignition temperatures might be determined by allowing the mixture of combustible gases and air to inflate soap bubbles and causing these to impinge upon a heated platinum wire. The short time of contact with the wire should reduce to a minimum any surface action such as that detailed above. The results obtained, however, are of uncertain value.[2]

**Flash-point.**—The temperature at which the vapour of a liquid becomes inflammable in air when ignited is usually termed its **flash-point.** For legal purposes it is often necessary to determine this temperature with accuracy, and carefully standardised apparatus is employed for the purpose. The flash-point of an oil is frequently a useful index of its purity. Thus, for example, the presence of rosin oil, flash-point 155° to 160° C., is readily detected in this manner, in linseed oil, flash-point 250° C. The following flash-points refer to common oils and spirits:[3]

| | Flash point ° C. |
|---|---|
| Linseed oil | 250 |
| Rosin oil | 155–160 |
| Paraffin illuminating oils | 38–50 |
| Turpentine | 35–40 |
| Rosin spirit | 35–40 |
| Naphtha | 16–21 |
| Methylated spirit | 14–16 |
| Ethyl alcohol, 99·6 per cent. | 11 |
| Ether | —41 |

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[1] McDavid, *Trans. Chem. Soc.*, 1917, **111**, 1003.

[2] White and Price, *ibid.*, 1919, **115**, 1248.

[3] Further data are given by Holm, *Zeitsch. angew. Chem.*, 1913, **26**, 273.

The minimum legal flash-point for illuminating oils in this country is 73° F., *i.e.* 22·8° C.

For binary mixtures of ethyl alcohol and water the following values have been obtained :[1]

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Ethyl alcohol, per cent. by weight . | 99·6 | 97 2 | 94·9 | 91·9 | 90 0 | 85·0 | 80·1 | 75·4 |
| Flash-point ° C. . . . . . | 11 | 13 | 15 | 16 | 16 5 | 17 5 | 18 5 | 20 5 |

The flash-point cannot be calculated by simple proportion from the flash-points of the constituents.[2] Increase of pressure tends to raise the flash-point.[3] Thus, in the case of a kerosene, the following data have been obtained :

| | | | | |
|---|---|---|---|---|
| Pressure in mm. . | 760 | 811 | 836 | 862 |
| Flash-point, ° C. . | 31 | 33 | 34 | 35·5 |

Flash-points determined in an oxygen atmosphere are appreciably lower than in air.

The foregoing results refer to what may be termed the *lower flash-point*, that is, the temperature of inflammation when the combustible vapour is present in sufficient quantity to reach the lower limit. There is a corresponding *upper flash-point*, which is seldom referred to and which may be determined by sparking in a more or less confined space. It represents the temperature of inflammation of the vapour at its higher limit.[4]

Several attempts have been made to connect the flash-point with certain other physical constants of the substances concerned, such as the vapour pressure and boiling-point,[5] but the most successful is that of Ormandy and Craven, who point out that, at their flash-points, different hydrocarbons exert approximately the same vapour pressure. The following relationship is found to hold to a rough approximation :

$$\underset{\text{(absolute T)}}{\text{Flash-point}} = k \times \underset{\text{(absolute T)}}{\text{boiling-point}},$$

where $k$ is a constant which varies according to the type of combustible and the nature of the flash-point, namely, whether higher or lower. In the case of the hydrocarbons a mean value of 0·736 has been obtained for the lower flash-point constant, and 0·800 for the higher. A few values are given in the table on p. 117.

The temperatures at which solids, in the compact form, will ignite in air without the application of any spark or other local high temperature, have occasionally been determined. The following are a few of the better-known results (p. 117).

## SLOW UNIFORM PROPAGATION OF FLAME.

In 1882 Mallard and Le Chatelier[6] gave the results of an investigation into the rate of propagation of flame in mixtures of air and a combustible

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[1] Ormandy and Craven, *J. Inst. Petrol. Tech*, 1922, 8, 145. See also *J Soc Chem. Ind.*, 1923, 42, 173A. [2] Sherman, Gray, and Hammerslag, *J. Ind. Eng. Chem.*, 1909, 1, 13.

[3] Ormandy and Craven, *loc. cit.*

[4] A convenient apparatus for determining both of these flash-points either below or above atmosphere temperature is described by Ormandy and Craven, *J. Inst. Petrol. Tech.*, 1922, 8, 145.

[5] See Charitschkoff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 138 ; Harker and Higgins, *Collected Researches, National Physical Laboratory*, 1912, 8, 38 ; Garner, *J. Inst. Petrol. Tech.*, 1921, 7, 26, 99.

[6] Mallard and Le Chatelier, *Bull. Soc. chim.*, 1882, [ii], 39, 369.

## UPPER AND LOWER FLASH-POINTS.

(Ormandy and Craven, 1922.)

| Substance. | Boiling-Point, ° C. | Lower Flash-point, ° C | Lower Constant, *l*. | Upper Flash-point, ° C. | Upper Constant, *k*. |
|---|---|---|---|---|---|
| Hexane . . . | 64 | −26 | 0·734 | 1 | 0·813 |
| Heptane . . | 98 | − 1 | 0·734 | 17 | 0·783 |
| Benzene . . | 80 | −12<br>(solid) | 0·739 | 10 | 0·802 |
| Toluene . . | 109 | 10 | 0·743 | 30 | 0·794 |
| Turps . . . | 150 | 38 | 0·736 | 55 | 0·775 |
| Methyl alcohol . | 64 | − 1 | 0·809 | 32 | 0·906 |
| Ethyl alcohol . | 78 | 11 | 0·810 | 32 | 0·870 |
| Acetone . . | 56 | −18 | 0·777 | 2 | 0·837 |
| Ether . . . | 34 | −41 | 0·756 | −27 | 0·802 |

| | Ignition Temperature, ° C. |
|---|---|
| Carbon—Diamond . . | 800–850 |
| Graphite . . | 690 |
| Charcoal . . | 345 |
| Sulphur—in air . . | 248,[1] 255[2] 261,[3] 363.[4] |
| in oxygen . | 257–264,[2] 282.[4] |
| Phosphorus—red . . | 255–260. |
| yellow . | *c.* 60. |

gas such as hydrogen and methane. It was observed that if the combustible mixture was ignited at the closed end of a horizontal tube, open to the air at the other end, the flame tended to travel with increasing velocity towards the open end. In a detonating mixture of hydrogen and air a speed of 300 metres per second was registered. If, on the other hand, the combustible mixture was ignited at the open end, the flame was observed to travel for a short distance at a uniform speed. This was followed by a vibratory movement, in the course of which the flame travelled backwards and forwards in an irregular manner, the mean speed from point to point along the tube being usually greater than that of the uniform movement. These vibrations usually continued to the end of the tube, but sometimes, during a particularly violent vibration, the flame might be extinguished, owing to contamination of the as yet unburnt mixture with the products of combustion.

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[1] Hill, *Pharm. J.*, 1907, 24, 358 ; *Chem. News*, 1890, 61, 125.

[2] M'Crea and Wilson, *Chem. News*, 1907, 96, 25. See *résumé* by Hill, *ibid.*, 1907, 95, 169.

[3] Blount, *ibid.*, 1890, 61, 153.

[4] Moissan, *Compt. rend.*, 1903, 137, 547.

The initial slow propagation of flame can be maintained at a uniform speed over a considerable distance of travel from the point of ignition with all combustible mixtures of gases under ordinary conditions of temperature and pressure, provided suitable precautions are taken.[1] The conditions most favourable to obtain and maintain this uniform movement are that the inflammable mixture should be contained in a long, straight, and horizontal tube open at one end and closed at the other; and that ignition should be effected at the open end of the tube by a source of heat not greatly exceeding in temperature the ignition-temperature of the mixture, and not productive of mechanical disturbance of the mixture. The speed of the uniform movement then depends on the composition of the mixture and on the diameter of the containing tube. Above a certain (small) diameter the material of which the tube is made does not appreciably affect the speed of the flame. With a tube of given diameter the speed of the uniform movement of flame in a mixture may—according to Mason and Wheeler—be regarded as a definite physical constant for that mixture.[1]

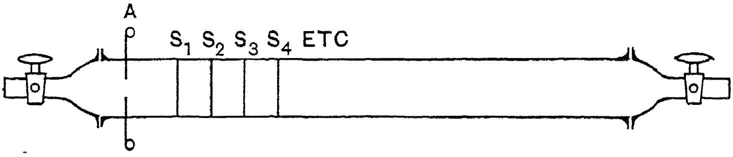

FIG. 19.—Apparatus used by Wheeler (1914).

Several methods have been adopted for the measurement of flame speeds. If the flames are sufficiently actinic to affect a photographic plate, permanent records may be obtained on revolving drums bearing the films. Mallard and Le Chatelier [2] employed this method in their researches on mixtures of carbon disulphide with nitric oxide or oxygen, the flames of which are well known to be highly actinic, whilst Mason and Wheeler [3] were able to apply the method with conspicuous success to mixtures of acetylene and air. The actual flame speed is obtained by comparison with the waves made simultaneously on the photographic drum by means of a tuning-fork of known frequency.

For the examination of flames, such as those of mixtures of methane and air, which are non-actinic, various devices have been employed. A useful one used by Wheeler consisted [4] in filling a horizontal tube with the gaseous mixture, the ends of the tube being closed, as shown in fig. 19, by flanged end-pieces, bearing taps. $S_1$, $S_2$, $S_3$ . . . were screen wires of copper, 0·025 mm. in diameter,[5] threaded vertically across the tube through fine holes pierced through the walls.

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[1] Mason and Wheeler, *Trans. Chem. Soc.*, 1917, **111**, 1044.

[2] Mallard and Le Chatelier, *Ann. Mines*, 1883, [8], 4, 312. Also Ellis, *Trans. Chem. Soc.*, 1923, **123**, 1435

[3] Mason and Wheeler, *Trans. Chem. Soc*, 1919, **115**, 578.

[4] Wheeler, *ibid*, 1914, **105**, 2606.

[5] Parker and A. V. Rhead (*ibid.*, 1914, **105**, 2150) used thin strips of Wood's alloy, melting-point 72° C. These were made by pouring the molten alloy down the channel produced by folding a piece of paper at an angle of 60° C.

In order to avoid including in the measurements of the speed of the flame any impetus that might be given by the igniting spark, the first screen-wire was fixed 40 cm. from the point of ignition. Other screen-wires were fixed 50, 100, 200, 300, and 400 cm. respectively from the first.

The method of recording the time of passage of flame along the tube was electrical. Each screen-wire carried a small electric current, the interruption of this current when the flame melted the wires being recorded by the movement of an electro-magnet.

The electric current passing through the screen-wires was sufficient to raise them nearly to red heat. This arrangement ensured the rapid melting of the wires as soon as the flame touched them, and therefore gave very uniform results; wires made from metals or alloys of low melting-point, which could not be drawn so fine or of so uniform a diameter as copper, were found to be unsatisfactory.[1]

All electrical connections through the screen-wires and chronograph having been established, the left-hand end-piece of the explosion-tube was removed (by sliding it downwards) and the mixture ignited at the now open end by passing an induction-coil spark at A.[2]

As is evident from the results shown graphically in figs. 20 and 21, the size of the tube exerts an important influence upon the flame speed. In tubes of small diameter, say less than about 5 cm., the cooling effect of the walls results in appreciable retardation of the flame speed. It will be observed that there is not much difference in speed in tubes from 5 to 10 cm. in diameter, whereas when the diameter of the tube is only 2·5 cm., the speed is reduced by about 30 per cent. Cooling by the walls thus interferes with the measurement of the true speed of the uniform movement of flame in mixtures of methane and air unless the diameter of the tube exceeds about 5 cm.

When, however, the diameter is increased above 10 cm., the speed of the flames is affected by the coming into play of another factor, namely, convection. This is noticeable with the fastest moving flames in tubes 10 cm. in diameter, the visible effect being a turbulence of the flame front. This is essentially a swirling motion in a direction nearly normal to the direction of translation of the flame front, which, as in tubes of smaller diameter, progresses at a uniform speed for about 150 cm. before backward and forward vibrations are set up. This swirling motion appears *ab initio*, and is due to rapid movement of the hot gases from below upwards by convection. In tubes of comparatively small diameter (5 to 9 cm.) this rapid movement is suppressed.

With tubes of diameter ranging from 9 cm. to 17 cm. there is an apparent retardation in the influence of the size of the tube. This was first observed by Parker [3] in 1915, but, as is evident from fig. 21, this effect is only temporary, for the maximum effect is not even reached with a diameter of 96·5 cm. But it may reasonably be objected that a pipe of so great a diameter is no longer to be regarded as a tube. On the other hand, there is a lower limit to the diameter of the tube that will allow a flame to pass through.

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[1] Mason and Wheeler, *Trans. Chem. Soc.*, 1917, 111, 1044.

[2] The influence of the nature of the spark upon ignition has been studied by Morgan and Wheeler, *ibid.*, 1921, 119, 239; Thornton, *Phil Mag.*, 1920, 40, 450; *Proc. Roy. Soc.*, 1916, [A], 92, 381; 1914, [A], 91, 17; 1914, [A], 90, 272; *Phil. Mag*, 1914, 28, 734; Wheeler, *Trans. Chem. Soc.*, 1920, 117, 903; Morgan, *ibid.*, 1919, 115, 94; Paterson and Campbell, *Proc. Physical Soc. London*, 1919, 31, 168; Sastry, *Trans. Chem. Soc.*, 1916, 109, 523; Terres and Plenz, *Chem Zentr.*, 1915, ii., 1278; *J. Gasbeleucht.*, 1914, 57, 990, 1001, 1016; Coward, Cooper, and Warburton, *Trans. Chem. Soc.*, 1912, 101, 2278.

[3] Parker, *ibid.*, 1915, 107, 328.

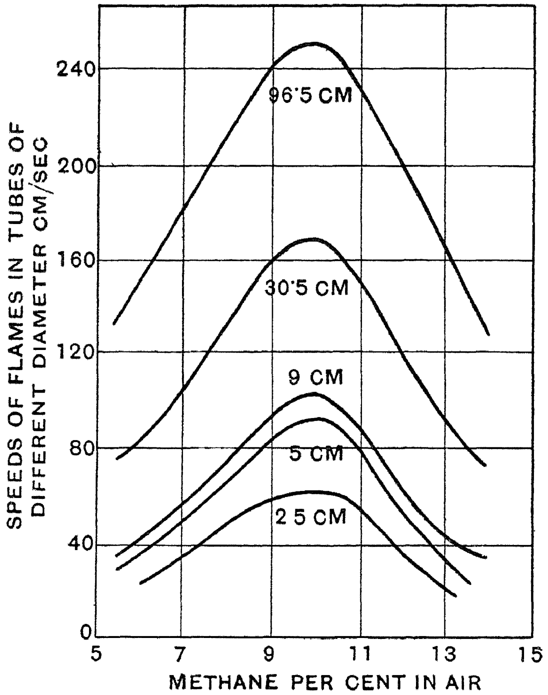

Fig. 20.—Speed of uniform movement of flame in tubes of different diameter (Mason and Wheeler, 1917.)

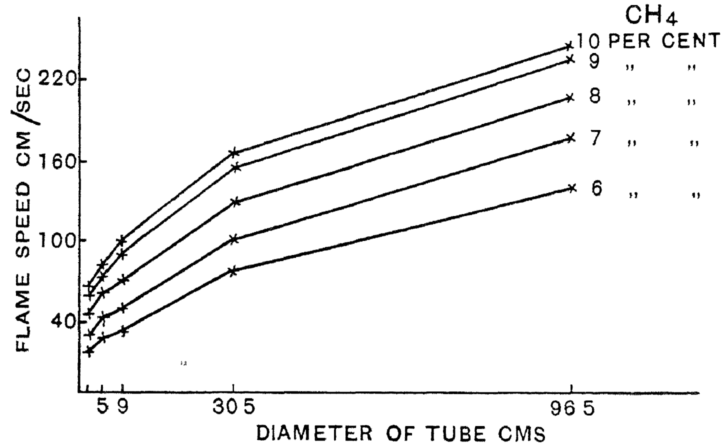

Fig. 21.—Influence of tube diameter upon the flame speed. (Mason and Wheeler, 1917.)

If the diameter of the tube is sufficiently small, the flame dies out after travelling a short distance. Still further reduction in the diameter of the tube renders it impossible for the flame to spread from the point of ignition. This was discovered by Davy,[1] and constituted the starting-point of his researches on the construction of his well-known safety lamp for use in coal mines. He found that in tubes $\frac{1}{7}$-inch in diameter (*i.e.* 3·63 mm.) explosive mixtures of firedamp and air could not be fired as no flame would pass along.[1]

Analogous results were obtained by Mallard and Le Chatelier,[2] who found the speeds of flame in a mixture of methane and air containing 10·4 per cent. of methane, using tubes of glass of different diameters, to be as follow:

| | | | | | |
|---|---|---|---|---|---|
| Diameter of tube, mm. . . | 3·2 | 5·5 | 8·0 | 9·5 | 12·2 |
| Speed of flame, cm. per sec. . | *nil* | 22 | 39 | 41 | 47 |

The methane was impure, it is true, but the result closely agrees with that found by Davy with firedamp. A more thorough investigation of the subject by Payman and Wheeler,[3] whilst yielding analogous results, has revealed several interesting features. One of the most important of these is that the apparent limits of inflammability of methane in air become narrowed as the diameter of the tube decreases, until with a diameter of 4·5 mm. only one of the seventeen mixtures tested, namely, that containing 9·95 per cent. of methane, would propagate flame. With 10·15 per cent. methane no flame would pass, whilst with 9·5 per cent. methane the flame only travelled 20 cm. and then became extinguished. With a tube of diameter 3·6 mm. no flame propagation

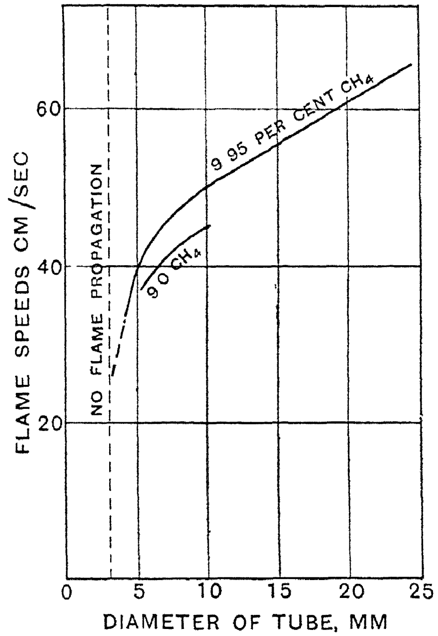

FIG. 22.—Influence of tube diameter upon the propagation of flame. (Payman and Wheeler, 1918.)

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[1] Davy, *Collected Works*, 1816, 6, 11.

[2] Mallard and Le Chatelier, *Ann. Mines*, 1883, [8], 4, 319.

[3] Payman and Wheeler, *Trans. Chem. Soc.*, 1918, 113, 656

occurred with any of the inflammable mixtures. The results obtained with 9·95 and 9·0 per cent. methane are shown in fig. 22. The nature of the tube itself is important, as Davy himself was aware. Metal tubes, on account of their greater cooling effect, are more efficient extinguishers of flame than glass. Since wire-gauze may be regarded as a series of thin, transverse sections of narrow metallic tubes joined together, the bearing of these results upon Davy's safety lamp is apparent.

Consideration of the curves shown in fig. 20 shows that the flame-speeds of mixtures of methane and air steadily rise to maximum values as the percentage of the combustible gas is raised from its lower limit of 5·6 to about 10 per cent. Further addition of methane reduces the speed until the flame is extinguished just beyond the upper limit value.

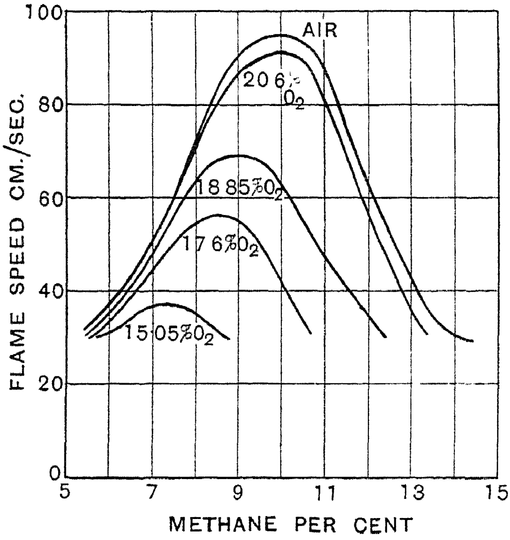

FIG. 23.—Flame speeds in methane-air mixtures diluted with nitrogen (Mason and Wheeler, 1917.)

This was to be anticipated for, beyond a certain value, excess of the combustible gas will usually function as a diluent. The shape of the curve, therefore, is typical.

Interesting results are shown in fig. 23, which gives the flame speeds of mixtures of methane and oxygen with varying proportions of the neutral diluent nitrogen.[1] Not only does the lower methane limit fall slightly with increase of oxygen, but it will be observed that there are great increases in the upper-limit values and in the flame speeds.

By decreasing the percentage of nitrogen from that present in the atmosphere to *nil*, the flame speeds show enormously enhanced values. This is clear from the data shown graphically in fig. 24.[2]

The author points out that the most striking results are those for mixtures of methane with pure oxygen. The speed is then 5500 cm.

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[1] The diameter of the tube was 5 cm.

[2] Payman, *Trans. Chem. Soc.*, 1920, 117, 54. These results are not *strictly* comparable numerically with those in fig. 23, since they were obtained in tubes 2·5 cm. in diameter, whilst Mason and Wheeler employed tubes of diameter 5 cm. The general characteristics, however, are the same.

per second—more than fifty times that attained in air. It will be further observed that the maximum speed of the flame is obtained with the mixture in which the methane and oxygen are present in combining proportions, namely, $CH_4+2O_2$. This result is in noteworthy distinction to that obtaining when the detonation-wave is developed in mixtures of methane and oxygen, for the mixture in which the speed of the detonation-wave is greatest contains equal proportions of methane and oxygen. The difference is the more striking when it is remembered that the uniform movement may give place to the detonation-wave after quite a short distance of travel of the flame.

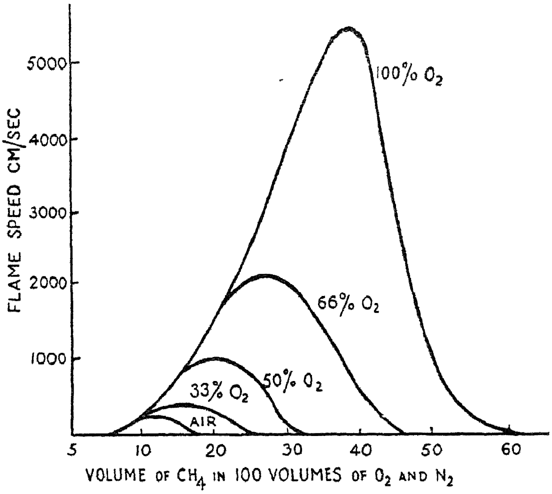

Fig. 24.—Flame speeds in methane-air mixtures enriched with oxygen. (Payman, 1920.)

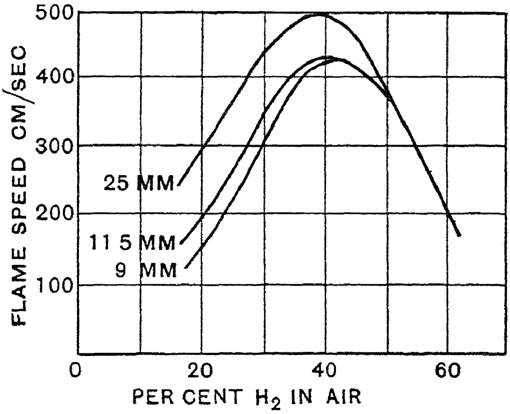

Fig. 25.—Flame speeds of hydrogen in air. (Haward and Otagawa, 1916.)

The flame-speeds of combustible mixtures of hydrogen and air are less easy to determine since the flame travels more rapidly and in some mixtures the explosion-wave may be set up after the flame has travelled but a short distance (about 2 metres) from the end of the tube.

Nevertheless a series of determinations has been published,[1] and these are shown in fig. 25. Glass tubes of three diameters were employed namely, 9, 11·5, and 25 mm. respectively. The curves show that an increase in diameter enhances the flame speed only in those mixtures in which the hydrogen is not present in considerable excess. It is interesting to note that the maximum flame speed is not attained with the mixture containing the hydrogen and oxygen in combining proportions, namely, 29·5 per cent. of hydrogen, but with a mixture containing about 40 per cent. of hydrogen. This is in peculiar contrast to the results obtained with mixtures of methane and oxygen. Le Chatelier suggested that as the thermal conductivity of hydrogen is six times that of air, it may well be that with mixtures containing more than one-third of their volume of hydrogen, the enhanced conductivity of the mixture more than compensates for its lower heating value.

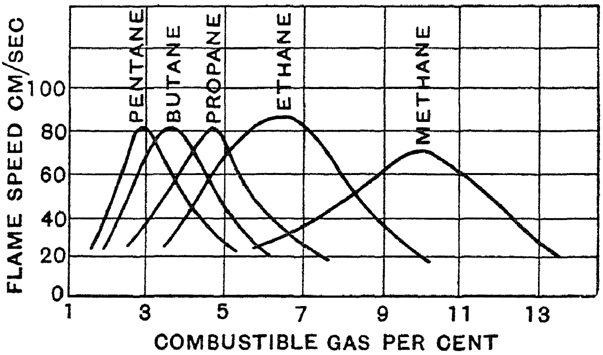

FIG. 26.—Flame speeds in combustible mixtures of paraffin hydrocarbons. (Payman, 1919.)

Measurements have also been made of the speed of the uniform movement in mixtures of air with each one of the hydrocarbons of the paraffin series up to and including pentane. The determinations were carried out with horizontal glass tubes, 2·5 cm. in diameter,[2] and the results are shown diagrammatically in fig. 26. With the exception of methane, the maximum speeds are approximately the same, namely, about 82 cm. per second. The value for methane is rather lower than this, being 67 cm. per second. Owing to the few data available for the thermal constants of the paraffin hydrocarbons, it is not easy to explain this difference. In each instance, the mixture having the maximum speed of flame contains more combustible gas than is required for complete combustion.

The higher and lower limit speeds tend to approach the same value of 20 cm. per second for all the gases. It is interesting to note that in every case, except that of methane, the maximum flame speed occurs with a mixture containing more of the combustible gas than is required for complete combustion.

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[1] Haward and Otagawa, *Trans. Chem. Soc.*, 1916, 109, 83. See also Payman, *ibid.*, 1919, 115, 1454.

[2] Payman, *ibid.*, 1919, 115, 1447.

Results obtained with carbon monoxide and air, and with mixtures of these two with other combustible gases are shown graphically in fig. 27.

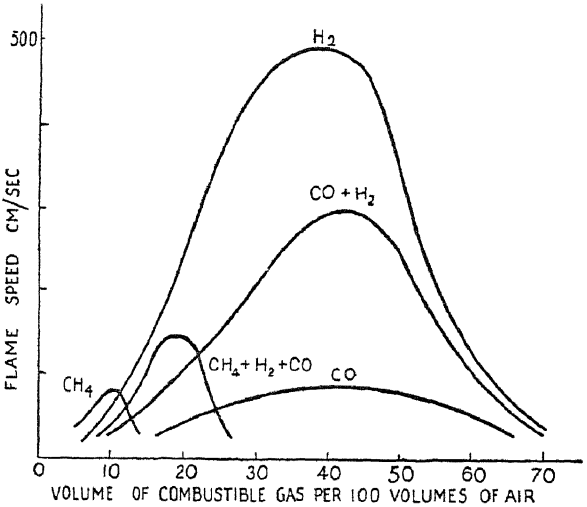

FIG. 27.—Flame speeds of carbon monoxide, hydrogen, and methane.

In the following table (p. 126) are given the maximum uniform flame speeds of various combustible mixtures, together with the flame speeds at approximately the upper and lower limits in horizontal tubes of diameter 2·5 cm.

**The Law of Speeds.**—Careful study of the rate of propagation of flame in the combustion of complex gaseous mixtures has led to the enunciation of the following law :[1]

> *Given two or more mixtures of air or oxygen with different individual combustible gases, in each of which mixtures the speed of propagation of flame is the same, all combinations of the mixtures of the same type*[2] *propagate flame at the same speeds under the same conditions of experiment.*

From this it follows that a mixture of a number of different combustible gases with air, for example, may be regarded as the algebraic sum of mixtures of each individual combustible gas with air, the proportions of the two[3] being such that the flame speed in it, if the mixture were burning alone, would be the same as in the complex mixture.

**Vertical Propagation of Flame.**[4]—In this case the effect of convection currents becomes increasingly pronounced. The tube in which the flame travels becomes a "chimney," and, with bottom ignition, the speed of the flame is enhanced by that of the draught. With top ignition the flame tends to burn at the mouth of the tube until all the combustible mixture has risen to the top.

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[1] Payman and Wheeler, *Trans. Chem. Soc.*, 1922, **121**, 363 ; Payman, *ibid.*, 1920, **117**, 48 ; 1919, **115**, 1446, 1454; Payman and Wheeler, *ibid.*, 1923, **123**, 1251.

[2] That is, all containing excess of oxygen or all containing excess of combustible gas.

[3] That is, combustible gas and air.

[4] Mason and Wheeler, *Trans. Chem. Soc.*, 1920, **117**, 1227.

| Gaseous Mixture. | Maximum Flame Speeds. | | Lower Limit Speeds. | | Upper Limit Speeds. | |
|---|---|---|---|---|---|---|
| | Combustible Gas. Per cent by Volume. | Flame Speed. cm./sec. | Combustible Gas Per cent by Volume | Flame Speed. cm./sec. | Combustible Gas Per cent. by Volume | Flame Speed. cm./sec |
| $H_2$+air . . | 36–40[1] | 500 | 6·19[2] | 10 | 71·39[2] | 50 |
| $CH_4$+air[3] . | 9·52 | 66·6 | 5·80 | 23·3 | 13·35 | 19·1 |
| $C_2H_6$+air[3] . | 6·53 | 85·6 | 3·30 | 18 1 | 10·60 | 19·7 |
| $C_3H_8$+air[3] . | 4·71 | 82·1 | 2·37 | 20·8 | 7·30 | 20·3 |
| $C_4H_{10}$+air[3] . | 3·66 | 82·6 | 1·95 | 20·1 | 6·53 | 20·3 |
| $C_5H_{12}$+air[3] . | 2·92 | 83·0 | 1·61 | 20·2 | 5·40 | 20·2 |
| $C_2H_4$+air[4] . | 8·45 | 113·7[3] | 3·55 | 25·8 | 14·00 | 22·2 |
| $C_2H_2$+air[5] . | 9·90 | 280·0 | 3·45 | 41·0 | 16·00 | 68·0 |
| $CH_4$+$H_2$+air . | 14·93 | 135·3 | 6·03 | 15·0 | 20·80 | 24·3 |
| 3$CH_4$+$H_2$+air . | 11·35 | 84·9 | 6·09 | 18·0 | 15·50 | 22·6 |
| CO+air[2] [6] . | 4·84 | 60·1 | 16·29 | 19·5 | 71·19 | 19·4 |
| $CH_4$+CO+air[2] . | 15·95 | 91·3 | 9·45 | 21·9 | 21·55 | 19·8 |
| $CH_4$+$H_2$+CO+air | 18·92 | 150·0 | 7·70 | 21·2 | 27·57 | 21·8 |
| CO+$H_2$+air[2] . | 45·92 | 315·2 | 9·25 | 18·2 | 71·34 | 44·4 |
| 3CO+$H_2$+air[2] . | 46·90 | 214·0 | 12·00 | 19·2 | 71·42 | 20·8 |
| Coal gas+air[2] . | 0·9 | 154·1 | 7·2 | 21·5 | 24·3 | 22·0 |
| Acetone+air[7] . | 5·45 | 96·1 | 2·70 | 55 0 | 8·20 | 30·7 |

## GASEOUS EXPLOSIONS.

When two or more gases interact with ever increasing velocity until a high maximum speed is attained, an **explosion**[8] is said to result. The velocity is many thousand times greater than of the slow, uniform propagation of flame dealt with in the previous section, and its accurate determination is a problem of considerable experimental difficulty.

In 1880 an explosion of coal gas occurred in Tottenham Court Road in London, and during the legal investigations subsequent thereto, the attention of scientists was directed to the fact that practically nothing was known of the rate at which an explosion-wave could travel. The following year Mallard and Le Chatelier[9] gave the results of an investigation on the subject carried out by themselves, and this was followed in

[1] Haward and Otagawa, *Trans. Chem. Soc.*, 1916, 109, 89.

[2] Payman, *ibid.*, 1919, 115, 1454.

[3] Payman, *ibid.*, p. 1436.

[4] Chapman, *ibid.*, p. 1677.

[5] Mason and Wheeler, *ibid.*, 1919, 115, 578. See also Haward and Sastry, *ibid.*, 1917, 111, 841. Numerical data are not given.

[6] Saturated with moisture at 12° C.; pressure 750 mm.

[7] Wheeler and Whitaker, *Trans. Chem. Soc.*, 1917, 111, 268.

[8] See also definition advanced by Langhaus, *Zeitsch. ges. Schiess. Sprengstoffw.*, 1918, 13, 310; *J. Chem. Soc. Abstr.*, 1919, ii., 327.

[9] Mallard and Le Chatelier, *Compt. rend.*, 1881, 93, 148.

1882 by the memoirs of Berthelot and Vieille.[1] In 1893 Dixon [2] reopened the question, and as his researches were carried out with such consummate skill and yielded results so concordant in their values, brief reference may here be made to his method of experiment. The explosion tubes consisted of leaden pipes ranging in length from 55 to 100 metres, and in diameter from 8 to 13 mm. As no appreciable difference could be detected in the velocity of the explosion-wave through the tubes when lying straight on the floor and when coiled on a drum about 2 feet in diameter, coiled tubes were used most frequently as their temperature admitted of easy control by immersion in a thermostat. It was found impossible to coil a small leaden pipe without stretching it somewhat—about 2 or 3 cm. The outside of the tube was therefore measured after each coil was wound on the drum, and the length of the axis of the pipe calculated.

Each end of the leaden tube was connected with a short, wider tube carrying a bridge of silver foil $W_1$, $W_2$ (fig. 28), and one of the tubes was fitted with a platinum spark gap S. The explosive mixture was admitted in a thoroughly dry condition—unless otherwise stated—the pressure determined, and the spark passed. The explosion-wave ruptured the silver-foil bridge $W_1$, passed through the leaden coil and, upon emerging at the other end, ruptured $W_2$. As these bridges were connected electrically with a chronometer, the time-interval between the ruptures was recorded, and from this the velocity of the explosion-wave was readily calculated.

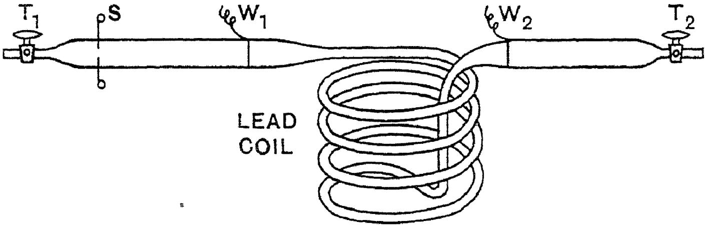

FIG. 28.—Dixon's apparatus for determining the velocity of an explosion-wave (1893).

The foregoing researches have sufficed to establish the following facts:

1. Both the composition and the diameter of the explosion tube are immaterial, provided the latter is above a certain minimum—about 5 mm.
2. The velocity of the explosion-wave after the passage of the spark increases rapidly until a high maximum is reached, after which it remains constant.

The results obtained by Berthelot and by Dixon for several typical gaseous mixtures are given in the following table. They exhibit a remarkably close agreement:

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[1] Berthelot and Vieille, *Compt. rend.*, 1882, 94, 101; 95, 151, 199; Berthelot, *ibid.*, 94, 149.

[2] Dixon, *Phil. Trans.*, 1893, 184, 97. See also the more recent paper by Dixon and Walls (*Trans Chem. Soc*, 1923, 123, 1025) on the propagation of the explosion-wave through hydrogen and carbon monoxide mixtures.

## VELOCITY OF EXPLOSION AT ROOM TEMPERATURE.

(Metres per second.)

| Gaseous Mixture. | Berthelot. | Dixon. |
|---|---|---|
| $2H_2+O_2$ . . | 2810 | 2821 |
| $H_2+N_2O$ . . | 2284 | 2305 |
| $CH_4+2O_2$ . . | 2287 | 2322 |
| $C_2H_4+3O_2$ . | 2210 | 2364 |
| $2C_2H_2+5O_2$ . | 2482 | 2391 |
| $C_2N_2+2O_2$ . | 2195 | 2321 |

3. Although Berthelot concluded that the velocity of the explosion-wave is independent of the initial pressure of the gases, Dixon found that this is approximately true only after a certain minimum pressure—about 1½ atmospheres—has been exceeded. In other cases the explosion velocity rises with the pressure. This is abundantly evident from the following data :

## INFLUENCE OF PRESSURE ON THE EXPLOSION VELOCITY.

(Dixon.)

Gaseous mixture . . $2H_2+O_2$.
Velocity . . . metres per second.

| Pressure, mm. | Velocity at 10° C. | Pressure, mm. | Velocity at 100° C. |
|---|---|---|---|
| 200 | 2627 | . . | . . |
| 300 | 2705 | 390 | 2697 |
| 500 | 2775 | 500 | 2738 |
| 760 | 2821 | 760 | 2790 |
| 1100 | 2856 | 1000 | 2828 |
| 1500 | 2872 | 1450 | 2842 |

Reduction of pressure reduces the intensity of explosion,[1] and for each gaseous mixture there appears to be a critical pressure, below which explosions will not take place. This pressure is a function of the chemical composition and proportions of the gases, the moisture content and the initial spark impulse. The completeness of combustion likewise falls with the pressure. Thus, for example, in one series of experiments with mixtures of methane and air, it was observed [2] that under a pressure of 40 mm. of mercury, 6 per cent. of the gas combined, whereas under 61 mm. 30 per cent. combined.

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[1] This receives further confirmation from the work of Parker, *Trans. Chem. Soc*, 1913, 103, 934.

[2] Stavenhagen and Schuchard, *Zeitsch angew. Chem.*, 1920, 33, 286.

4. The foregoing table also illustrates the retarding influence of rise of temperature upon the velocity of explosion, and similar effects were observed with other gases.

5. The influence of water-vapour upon the rate of explosion of oxygen and carbon monoxide was studied with interesting results. The maximum velocity was attained when the mixture was saturated at 35° C., *i.e.* it contained some 5·6 per cent. of water-vapour. Further addition of steam is seen to retard the reaction.

## INFLUENCE OF WATER-VAPOUR UPON THE VELOCITY OF EXPLOSION.

(Dixon.)

| Gaseous Mixture. | Water-Vapour. Per cent. | Velocity. Metres per Second. |
|---|---|---|
| Dried with $P_2O_5$ . . . . . | . . | 1264 |
| Moderately dry . . . . . . | . . | 1305 |
| Saturated with water-vapour at 10° C. . | 1·2 | 1676 |
| ” ” ” 20° C. . | 2·3 | 1703 |
| ” ” ” 28° C. . | 3·7 | 1713 |
| ” ” ” 35° C. . | 5·6 | 1738 |
| ” ” ” 45° C. . | 9·5 | 1693 |
| ” ” ” 55° C. . | 15·6 | 1666 |
| ” ” ” 65° C. . | 24·9 | 1526 |
| ” ” ” 75° C. . | 38·4 | 1266 |

6. Addition of an inert gas to an explosive mixture usually results in a retardation of the explosion-wave. If one of the combustible gases is in excess, it is liable to behave like an inert gas of similar volume and density. This is evident from a consideration of the data in the following table:

## INFLUENCE OF INERT GASES UPON THE VELOCITY OF EXPLOSION AT ORDINARY TEMPERATURE.

(Dixon.)

| Gaseous Mixture. | Velocity. Metres/Sec. | Gaseous Mixture. | Velocity. Metres/Sec. | Gaseous Mixture. | Velocity. Metres/Sec. | Gaseous Mixture. | Velocity. Metres/Sec. |
|---|---|---|---|---|---|---|---|
| $2H_2+O_2$ | 2821 | $2H_2+O_2$ | 2821 | $C_2H_4+2O_2$ | 2581 | $C_2H_4+2O_2$ | 2581 |
| $2H_2+O_2+O_2$ | 2328 | $2H_2+O_2+N_2$ | 2426 | $C_2H_4+2O_2+O_2$ | 2368 | $C_2H_4+2O_2+N_2$ | 2413 |
| $2H_2+O_2+3O_2$ | 1927 | $2H_2+O_2+3N_2$ | 2055 | $C_2H_4+2O_2+2O_2$ | 2247 | $C_2H_4+2O_2+2N_2$ | 2211 |
| $2H_2+O_2+5O_2$ | 1707 | $2H_2+O_2+5N_2$ | 1822 | $C_2H_4+2O_2+4O_2$ | 2118 | $C_2H_4+2O_2+4N_2$ | 2024 |
| $2H_2+O_2+7O_2$ | 1281 | $2H_2+O_2+7N_2$ | none | $C_2H_4+2O_2+6O_2$ | 1980 | $C_2H_4+2O_2+6N_2$ | 1878 |
|  |  |  |  | $C_2H_4+2O_2+8O_2$ | 1856 | $C_2H_4+2O_2+8N_2$ | 1734 |

Excess of hydrogen, on the other hand, actually accelerates the explosion velocity unless present in too great a quantity. This is evident from the following data :

### RATE OF EXPLOSION OF ELECTROLYTIC GAS WITH EXCESS OF HYDROGEN.

(Dixon.)

| Gaseous mixture . . | $2H_2+O_2$ | $2H_2+O_2+2H_2$ | $2H_2+O_2+4H_2$ | $2H_2+O_2+6H_2$ |
|---|---|---|---|---|
| Explosion velocity, metres/sec. | 2821 | 3268 | 3527 | 3532 |

A similar acceleration has been observed on addition of excess of hydrogen to mixtures of nitrous oxide and hydrogen.

7. Finally, it has been established that in the explosion-wave, the combustion of electrolytic gas is not complete. In the explosion of carbon monoxide and oxygen a residuum of unburned gas is likewise found.

**Explosion Pressures.**—The propagation of the explosion-wave in gases is accompanied by a very high pressure lasting for a very short time. The early measurements of Bunsen [1] were effected by exploding gaseous mixtures in a small cylinder fitted with a movable lid attached to a lever. The latter was weighted until the force of the explosion was unable to force the lid off. The results for hydrogen and carbon monoxide were as follow :

| | Pressure. |
|---|---|
| $2H_2+O_2$ . . . . | 9·5 atmospheres. |
| $2CO+O_2$ . . . . | 10·1 ,, |

Closely similar results were obtained by Berthelot and Vieille.

Modern methods [2] consist in exploding gaseous mixtures in metallic cylinders and automatically recording the pressures exerted against pistons working with springs. Neither the temperatures [3] nor the pressures obtained in practice are equal to those to be expected from theoretical considerations, and several explanations have been offered, namely :

(1) Dissociation of the gaseous products.

(2) Incomplete combustion.

(3) Variation in specific heats of gases under the special conditions, which render the theoretical calculations uncertain.

4. Loss of heat by radiation.[4]

Probably each of these factors is contributory to the main effect.

**Explosion Limits.**—Attention has already been directed to the influence of inert gases upon the rate of travel of the explosion-wave through a combustible mixture. In general the velocity falls until a certain dilution is reached at and beyond which no explosion takes place. This is explained by the fact that the heat generated by union of the combustible gases is largely absorbed in raising the temperature of the indifferent gas instead of being employed in propagating the explosion. As is to be anticipated, therefore, by raising the initial temperature of the gases prior to firing, the dilution with inert gas may be carried further than in the cold. In other words, the lower limit of explosion of the combustible gas is depressed.[1]

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[1] Bunsen, *Gasometrische Methoden* (Braunschweig, 1877).

[2] See Clerk, *Gas, Petrol, and Oil Engine* (Longmans, 1909), vol. i. ; Hopkinson, *Proc. Roy. Soc*, 1906, [A], 77, 387 On the pre-pressure interval see Morgan, *Trans Chem. Soc*, 1923, 123, 1304 ; *Engineering*, 1919, p. 535 ; David, *ibid*, 1922, p 791 ; Wheeler, *Trans. Chem Soc*, 1918, 113, 840 ; Bairstow and Alexander, *Proc Roy. Soc*, 1905, [A], 76, 340

[3] See Blom (*Zeitsch. ges. Schiess. Sprengstoffw.*, 1916, 11, 219 ; *J. Chem. Soc. Abstr.*, 1919, ii, 277) who gives a series of corrections and formulæ ; Muraour, *Compt. rend* 1919, 169, 723

[4] See, for example, David, *Proc. Roy. Soc.*, 1920, [A], 63, 183.

Teclu [2] gives the following explosion limits for mixtures of combustible gases and air, the method of exploding consisting in firing by an electric spark:

## EXPLOSION LIMITS IN AIR.

(Teclu, 1907.)

| Gas | Lower Limit. Per cent by Volume. | Upper Limit. Per cent. by Volume |
|---|---|---|
| Hydrogen . . . . | 9·73–9·96 | 62·75–63·58 |
| Coal-gas. . . . | 4·36–4·82 | 23·35–23·63 |
| Methane . . . . | 3·20–3·67 | 7·46–7·88 |
| Acetylene . . . . | 1·53–1·77 | 57·95–58·65 |

Closely connected with this is the problem of the completeness of combustion of gaseous mixtures when diluted with inert gases. This has been investigated by Parker[3], who finds that the effect of increase of initial temperature is much less in the case of hydrogen mixtures than with methane or carbon monoxide mixtures. The lower limit of hydrogen is much the same whether mixed with air or oxygen, but for carbon monoxide, methane, and coal-gas, the lower limits in oxygen are greater than in air, probably on account of the greater specific heat of oxygen.

**Valency.**—Oxygen is usually regarded as a divalent element, but many compounds have been prepared for which it is difficult to write suitable structural formulæ without assuming oxygen to have a valency of four. Thus, in 1888, Heyes [4] suggested that in such oxides as $BaO_2$ and $MnO_2$ one of the oxygen atoms is tetravalent, the general formula for the oxides being $M=O=O$. This enables a distinction to be made between these substances and compounds of the nature of carbon dioxide.

Friedel [5] had already shown in 1875 that methyl ether combines with hydrogen chloride to give an oxonium salt $(CH_3)_2O.HCl$, and it is difficult to avoid the assumption that oxygen is here tetravalent. Its formula may be written as

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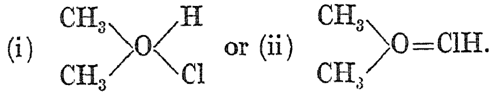
[1] Roszkowski, *Zeitsch. physikal. Chem.*, 1891, 7, 485.

[2] Teclu, *J. prakt. Chem.*, 1907, 75, 212.

[3] Parker, *Trans. Chem. Soc.*, 1913, 103, 934.

[4] Heyes, *Phil. Mag.*, 1888, 25, 221

[5] Friedel, *Bull. Soc. chim.*, 1875, [2], 24, 160, 241.

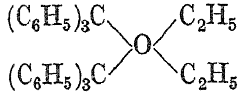


$$\text{(i)}\ \begin{matrix} CH_3 & & H \\ & \rangle O \langle & \\ CH_3 & & Cl \end{matrix} \quad \text{or (ii)}\ \begin{matrix} CH_3 & & \\ & \rangle O{=}ClH. & \\ CH_3 & & \end{matrix}$$

The second formula harmonises with the fact that whilst hydrogen chloride is a very stable substance, the oxonium salt readily dissociates, and it is not improbable that the complex (ii) is formed first, which then undergoes more or less complete rearrangement to (i), the two forms remaining in equilibrium.[1]

As shown in Chapter X., water is believed to be associated to a considerable extent to dihydrol $(H_2O)_2$ and, at low temperatures even to trihydrol molecules, $(H_2O)_3$. Assuming the strictly monovalent nature of hydrogen, a higher valency than two is required for oxygen. Thus dihydrol may be written $H_2{=}O{=}O{=}H_2$, and to trihydrol a cyclic formula may be given.

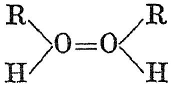
Triphenyl methyl, $(C_6H_5)_3C$, unites with ethyl ether to form [2]



$$\begin{matrix} (C_6H_5)_3C & & C_2H_5 \\ & \rangle O \langle & \\ (C_6H_5)_3C & & C_2H_5 \end{matrix}$$

in which the oxygen is clearly tetravalent. The same may be said of compounds containing water or alcohol of crystallisation.

Beckmann,[3] in 1890, directed attention to the interesting fact that substances exhibiting association in benzene solution frequently possess hydroxyl groups; and this has been confirmed by later investigators.[4] Careful study of the surface tensions of liquid phenols and various organic hydroxy derivatives has led to highly interesting results.[5] Not only are phenolic derivatives associated like fatty alcohols, but the association may undergo steric hindrance by the introduction of groups, such as $NO_2$, in the ortho position. This is explained on the assumption that association is conditioned by the hydroxyl oxygen which functions as a tetravalent atom. Thus



$$\begin{matrix} R & & & & R \\ & \rangle O & = & O \langle & \\ H & & & & H \end{matrix}$$

If, now, a polyvalent element or group is introduced into the ortho position, the tendency is for the extra valencies of the oxygen to be saturated intramolecularly, so that association with external molecules becomes less easy. Thus, in the case of ortho-chlorophenol the valencies are assumed to be distributed as follows :

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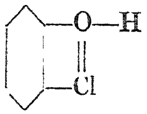
[1] Friend, *The Theory of Valency* (Longmans, 1909), p. 96 Analogous derivatives of dimethyl pyrone (Collie and Tickle, *Trans. Chem. Soc.*, 1899, 75, 710) and of acetone (Archibald and M'Intosh, *ibid*, 1904, 85, 919) have likewise been prepared.

[2] Gomberg, *Ber.*, 1900, 33, 3150; 1901, 34, 2726; 1902, 35, 2397; 1903, 36, 376, 3928; *Amer. Chem. J.*, 1901, 25, 317.

[3] Beckmann, *Zeitsch. physikal. Chem.*, 1890, 6, 437.

[4] Auwers and his co-workers, *Zeitsch. physikal. Chem.*, 1893, 12, 689; 1894, 15, 33; 1895, 18, 595; 1896, 21, 337; 1899, 30, 300; 1900, 32, 39; 1903, 42, 513; *Ber.*, 1895, 28, 2878; 1898, 31, 3037.

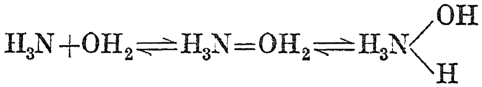
[5] Hewitt and Winmill, *Trans. Chem. Soc.*, 1907, 91, 441.



Ammonium hydroxide frequently behaves as if its atoms were arranged as follows :

$$H_3N=O=H_2.$$[1]

Probably when ammonia dissolves in water, equilibrium is set up between the several molecules as indicated below :



$$H_3N+OH_2 \rightleftharpoons H_3N=OH_2 \rightleftharpoons H_3N\begin{matrix}\diagup OH\\ \diagdown H\end{matrix}$$

In some cases of free oxidation it would appear that the whole molecule of oxygen takes part. Thus, when the alkali metals oxidise in air, peroxides are formed, from which the extra atom of oxygen may be liberated with comparative ease. This, it has been suggested,[2] is most conveniently explained on the assumption that the combination proceeds as follows :

$$O=O+2Na \rightarrow O=O=Na_2,$$

and in support of this may be cited the observations of many other investigators [3] who find that whole molecules of oxygen are absorbed in various reactions. It is difficult to account for this save on the assumption that oxygen can function as a tetravalent atom.[4] The third and fourth valencies of oxygen have been variously named as *crypto* valencies,[5] *auxiliary* valencies,[6] *neutral affinities*,[7] *electrical double valencies*,[8] and *residual* or *latent* valencies.[9]

Oxygen is not known with certainty to function as a monovalent element.[10]

**Physiological Properties.**—A supply of free oxygen is necessary, not only for the continuance of human life, but for that of all organisms with the exception of certain lower forms which, on account of their common characteristic, are termed *anærobic*.[1] With the higher animals the oxygen is absorbed by diffusion[2] through the lungs, and forms with the hæmoglobin of the blood an additive compound[3] which readily yields its oxygen for oxidising purposes in the various parts of the body, the resulting carbon dioxide being carried back to the lungs whence it passes into the atmosphere. The nature of the respiratory process as one of slow combustion was recognised by Lavoisier,[4] and it is the heat evolution caused by this oxidation of organic carbonaceous matter that maintains the temperature of the living body. An increase in the proportion of the oxygen causes a more rapid absorption of oxygen into the blood and will therefore increase the amount of oxidation occurring in the body.. Although this may serve a useful purpose in assisting the maintenance or stimulation of the vitality of persons suffering from exhaustion or great physical strain,[5] an increased pressure of the atmosphere or of oxygen, for prolonged periods, may cause harm from the excessive oxidation and stimulation induced, as well as from the liability of the blood to yield bubbles of previously dissolved oxygen when the pressure is reduced.[6] Various types of animals are affected to different extents by an increased proportion of oxygen in the atmosphere.[7]

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[1] Cain, *Mem. Manchester Phil. Soc.*, 1904, 48, xiv., 1–11.

[2] Engler and Wild, *Ber.*, 1897, 30, 1669.

[3] Erdmann and Kothner, *Annalen*, 1897, 294, 55; Bach, *Compt. rend.*, 1897, 124, 2, 951; Engler and Weissberg, *Ber.*, 1898, 31, 3046; Engler, *ibid.*, 1900, 33, 1111; Manchot, *ibid.*, 1906, 39, 1170; *Annalen*, 1902, 325, 95; Manchot and Herzog, *Ber.*, 1900, 33, 1742.

[4] Other data dealing with the tetravalent nature of oxygen are given by Knox and Richards, *Trans. Chem. Soc.*, 1919, 115, 508; Kendall, *J. Amer. Chem. Soc.*, 1917, 39, 2303; 1916, 38, 1309; 1914, 36, 1722; M‘Intosh and co-workers, *ibid.*, 1912, 34, 1273; 1911, 33, 70; 1910, 32, 542, 1330; 1908, 30, 1097; 1906, 28, 588; 1905, 27, 26, 1013; *Trans. Chem. Soc.*, 1905, 87, 784; 1904, 85, 919, 1098; Smedley, *ibid.*, 1909, 95, 231; Criticism by Redgrove, *Chem. News*, 1909, 99, 109; Thomlinson, *ibid.*, 185.

[5] Bülow and Sicherer, *Ber.*, 1901, 34, 3920.

[6] Werner, *Neuere Anschauungen auf dem Gebiete der anorganische Chemie* (Braunschweig, 1905).

[7] Spiegel, *Zeitsch. anorg. Chem.*, 1902, 29, 365.

[8] Arrhenius, *Theorien der Chemie* (Leipzig, 1906).

[9] Friend, *Trans. Chem. Soc.*, 1908, 93, 260; *The Theory of Valency* (Longmans, 1909).

[10] The evidence of Porter and Thurber (*J. Amer. Chem. Soc.*, 1921, 43, 1194) is not conclusive.

It is an interesting fact that the solubility of oxygen in blood does not follow Henry's Law, according to which the solubility of a gas is proportional to the pressure. Experiment shows that large amounts of oxygen are absorbed at low pressures by blood as compared with high pressures. The explanation usually offered is that the oxygen combines with the hæmoglobin of the blood to form the characteristically bright red oxyhæmoglobin of arterial blood which readily dissociates when the partial pressure of oxygen is reduced.[8] This, however, cannot be the whole explanation for several reasons. Thus, for example, complete absorption of oxygen is not effected even under a pressure of 10 atmospheres. Wolfgang Ostwald,[9] in 1907, directed attention to the fact that the amounts of oxygen and carbon dioxide absorbed by the blood at various pressures are expressed by the adsorption formula, namely—

$$\frac{x}{m}=kp^{\frac{1}{n}}$$

where $k$ and $n$ are constants, and $x$ is the amount of gas adsorbed by $m$ grams of blood under a pressure $p$. It appears probable, therefore, that adsorption of the gases takes place, probably on the surface of the disperse phase in the blood.

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[1] Pasteur, *Compt. rend.*, 1863, 56, 416; 1861, 52, 344.

[2] Douglas and Haldane, *Proc. Roy. Soc.*, 1911, [B], 84, 1; 1910, [B], 82, 331; *J. Physiol.*, 1912, 44, 305.

[3] Barcroft and Hill, *ibid.*, 1910, 39, 411.

[4] Lavoisier, *Mem. Acad. Sci.*, 1780, p. 355; 1789, p 185.

[5] Hill and Flack, *Proc Physiol. Soc.*, 1909, p. 33; Hill and Mackenzie, *ibid.*, p 38.

[6] The influence of variation of the relative proportions of oxygen and other gases in the atmosphere is discussed in Chap. VI.

[7] See, for example, Hill and Macleod, *Proc. Roy. Soc.*, 1902, 70, 454, 455.

[8] See Henri, *Compt. rend.*, 1904, 138, 572.

[9] Ostwald, *Kolloid Zeitsch*, 1907, 2, 264, 294. See also Brown and Hill, *Proc. Roy. Soc.*, 1923, [B], 94, 297; Hartridge and Roughton, *ibid.*, p 336; Adam, *ibid.*, p 496; Bayliss, *Nature*, 1923, 111, 666.

It is interesting to note that the amount of oxygen thus taken up by the blood is very much greater than that absorbed by pure water. This is evident from the following data :

| Solvent. | c.c. Oxygen measured at N T.P. absorbed by 100 c c. of Solvent from the Atmosphere. |
|---|---|
| Water | 0·7 |
| Dog's blood | 24 |
| Human blood | 18–19 |

The mean heat of reaction of oxygen with hæmoglobin at 22° C. is given [1] as 6950 calories, whilst that of carbon monoxide and hæmoglobin is 14,700 calories. The difference is noteworthy in view of the well-known poisoning action of the latter gas. In view of the wide discrepancies between the individual results, however, further investigation of the subject would appear desirable.

**Applications.**—It is clear that a supply of free oxygen will be of value to men working under such conditions as preclude a sufficient natural supply of this gas ; examples of such conditions are met during rescue work in mines when the air has been vitiated by fire or by an explosion. Oxygen is also administered to persons suffering from great exhaustion due to illness, suffocation, or excessive exertion.

The autogenous welding and cutting of iron and steel also calls for a supply of free oxygen, a fairly high degree of purity being desirable. Blowpipes are constructed for the production of an acetylene or hydrogen flame fed with oxygen gas, the relative supplies of oxygen and combustible gas being so regulated that the flame is mainly of a reducing character; two iron surfaces, which need not be previously cleaned, when placed edge to edge and heated at the joint, can be made to yield a weld due to the blending of the clean molten metal. In another type of blowpipe the oxy-hydrogen or oxy-acetylene flame is used for heating the metal whilst a second jet, inside or outside this flame, directs a stream of oxygen on to the heated spot at which oxidation therefore occurs rapidly ; by gradually moving the blowpipe it is thus possible to cut thick sheets expeditiously and cleanly to any desired shape.

The oxy-hydrogen or oxy-coal-gas flame is also commonly employed for the production of a high temperature and brilliant light ; thus the dazzling luminosity of a piece of lime, magnesia, or zirconia heated by the oxy-coal-gas flame renders possible the convenient *limelight* and similar methods for illuminating purposes. Blowpipe and other flames can also be fed with oxygen or with air enriched with oxygen for the fusion of such metals as those of the platinum group, and for various purposes in the glass and ceramic industries.[2]

Oxygen has been used for enriching the blast supplied to blast furnaces in pig-iron production, with consequent economy in the consumption of coke. This process yields particularly favourable results in the manufacture of ferro-silicon.[3]

In the fixation of nitrogen by the electric-arc process [4] it is found that the efficiency is greatly enhanced by increasing the oxygen content of the air prior to sparking.

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[1] Adolph and Henderson, *J. Biol. Chem.*, 1922, 50, 463.

[2] See Fletcher, *J. Soc. Chem. Ind.*, 1888, 7, 182.

[3] See this series, Vol. IX., Part III. ; also Johnson, *Met. Chem. Eng.*, 1915, 13, 483; Richards, *ibid.*, 1910, 8, 123 ; and account in *Engineering*, 1913, 96, 374.

[4] See this series, Vol. VI.

An interesting use to which liquid oxygen has been experimentally applied, and one which may have important developments, is the formation of an explosive when mixed in cartridges with finely divided combustible substances such as sulphur, charcoal, or cotton-wool. Such an explosive possesses the considerable advantage that, if it is not used within a few minutes, its dangerous properties disappear, and the risk of accident is greatly reduced. A portion of the Simplon Tunnel was experimentally bored with an explosive of this type. If the mixture of liquid oxygen and combustible material is ignited in the open, rapid but quiet combustion occurs, similar to that of a mixture of charcoal and nitre. Yellow phosphorus dipped in liquid oxygen also becomes highly explosive.[1]

**Detection and Estimation.**—Oxygen is usually recognised by its power of reigniting a glowing splinter, the only other gas possessing this power being nitrous oxide, which, however, is readily distinguished by its lack of reactivity towards nitric oxide and by leaving an equal volume of residual nitrogen when such a substance as phosphorus is burned in it. For the detection of free oxygen in a gaseous mixture quantitative analysis is usually resorted to, in which the oxygen is absorbed by some oxidisable substance, for example by moist phosphorus,[2] heated copper, or by sodium hyposulphite, or pyrogallol dissolved in a solution of an alkali hydroxide (preferably potassium hydroxide [3]), care being taken in the case of the alkaline absorbents that carbon dioxide has been previously removed. A sensitive reagent for the detection of traces of oxygen in a gas is supplied by an alkaline solution of ferrous sulphate and catechol, a red coloration indicating the presence of free oxygen.[4] When present in small quantities only this reaction may be used for estimating the gas calorimetrically. It is frequently necessary to determine the volumes of dissolved oxygen in water and other liquids. For accounts of these methods the reader is referred to pp. 35–36.

Oxygen in organic compounds is almost invariably estimated "by difference," because, although this procedure has the disadvantage of throwing on to the oxygen figure the sum total of the errors in the estimation of the other constituents, the results thus obtained are generally more satisfactory than those obtained by a direct determination. Methods for the direct estimation of oxygen in organic compounds have been proposed, and in some special cases may prove of use.[5]

**Atomic Weight.**—After the enunciation of the Atomic Theory by John Dalton at the beginning of last century, the atomic weight of hydrogen was taken as unity—hydrogen being the lightest element known—and all other atomic weights were expressed relatively thereto. A serious difficulty arose, however, in that the atomic weight of the majority of elements cannot be determined directly with reference to hydrogen. Since most of the elements combine with oxygen, it was evident that if their atomic weights were expressed relatively to this element, any revision of the ratio

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[1] Piutti, *Atti R. Accad. Lincei*, 1915, v., 24, ii., 252.

[2] See Watson, *J. Chem. Soc. Trans.*, 1911, 99, 1460.

[3] Henrich, *Ber.*, 1915, 48, 2006; Henrich and Kuhn, *Zeitsch. angew. Chem*, 1916, 29, 149. See also Shipley, *J. Amer. Chem. Soc.*, 1916, 38, 1687.

[4] Binder and Weinland, *Ber*, 1913, 46, 255.

[5] See, for example, Boswell, *J. Amer. Chem. Soc*, 1913, 35, 284.

hydrogen : oxygen

would not necessitate recalculation of a large part of the atomic weight table. Accordingly, Wollaston chose oxygen as his standard with an atomic weight of 10. Berzelius suggested O=100, as this higher figure avoided the necessity of attributing to hydrogen a value less than unity. During succeeding years various standards were proposed until, in 1858 to 1860, Cannizzaro suggested the adoption of the round figure O=16·00. The International Atomic Weight Committee, appointed in 1889, mainly on the initiative of Brauner, took as standard H=1, but in 1905 adopted

**O=16·000,**

and expressed all other atomic weights relatively thereto.[1]

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[1] For a full account of the determinations of the ratio hydrogen : oxygen, see this series, Vol. II.

# CHAPTER V.

## OZONE.

Formula, $O_3$. Molecular weight, 48.

**Occurrence and History.**[1]—In 1785 van Marum drew attention to the fact that the air in the neighbourhood of an electrical machine in action possesses a characteristic odour; and it is stated that this "electrified air" was shortly afterwards used by Cavallo[2] as a remedy for fœtid ulcers, its power of removing unpleasant odours being thus early recognised. In 1801 Cruickshank observed that a similar odour was evolved during the electrolysis of water, and J. Davy, in 1826, recognised the presence of "electrified air" in the atmosphere during storms and electrical disturbances. Fourteen years later Schönbein[3] concluded that the odour indicated the presence of a new gas, to which he gave the name of *ozone*, from Greek ὄζω, I smell.

It was at first believed that ozone was a compound of hydrogen and oxygen, but the observation of Marignac[4] that the gas can be prepared from pure, dry oxygen disposed of this idea, and led Marignac and de la Rive[5] to the conclusion that ozone is a peculiar form or allotrope of oxygen. In 1848 Hunt,[6] judging by analogy with the formulæ $SeO_2$ and $SO_2$ for the oxides of selenium and sulphur respectively, suggested that ozone is an oxide of oxygen, of formula $O . O_2$ or $O_3$.

In 1860 Andrews and Tait[7] demonstrated that pure, dry oxygen undergoes appreciable contraction during ozonisation, thus indicating that ozone is a kind of condensed oxygen, of higher density and greater molecular weight, and to this extent supporting the suggestion of Hunt. Odling,[8] in the following year, suggested that the simplest way of regarding the conversion of oxygen into ozone lay in assuming the change to take place according to the equation

$$3O_2=2O_3.$$

The correctness of this assumption was experimentally proved by Soret in 1866, and confirmed by Brodie in 1872 (see p. 155).

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[1] Leeds, *Chem. News*, 1880, 41, 138; 1884, 50, 215.

[2] Cavallo, see *Ozone and Antozone* by C. Fox (Churchill).

[3] Schönbein, *Pogg. Annalen*, 1840, [2], 50, 616; 1843, 59, 240; 1844, 63, 520. See also *J. Chem. Soc.*, 1869, 22, 124.

[4] Which has since been confirmed by various investigators. See Shenstone and Cundall, *Trans. Chem. Soc.*, 1887, 51, 610; Shenstone, *ibid.*, 1893, 63, 938; Baker, *ibid.*, 1894, 65, 617.

[5] Marignac and de la Rive, *Archives d' Electricité*, 1845, 5; *Compt. rend.*, 1845, 20, 1291.

[6] Hunt, see Leeds, *loc. cit.*

[7] Andrews and Tait, *Phil. Trans.*, 1860, 150, 113; *J. Chem. Soc.*, 1860, 13, 344. See also Fremy and Becquerel, *Ann. Chim. Phys.*, 1852, 35, 62; *Compt. rend.*, 1852, 34, 399.

[8] Odling, *Manual of Chemistry*, 1861, p. 94.

Ozone occurs in small quantities in the atmosphere as is evidenced by certain absorption bands in solar and stellar spectra.[1] It is also present in certain natural waters in sufficient quantity to be recognisable by the smell.[2]

**Preparation by Physical Processes.**—The preparation of ozone from oxygen is a markedly endothermic process, being accompanied by the absorption of 34 calories per gram molecule of the gas. Thus

$$3(O_2)=2(O_3)-2\times 34{,}500 \text{ calories.}$$

Hence its formation from oxygen by exposing this gas to high temperatures is to be expected. According to a calculation by Nernst[3] the percentages of ozone in equilibrium with oxygen at certain high temperatures are as follow:

| Temperature, ° C. | Ozone, per cent |
|---|---|
| 2183 | 0·1 |
| 3230 | 1 |
| 6640 | 10 |

This equilibrium is represented by the equation

$$3O_2 \rightleftharpoons 2O_3.$$

Increase of pressure will favour the formation of ozone inasmuch as the transformation is accompanied by a decrease in volume.

At high temperatures, however, the decomposition of ozone into oxygen is practically instantaneous. Indeed, oxygen containing only 1 per cent. of ozone would at 1000° C. have its ozone content reduced to 0·001 per cent. in 0·0007 seconds;[4] and even at 250° to 300° C. decomposition is very rapid.

Hence, no ozone can be expected in the cooled gas unless the cooling is effected so expeditiously that the gas almost immediately attains a low temperature at which decomposition occurs relatively slowly. Thus Troost and Hautefeuille[5] were able to detect ozone in the oxygen issuing from a strongly heated tube through which there passed a concentric silver tube cooled internally by a current of water; with this device of a "hot and cold tube" some of the ozone produced from the oxygen near the heated surface passes to the cold surface and so, becoming rapidly cooled, escapes the reverse decomposition into oxygen at intermediate temperatures. For a similar reason ozone can be detected in air or oxygen which has been rapidly removed from contact with a Nernst filament, and in liquid air under the surface of which a platinum wire has been raised to a white heat by means of an electric current.

By the electrical heating of a Nernst filament to 2000° C., whilst immersed in liquid oxygen, an ozone content of 3·9 per cent. by weight has been obtained. Closely connected with this result is the occurrence of ozone in liquid air at the surface of or under which combustible substances such as hydrogen, carbonic oxide, acetylene, charcoal, and wood have been burned.[1]

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[1] Fowler and Strutt, *Proc. Roy. Soc.*, 1917, [A], 93, 577; Hartley, *Trans. Chem. Soc.*, 1881, 39, 60, 111; Meyer, *Annalen Physik*, 1903, 12, 849. See this Vol., Chap. VI.

[2] Nasini and Porlezza, *Atti R. Accad. Lincei*, 1912, [5], 21, ii., 740, 803.

[3] See Nernst, *Zeitsch. Elektrochem.*, 1903, 9, 891.

[4] Clement, *Annalen*, 1904, 14, 334.

[5] Troost and Hautefeuille, *Compt. rend.*, 1877, 84, 946

The tendency for ozone to be formed at elevated temperatures is further illustrated by the presence of the gas in the oxyhydrogen flame.[2] It should be mentioned, however, that the observations of many of the earlier investigators[3] on the occurrence of ozone in the neighbourhood of flames are unfortunately rendered uncertain by the probable simultaneous presence of oxides of nitrogen which respond to the same test, namely, the liberation of iodine from potassium iodide, as was employed for detecting ozone (see pp. 177–179).

It is worthy of note that, whereas slow cooling of the heated gas will cause the disappearance of any ozone which may have been produced, any oxides of nitrogen will persist in the cooled gas.

Oxygen is also converted into ozone by the action of ultra-violet light,[4] of cathode rays,[5] and of radium radiation.[6]

The change, however, is only partial; indeed, it has been demonstrated experimentally that the action of ultra-violet light leads to an equilibrium, ozone being partially decomposed if present in relatively large quantity.[7] Solar radiation at an altitude of 4360 metres does not appear able to convert oxygen into ozone.[8]

Appreciable quantities of ozone are produced when liquid air or oxygen is exposed to the rays emitted by a spark discharge between zinc electrodes.[9] The most convenient method of producing ozone consists in allowing a silent[10] or glow electric discharge[11] to pass through air or preferably oxygen, a procedure first adopted by Siemens in 1857. Simply subjecting oxygen to electric sparks will not produce any quantity of ozone, as the gas is decomposed by the sparks practically as soon as it is formed. Even at −194° C. the spark discharge only yields about 1 per cent. of ozone, and this is probably attributable to the silent discharge simultaneously occurring.[12] The apparatus employed for the preparation of ozone on a small scale usually consists of two concentric tubes, coated with metal foil or some other conducting material, and connected with the terminals of an induction coil or electric machine. A slow current of oxygen is caused to traverse the space between the two tubes and thus becomes submitted to the action of the discharge. It is advisable to dry the gas before use,[1] because it is probable that the presence of water-vapour favours the formation of hydrogen peroxide at the expense of the ozone, and also, if nitrogen is present, causes the production of oxides of nitrogen.[2] Many modifications of this apparatus have been introduced; the diagram represents a small experimental apparatus in which water or dilute sulphuric acid provides the conducting surfaces.

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[1] F. Fischer and co-workers, *Ber.*, 1906, 39, 940, 2557, 3631; 1907, 40, 443, 111.

[2] Manchot, *ibid.*, 1909, 42, 3948; 1910, 43, 750.

[3] See, for example, Than, *J. prakt. Chem.*, 1870, [2], 1, 415; Cundall, *Chem. News*, 1890, 61, 119; Maquenne, *Bull. Soc. chim.*, 1905, 33, 510.

[4] Fischer and Braehmar, *Ber.*, 1905, 38, 2633; 1909, 42, 2228; Johnson and M'Intosh, *J. Amer. Chem. Soc.*, 1909, 31, 1146; van Aubel, *Compt. rend.*, 1909, 149, 983; 1910, 150, 96; Warburg, *Sitzungsber Preuss. Akad. Wiss. Berlin*, 1914, p. 872 Contrast Bordier and Nogier, *Compt. rend.*, 1908, 147, 354; Courmont, Nogier, and Rochaix, *Compt. rend.*, 1909, 149, 160.

[5] Goldstein, *Ber.*, 1903, 36, 3042.

[6] Nasini and Levi, *Atti R. Accad. Lincei*, 1908, 17, ii., 46; P. and M. Curie, *Compt. rend.*, 1899, 129, 823; Richarz and Schenk, *Sitzungsber. K Akad Wiss. Berlin*, 1904, 13, 490; Lind, *Monatsh.*, 1912, 33, 295; *Amer. Chem. J*, 1912, 47, 397; *Le Radium*, 1912, 9, 104.

[7] Regener, *Ann. Physik*, 1906, 20, 1033; von Bahr, *ibid.*, 1910, 33, 598; Weigert, *Zeitsch. physikal. Chem.*, 1912, 80, 78; Warburg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 216; 1913, 644.

[8] Bayeux, *Compt. rend.*, 1919, 169, 957.

[9] Warburg, *Ber. deut. physikal. Ges.*, 1915, 17, 194.

[10] See Shenstone and Evans, *Trans. Chem. Soc.*, 1898, 73, 246.

[11] The distribution of ozone in the direct current corona has been studied by Rideal and Kunz, *J. Physical. Chem.*, 1920, 24, 379; Anderegg, *J. Amer. Chem. Soc.*, 1917, 39, 2581.

[12] Briner and Durand, *Compt. rend.*, 1907, 145, 1272. See also Goldstein, *Ber.*, 1903, 36, 3042.

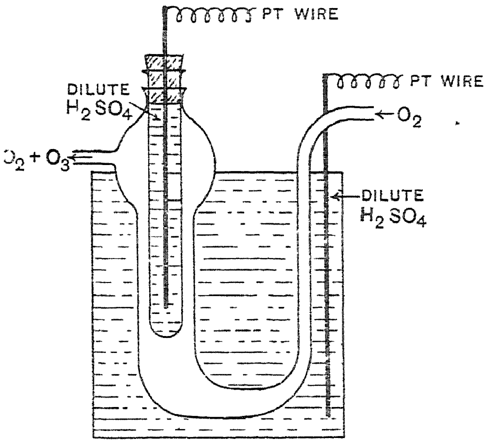

Fig. 29.—Preparation of ozone (Brodie, 1872).

By lowering the temperature it is possible greatly to increase the yield of ozone which, under ordinary conditions, is less than 10 per cent. of the oxygen. By immersing an ozonising apparatus in a cooling mixture of ether and solid carbon dioxide and so working at −78° C., a yield of 11 per cent. has been obtained.[3] whereas in liquid air it was found possible to convert 99 per cent. of the oxygen into ozone, the best results being obtained at this temperature with a pressure of 100 mm., the ozone liquefying out as it is formed.

For demonstration purposes a useful ozoniser of extreme simplicity can be made by drawing out a piece of combustion tubing, some 18 inches in length, to the shape shown in fig. 30, and fitting a rubber cork

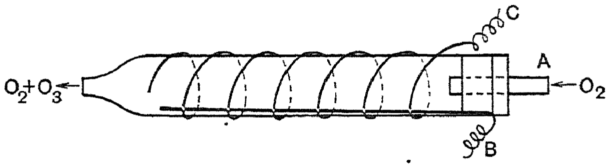

Fig. 30.—A simple ozoniser.

carrying a glass tube A into the wider end, simultaneously entrapping a piece of platinum or aluminium wire B of sufficient length to reach almost down to the restricted end of the tube. A second piece of wire

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[1] Warburg and Leithäuser, *Ann. Physik*, 1906, [4], 20, 751.

[2] The results of Shenstone (*Trans. Chem. Soc.*, 1897, 71, 471), which led to the idea that moisture hinders the formation of ozone, appear to have been due to the presence of nitrogen, which gives rise to nitrogen peroxide; this is known to accelerate the spontaneous decomposition of ozone.

[3] Briner and Durand, *Compt. rend.*, 1907, 145, 1272. See also Goldstein, *Ber.*, 1903, 36, 3042.

C is coiled round the outside of the tube, and both B and C are connected to the terminals of a Ruhmkorff coil. Oxygen is admitted through A, and a stream of ozonised oxygen escapes at the open end. The apparatus may advantageously be fixed on to a wooden stand, and, although its efficiency is not great, it possesses the advantage of being transparent.

Various other forms of ozonisers have been described, but for accounts of these the reader is referred to the subjoined references.[1]

Obtained in this way, ozone may be purified by fractional distillation at low temperatures, the boiling-point of ozone being some 63° above that of oxygen. The ozonised oxygen is liquefied by cooling in liquid air. The deep blue liquid thus obtained evolves mainly oxygen under reduced pressure and at a certain composition separates into two layers. The upper dark blue layer consists of a solution of ozone in liquid oxygen; the lower deep violet-black layer is a solution of oxygen in ozone and contains, at $-183°$ C., some 30 per cent of oxygen.[2] All but mere traces of oxygen are removed in a single fractionation of this liquid,[3] and by careful manipulation pure ozone, B.P. $-112{\cdot}4°$ C., may be obtained.

**Preparation by Chemical Processes.**—Ozone is formed to some extent during the slow combustion of certain substances such as phosphorus. In the case of phosphorus the occurrence of the ozone appears to be connected with the phosphorescence because substances which, by their presence, inhibit the phosphorescence, also prevent the formation of ozone.[4]

The formation of the ozone is probably due to the oxidation proceeding by the addition of whole molecules of oxygen to the oxidisable substance with the primary production of peroxidic substances which subsequently eliminate an atom of oxygen for each molecule originally absorbed; the atoms of oxygen then combine with one another and also possibly with molecules of oxygen, yielding ozone. Ozone is also frequently present in flames.[5]

The oxygen obtained by many chemical processes is frequently contaminated with ozone.

Fluorine decomposes water in the cold with such vigour that a portion of the liberated oxygen is ozonised. By passing a current of fluorine into water maintained at 0° C., Moissan was able to obtain a supply of oxygen containing 14·4 per cent. of ozone.[6] Small yields are obtained by the action of concentrated sulphuric acid upon powerful oxidisers such as barium peroxide, potassium bichromate, or permanganate.

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[1] Ramaiah and Swamy, *Chem. News*, 1920, 121, 193; Lechner, *Zeitsch. Elektrochem.*, 1911, 17, 414; Krüger, *Festschrift W. Nernst*, 1912, 240; Russ, *Zeitsch. Elektrochem.*, 1906, 12, 409; Harries, *Ber.*, 1906, 39, 3667; Jannasch and Gottschalk, *J. prakt. Chem.*, 1906, 73, 497; Kausch, *Elektrochem. Zeit.*, 1905, 12, 69, 91; Pohl, *Ber. Deut. physikal Ges.*, 1906, 4, 10; Warburg, *Ann. Physik*, 1905, 17, 1; 1906, 20, 734, 751; Gray, *Physical Review*, 1904, 19, 362; Wright, *Amer. J. Sci.*, 1872, 4, 26; *Chem. News*, 1872, 26, 213; Brodie, *Phil. Trans*, 1872, 162, 435; Houzeau, *Compt. rend.*, 1870, 70, 1286; 1872, 74, 256; von Babo, *Annalen. Suppl.*, 1863, 2, 265; von Babo and Claus, *ibid*, p. 297; *Annalen*, 1866, 140, 348; von Siemens, *Pogg. Annalen*, 1857, 102, 120.

[2] Riesenfeld and Schwab, *Zeitsch. Physik*, 1922, 11, 12; *Ber*, 1922, 55, [B], 2088.

[3] Karrer and Wulf, *J Amer Chem. Soc.*, 1922, 44, 2391.

[4] See Russell, *Trans. Chem. Soc.*, 1903, 83, 1263.

[5] Loew, *Zeitsch. Chem.*, 1870, 6, 65, 269; Manchot, *Ber.*, 1909, 42, 3948; Fischer and Braehmar, *ibid.*, 1906, 39, 940.

[6] Moissan, *Ann. Chim. Phys.*, 1891, [6], 24, 224.

In the last-named case the reaction is dangerously explosive and should only be carried out with small quantities of the reagents. Ozone is also formed during the decomposition by heat of potassium chlorate, and by the action of nitric acid, preferably of density 1·33, on ammonium persulphate[1] carefully warmed up to 65° to 75° C. The liberated gases are washed with caustic-potash solution and contain from 3 to 5 per cent. of ozone.

Ozone is produced during the electrolysis of neutral or alkaline solutions of potassium fluoride in consequence of the action of the fluorine momentarily produced at the anode upon the water in its vicinity.[2] Electrolysis of aqueous hydrogen fluoride is stated to have yielded [3] ozonised oxygen containing from 0·475 to 3·48 per cent. of ozone by volume.[4] With a saturated solution of potassium fluoride at 0° C. a yield of 0·65 per cent. ozone has been obtained for a short time, but the percentage of ozone tends to fall with the duration of the experiment. Variation of current density from 5 to 10 amperes per sq. decimetre does not appear to have any appreciable effect upon the yield.[4]

But perhaps the most satisfactory chemical process for the preparation of ozone is the electrolysis of dilute sulphuric acid. A 15 per cent. solution of acid is recommended, coupled with a high current density, namely, 80 amperes per sq. cm., at the (platinum) anode. With a platinum-foil anode sealed into glass so that only a thin edge is obtained projecting to an extent of about one-tenth of a millimetre, it is possible to produce oxygen containing over 20 per cent. of ozone by volume.[5]

The amount of ozone has been increased to 37 per cent. when calculated in terms of the gas liberated at the anode by the direct current by superimposing an alternating current on the last named.[6] This rise in efficiency is attributable to the depolarising action of the alternating current. The actual concentration of the ozone is, however, only 6 per cent. of the anodic gases owing to dilution with the gas liberated by the alternating current.

**Commercial Production of Ozone.**—The electrical method is the only one suitable for the technical production of ozone, and the conditions necessary for ensuring a maximum efficiency have been carefully studied by many investigators. Thus it is found that a larger yield of ozone is obtained when oxygen is passed through the ozoniser instead of air. Moisture exerts a noteworthy retarding influence,[7] and the gas should therefore be dried prior to passing into the ozoniser. Rise of temperature likewise reduces the ozone production,[8] as is evident from the following data:

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[1] Malaquin, *J. Pharm. Chim.*, 1911, 3, 329.

[2] Pauli, *Zeitsch. Electrochem*, 1897, 3, 474.

[3] Grafenberg, *Zeitsch. anorg. Chem.*, 1903, 36, 355.

[4] Prideaux (*Trans. Farad. Soc.*, 1906, 2, 34), using a current density of 100 amperes per sq. decimetre, obtained a yield of only 0·23 volume per cent. of ozone.

[5] F. Fischer and Bendixsohn, *Zeitsch. anorg. Chem.*, 1909, 61, 13, 153: F Fischer and Massenez, *ibid.*, 1907, 52, 202, 229.

[6] Archibald and von Wartenberg, *Zeitsch Elektrochem.*, 1911, 17, 812.

[7] Warburg and Leithauser, *Ann. Physik*, 1906, [4], 20, 751.

[8] Beill, *Monatsh.*, 1893, 14, 71; see also Cermak, *Chem. Zentr.*, 1906, ii., 585; *Ber. Deut physikal. Ges.*, 1906, 4, 268; Briner and Durand, *Compt. rend.*, 1907, 145, 1272; Job, *VII. Internat. Cong. Applied Chem.*, 1909, sec. ii., p. 143; Linder, *Trans. Amer. Inst. Chem. Eng.*, 1910, 3, 188. Puschin and Kauchtschev (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 576) find that rise of temperature from 0° to 28° C. favours the ozone production, whilst further rise diminishes it.

## EFFECT OF TEMPERATURE ON OZONE PRODUCTION.

(Beill 1893.)

| Temperature, ° C. | Ozone. Per cent. by Volume. | Temperature, ° C. | Ozone Per cent. by Volume. |
|---|---|---|---|
| −73 | 10 | 35 | 3 |
| −46 | 9·2 | 78 | 1·3 |
| −20 | 7·9 | 100 | 0·8 |
| 0 | 5·2 | 132 | 0·3 |
| 20 | 4·7 | | |

The character of the discharge is important, sparking being fatal to efficiency. Alternating currents are usually employed, and the percentage of ozone is found to rise with the frequency until a certain maximum value is reached[1] which varies with the voltage,[2] being 1240 periods per second at 6500 volts, 950 at 7000 volts, and 660 at 8000 volts in one series of experiments, the rate of passage of air through the ozoniser remaining constant. Increase in the rate of air-flow displaces the point of maximum ozone production in the direction of increasing frequency.

The influence of pressure up to 5 atmospheres has been studied,[3] and the results show that the optimum point for the production of ozone lies between 0·5 and 1 atmosphere.

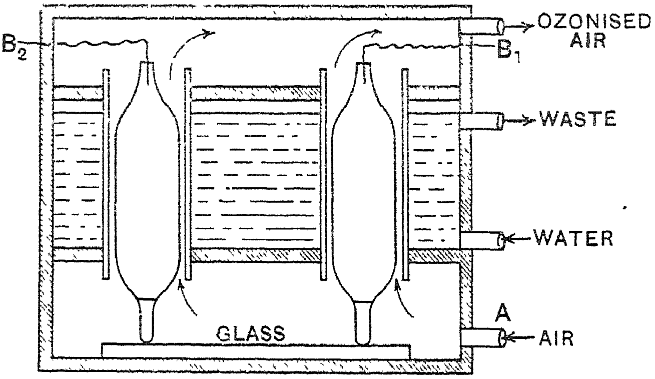

Fig. 31.—The Siemens-De Frise ozoniser.

The *Siemens–De Frise* ozoniser is one of the best known, and is shown in diagrammatic section in fig. 31. Six or eight glass cylinders, measuring some 3 feet in height and 10 inches in diameter, are fixed, two abreast, in a cast-iron box which is divided into three horizontal compartments. Water is passed through the middle chamber to keep the apparatus cool. Each glass cylinder holds one of aluminium, which rests on a glass plate on the bottom of the lowest compartment and is thus insulated from the metal box. It is further separated from the glass cylinder by an annular space about $\frac{1}{16}$ inch wide, up which a current of air continually passes. The cast-iron box is earthed, whilst the aluminium cylinders are raised to a potential of nearly 40,000 volts. The air entering at A (fig. 31) escapes at B charged with ozone.

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[1] Warburg and Leithauser, *Ann. Physik*, 1909, [4], 28, 1, 17. For other electrical data, see Warburg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1903, p. 1011; A. W. Gray, *ibid.*, 1903, p. 1016; *Ann. Physik*, 1904, [4], 13, 477, Ewell, *Physical Review*, 1906, p. 232; Fischer and Braehmer, *Ber.*, 1905, 38, 2633; Lechner, *Zeitsch. Elektrochem.*, 1911, 17, 414; Archibald and von Wartenberg, *ibid.*, p. 812.

[2] Puschin and Kauchtschev, *loc. cit.*

[3] von Wartenberg and Mair, *Zeitsch. Elektrochem.*, 1913, 19, 879.

The *Vosmaer* ozoniser consists of a series of parallel iron tubes through which the air to be ozonised is made to pass. A strip of metal with a saw-like edge passes down the length of each tube inside, but is insulated on porcelain supports. The tubes are connected to one pole of a high tension transformer, and the metal strips to the other, an alternating current being used. The advantage of this apparatus lies in the fact that no dielectric other than the porcelain supports and the air to be ozonised is required. A series of these tubes constitutes a "battery."

**Physical Properties.**—The characteristic odour of ozone can always be observed in the atmosphere, near electrical apparatus working with a high voltage; indeed, so penetrating is the odour that it will betray the presence of one part in 2½ millions of air.[1] As already mentioned, it was this odour that led Schönbein to suggest the name *ozone* for the gas.

The blue colour of ozone is easily perceptible in the gas obtained by evaporation of the liquid and can also be detected in oxygen containing only 10 per cent. of ozone [2] if layers of at least 1 metre in depth are examined. Ozone exerts so marked an absorption for ultra-violet light,[3] especially in the neighbourhood of 258 $\mu\mu$, as to allow the amount of ozone in ozonised oxygen to be determined photo-electrically.

Ozonised oxygen is appreciably denser than pure oxygen. A litre of ozone at N.T.P. would weigh 2·1445 grams, whereas oxygen weighs only 1·4289. Its density, therefore, is 1·50, where that of oxygen is taken as unity. The contraction accompanying the formation of ozone from oxygen was first observed by Andrews and Tait in 1860. The higher density of ozone is indicated by the relative velocities of diffusion of pure oxygen and ozonised oxygen, the results of Soret and of Ladenburg obtained with a mixture of known ozone content indicating for ozone a vapour density 1·5 times that of oxygen (see p. 155).

Ozone is distinctly more soluble in water than oxygen, but it has not been found possible to obtain concordant figures for the solubility, because in aqueous solution the gas decomposes so rapidly that equilibrium [4] is difficult to attain. Moufang [5] states that 1 litre of water dissolves about 10 mg. of ozone at 2° C., but only 1·5 mg. at 28° C. If this is correct, the solubility curve is remarkably steep.

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[1] Hartley states that one part of ozone per 2½ million parts of air by volume is detectable by the sense of smell (*Trans. Chem. Soc*, 1881, 39, 111).

[2] Hautefeuille and Chappuis, *Compt. rend.*, 1880, 91, 522; Chappuis, *Compt. rend.*, 1880, 91, 985.

[3] Hartley, *Trans. Chem. Soc.*, 1881, 39, 57; Fabry and Buisson, *Compt. rend.*, 1913, 156, 782; Krüger and Moeller, *Physikal. Zeitsch*, 1912, 13, 729; Hallwachs, *Ann. Physik*, 1909, 30, 602; Ladenburg and Lehmann, *Ber. Deut. phys. Ges.*, 1906, 4, 125

[4] Schone, *Ber.*, 1873, 6, 1224; Mailfert, *Compt. rend.*, 1894, 119, 951, Inglis, *Trans. Chem. Soc.*, 1903, 83, 1012; Ladenburg, *Ber.*, 1898, 31, 2510.

[5] Moufang, *Woch. Brauerei*, 1911, 28, 434. Mailfert (*Compt. rend.*, 1894, 119, 951) found that 1000 grams of water at 0° C could absorb 39·4 mgms. of ozone. See also Ladenburg, *Ber.*, 1898, 31, 2510.

The solution possesses the characteristic odour and oxidising properties of the gas. In dilute acid solution ozone is much more stable and the absorption coefficient in decinormal sulphuric acid has been experimentally determined as 0·487 at 0.[1]

The "ozone water" of commerce usually contains no ozone. Its activity is due to such substances as hypochlorites, etc.

Carbon tetrachloride dissolves approximately seven times as much ozone as does water, and when oxygen containing 6 per cent. of ozone is passed through the former solvent a distinctly blue solution is easily obtained.[2]

The specific heat ratio has been determined by extrapolation from observed values for mixtures of oxygen and ozone and leads to the value

$$\gamma=1{\cdot}29.$$

The magnetic properties of ozone are more marked than those of oxygen.[3]

The gas can be liquefied by cooling,[4] or by combined cooling and pressure, but great care is necessary in working with liquid ozone because in the liquid or compressed state the substance is exceedingly unstable, and tends to explode if the pressure is suddenly reduced or the temperature suddenly raised;[5] contact with grease or organic matter generally also may cause liquid ozone to explode.

Liquid ozone has a deep blue, almost black, colour, and is opaque in layers exceeding 2 mm. in thickness. It boils under ordinary pressure at −112·4° C.[6]; the considerable difference between the boiling-points or liquefying-points of ozone and oxygen supplies a convenient method for separating the former from a mixture of the two gases, oxygen remaining uncondensed at temperatures far below the temperature of liquefaction of ozone.

On cooling liquid ozone in liquid hydrogen, it solidifies in violet-black crystals, melting at −249·7° C. Its critical temperature is −5° C.; critical density 0·537; critical pressure 64·8 atmospheres. Its density at the boiling-point is 1·46.[7]

**Chemical Properties.**—Ozone is an endothermic substance, its formation from gaseous oxygen being attended by a large absorption of heat, namely 34,500 calories per gram molecule at constant volume.[8] Thus

$$3(O_2)=2(O_3)-2\times 34{,}500 \text{ calories.}$$

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[1] Luther, *Zeitsch. Elektrochem.*, 1905, 11, 832; Rothmund, *Festschrift W Nernst*, 1912, 391; Rothmund and Burgstaller, *Monatsh*, 1913, 34, 665. Mailfert, *Compt. rend*, 1894, 119, 951; Leeds, *Ber*, 1879, 12, 1831; Carius, *Ber.*, 1872, 5, 520; 1873, 6, 806.

[2] Fischer and Tropsch, *Ber.*, 1917, 50, 785. [3] Becquerel, *Compt. rend*, 1881, 92, 348.

[4] It liquefies with ease at atmospheric pressure at −181° C. (Olszewski, *Monatsh.*, 1887, 8, 230). Hautefeuille and Chappuis (*Comp. rend*, 1880, 91, 522, 1882, 94, 1249) liquefied the gas under pressure at −23° C.

[5] Erdmann (*Ber.*, 1904, 37, 4737) describes a convenient apparatus for experiments with liquid ozone.

[6] Riesenfeld and Schwab, *Zeitsch. Physik*, 1922, 11, 12; *Ber*, 1922, 55, [B], 2088. Olszewski (*Monatsh*, 1887, 8, 69) gives −106° C. (hydrogen thermometer); Troost (*Compt. rend*, 1898, 126, 1751) −116° C.; Ladenburg (*Ber.*, 1898, 31, 2508) −125° C

[7] Riesenfeld and Schwab, *loc. cit.*

[8] Kailan and Jahn, *Zeitsch. anorg. Chem.*, 1910, 68, 243; Jahn, *ibid.*, 1908, 60, 337; see also Berthelot, *Ann. Chim. Phys.*, 1877, 10, 162.

This figure has been obtained by decomposing ozone and noting the heat evolution.

As might be anticipated from its endothermic nature, ozone is unstable, and decomposes slowly even at the ordinary temperature.[1] At 300° to 400° C. its decomposition is practically instantaneous.

A phosphorescent light is observed on heating ozonised oxygen to 350° C. A more powerful phosphorescence results on decomposing the vapour of liquid ozone with a hot glass rod.[2]

Exposure to ordinary light accelerates the decomposition,[3] even red and yellow light exerting some influence.[4] Ultra-violet light is particularly reactive,[3] but leads to an equilibrium, inasmuch as oxygen is converted into ozone under the like influence.[5] Ozone is more chemically reactive in sunlight than in the dark.[6]

It is interesting to note that, whereas admixture with carbon dioxide, nitrogen, and oxygen does not considerably affect the rate of decomposition, the presence of water-vapour, chlorine, or nitrogen dioxide causes a marked acceleration.[7]

Certain substances, such as platinum black, copper oxide, and the dioxides of lead and manganese, exert a catalytic effect on the decomposition of ozone, and solutions of the alkalis have a similar effect. The final result in all these decompositions is represented by the equation

$$2O_3=3O_2,$$

and although the mechanism of the decomposition is not exactly understood, yet in the gaseous state and in solution its reaction is generally bimolecular.[8]

Ozone is remarkable for its chemical activity which is manifested in several ways, namely :

1. Oxidation, during the process of which there is no change in volume in so far as the ozone itself is concerned, each molecule of ozone yielding a molecule of oxygen, the third oxygen atom entering the oxidised product. This is the most usual type of oxidation.
2. Oxidation in which all three atoms of oxygen are absorbed in oxidising.
3. The formation of addition products such as ozonates, ozonides, and oxozonides, in which the ozone molecule as a whole is attached to the final product.

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[1] Clark and Chapman, *Trans. Chem. Soc*, 1908, 93, 1638; Clement, *Ann. Physik*, 1904, 14, 334; *Sitzungsber K. Akad. Wiss. Berlin*, 1901, 48, 1126; Perman and Greaves, *Proc. Roy Soc*, 1908, 80, [A], 353; Chapman and Jones, *ibid*, 1910, 97, 2463; 1911, 99, 1811; Fischer and Tropsch, *Ber.*, 1917, 50, 765.

[2] Beger, *Zeitsch. Elektrochem.*, 1910, 16, 76; Stuchtey, *Zeitsch. Wiss Photochem.*, 1920, 19. 161.

[3] Houzeau, *Compt. rend.*, 1872, 74, 1267; von Bahr, *Ann. Physik*, 1910, 33, 598; Weigert, *Zeitsch. physikal. Chem*, 1912, 80, 78. Compare Russ, *Zeitsch. Electrochem.*, 1906, 12, 409.

[4] Griffith and Shutt, *Trans. Chem. Soc.*, 1921, 119, 1948.

[5] See p. 140, where further references are given.

[6] Besson, *Compt. rend*, 1895, 121, 125.

[7] Warburg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, p. 644; 1912, p. 216; Weigert, *Ann. Physik*, 1907, 24, 243; Chapman and Jones, *Trans. Chem. Soc*, 1910, 97, 2463, 1911, 99, 1811. Shenstone (*Trans. Chem. Soc*, 1897, 71, 477) believed moist ozone to be more stable than dry. That was incorrect.

[8] In addition to the foregoing references, see Rothmund and Burgstaller, *Monatsh.*, 1913, 34, 665.

These processes may now be considered in turn.

1. The reactions normally falling under this heading may be subdivided into two groups, namely—

(*a*) Reactions resulting in pure oxidation of the substance ozonised.

(*b*) Reactions resulting in the reduction both of the ozone and the substance treated.

(*a*) *Reactions involving Oxidation.*—The majority of the reactions with ozone fall under this subdivision. Hydrogen and nitrogen are not affected by ozone under ordinary conditions, but iodine,[1] sulphur, arsenic, antimony, and the various allotropes of phosphorus are converted into oxides and, in the presence of moisture, into the corresponding acids.

Under the influence of ultraviolet light from a quartz mercury vapour lamp, however, ozone is capable of oxidising dry hydrogen, the following reactions taking place :—

$$\text{(i) } 2O_3 = 3O_2;$$
$$\text{(ii) } H_2 + O_3 = H_2O + O_2.$$

Reaction (i) is normally slow, but is greatly accelerated by even small quantities of hydrogen. Hydrogen peroxide does not appear to be formed under these conditions.[2]

Under the influence of ozone all the common metals excepting gold and platinum are converted, superficially if the metal is massive, into oxides ; thus silver becomes coated with a black film of a peroxide.

Combined hydrogen is frequently oxidised to water as in hydrogen sulphide[3] and palladium hydride which yield the free element and water ; also phosphine and ammonia, in which not only is the hydrogen oxidised, but also the other element present giving acid fumes. Hydrogen chloride, bromide, and iodide are oxidised with liberation of the halogen element,[4] a condition of equilibrium being reached in the case of the first named.

Heated with steam to 120° C., hydrogen sulphide is partially, but not completely oxidised to sulphuric acid by ozonised air.[5]

Carbon monoxide is slowly[6] oxidised by ozone at ordinary temperatures, the reaction being favoured by light and moisture.[7] At 250° C. the oxidation proceeds rapidly,[8] and by bubbling the gases emerging from the ozoniser through lime-water or baryta-water, the presence of carbon dioxide is readily demonstrated.

Sulphur dioxide and nitrous fumes are rapidly oxidised by moist ozone, with formation of sulphuric and nitric acids respectively.[9]

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[1] Muir, *Trans Chem. Soc.*, 1909, 95, 656 ; Fichter and Rohner, *Ber.*, 1909, 42, 4093.

[2] Weigert and Bohm, *Zeitsch. physikal. Chem.*, 1915, 90, 189 ; Weigert, *ibid.*, 1912, 80, 78 ; *Ber.*, 1913, 46, 815.

[3] See Schwarz and Munchmeyer, *Chem Zentr.*, 1914, i., 56.

[4] Volta, *Gazzetta*, 1879, 9, 521 ; Ogier, *Compt rend.*, 1877, 85, 957 ; 1878, 86, 722 ; Jahn, *Zeitsch. anorg. Chem.*, 1904, 42, 203.

[5] Bresciana, *Ann. Chim. Applicata*, 1915, 4, 343.

[6] Berthelot, *Compt. rend.*, 1879, 87, 50 ; Waters, *Amer. Chem J.*, 1903, 30, 50. Compare Schwarz and Munchmeyer, *loc. cit.*

[7] Clausmann, *Compt. rend.*, 1910, 150, 1332 ; Remsen and Southworth (*Ber*, 1875, 8, 1414) failed to detect any oxidation under the influence of sunlight.

[8] Jones, *Amer. Chem. J.*, 1903, 30, 40.

[9] Berthelot, *Ann. Chim. Phys.*, 1878, 14, 367 ; Schwarz and Munchmeyer, *loc cit.* Helbig, *Atti R. Accad. Lincei*, 1902, 11 (ii), 311 ; 1903, 12 (i), 211. Russ and Pokorny, *Monatsh.*, 1913, 34, 1027.

In the case of sulphur dioxide at temperatures below 40° C. all three atoms of oxygen in the ozone molecule are utilised. Thus

$$3SO_2+O_3=3SO_3.$$

But with nitrogen peroxide,[1] one molecule of ozone is required per molecule of peroxide at 25° C. Thus

$$N_2O_4+O_3=N_2O_5+O_2.$$

Potassium iodide in aqueous solution is oxidised to free iodine, the reaction having been extensively applied in the early history of ozone, but it has now somewhat lost in favour because a similar effect can be produced by nitrogen peroxide or chlorine.[2] If the action of the ozone is prolonged, the oxidation may proceed further to the formation of hypoiodite, iodate, and periodate.[3]

$$2KI+H_2O+O_3=2KOH+O_2+I_2.$$

In a similar manner potassium bromide yields bromine and potassium hydroxide, but the further formation of hypobromite and bromate is less rapid than the analogous reaction with potassium iodide.[4]

Ozone oxidises alkali nitrites in aqueous solution to nitrates, the reaction taking place quantitatively according to the equation [5]

$$NaNO_2+O_3=NaNO_3+O_2.$$

This reaction has been made use of in the determination of atmospheric ozone.

Many other inorganic salts are oxidised by ozone; solutions of manganese and lead salts yield the corresponding brown dioxides unless the solution contains a relatively large quantity of nitric or sulphuric acid when the former class of salts gives rise to permanganic acid.[6] Chromic salt solutions are transformed into chromic acid, potassium ferrocyanide gives the ferricyanide, ferrous, stannous, and bismuthous salts yield precipitates of the ferric, stannic, and bismuthic hydroxides, whilst silver solutions form a precipitate of black silver peroxide. Metallic sulphides, *e.g.* lead sulphide, are changed into the corresponding sulphates.[7] Alkali thiosulphates yield chiefly sulphate and dithionate.[8]

Some of the thiosulphate appears to be catalytically decomposed, depositing sulphur in accordance with the equation [9]

$$Na_2S_2O_3=Na_2SO_3+S.$$

The sulphite is then oxidised to sulphate by ozone.

The oxides and hydroxides of the metals generally are raised to the highest degree of oxidation of the metal, thus ferric hydroxide in the presence of alkali yields a ferrate. With the alkali hydroxides, however, ozone forms additive compounds or highly oxidised compounds of a special type; crushed potassium hydroxide absorbs ozone forming a brown substance, *potassium ozonate*, of uncertain composition but probably $KHO_4$ or $K_2O_4$.[1] This reaction may be regarded in two ways, namely: (i) as oxidation by addition of the whole ozone molecule. Thus

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[1] Wulf, Daniels and Karrer, *J. Amer. Chem. Soc.*, 1922, 44, 2398.

[2] See pp. 154 and 178.

[3] Engler and Wild, *Ber.*, 1896, 29, 1929.

[4] Garzarolli-Thurnlack, *Monatsh.*, 1901, 22, 955.

[5] Usher and Rao, *Trans. Chem. Soc.*, 1917, 111, 799.

[6] Maquenne, *Compt. rend.*, 1882, 94, 795.

[7] Mailfert, *Compt. rend*, 1882, 94, 860, 1186; Yamauchi, *Amer. Chem. J.*, 1913, 49, 55; Jannasch and Gottschalk, *J. prakt. Chem*, 1906, 73, 497.

[8] Riesenfeld and Egidius, *Zeitsch. anorg. Chem*, 1914, 85, 217.

[9] Yamauchi, *Amer. Chem. J.*, 1913, 49, 55.

$$KOH+O_3=KHO_4.$$

In that case the reactions would fall into the third category (pp. 147, 151). But (ii) it has been suggested that during the process of alkali ozonation the ozone molecule decomposes into molecular and atomic oxygen, the latter, only, acting upon the alkali to form the ozonate.[2] When freshly prepared, potassium ozonate is orange in colour like potassium bichromate, but on keeping, and on treatment with water, it decomposes into the hydroxide, oxygen, and potassium tetroxide. Rubidium, cæsium, and possibly sodium yield orange-red ozonates. Liquid ammonia, to which a small quantity of water has been added, appears to behave in an analogous manner towards ozone, the liquid becoming orange-red, but the coloration persists only at temperatures below −50° C.[3] By prolonging the reaction, the ammonia is converted into ammonium nitrate, with traces of nitrite.[4] Hydroxylamine readily reacts with ozone, the nitrate alone being formed.[4] Hydrazine hydrate is converted mainly into nitrogen and water.

From the fact that the presence of at least a trace of water is necessary to effect oxidation processes by ozone, it is of interest to note that water is not oxidised by ozone to hydrogen peroxide; indeed, in the presence of hydrogen peroxide, ozone in alkaline solution [5] decomposes according to the equation

$$H_2O_2+O_3=H_2O+2O_2,$$

whilst in acid solution, except in the presence of a large excess of hydrogen peroxide, there is a tendency for an undue proportion of ozone to undergo decomposition.

Ozone affects a photographic plate.[6] It is also stated to cause the explosion of nitrogen chloride, nitrogen iodide, and also of nitroglycerine.[7]

Towards organic substances ozone is strikingly active. Organic colouring matters are bleached; for example, indigo is oxidised to isatin.[8] Turpentine rapidly absorbs the gas, and if the liquid is exposed on filter paper in an atmosphere of ozone, inflammation may occur.[9] India-rubber is rapidly attacked and so is of little value for connections in ozone apparatus. Alcohol is oxidised into acetaldehyde and even cellulose is oxidised, giving an indefinite peroxide compound.[1] The oxidation of an alcoholic solution of tetramethyl-*p*-di-aminodiphenylmethane by ozone produces a violet colour; this solution, applied conveniently on absorbent paper (as "tetramethyl base paper"), supplies a delicate test for ozone, possessing the additional advantage of distinguishing this gas from nitrogen dioxide, with which a yellow colour is formed,[2] and from hydrogen peroxide, with which no colour is obtained.

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[1] Baeyer and Villiger, *Ber.*, 1902, 35, 3038; Bach, *Ber.*, 1902, 35, 3424; Manchot and Kampschulte, *Ber.*, 1907, 40, 4984; Traube, *Ber.*, 1912, 45, 2201.

[2] Traube, *Ber.*, 1916, 49, 1670; 1912, 45, 2201.

[3] Manchot and Kampschulte, *Ber*, 1907, 40, 4984; Manchot, *Ber.*, 1913, 46, 1089.

[4] Strecker and Thienemann, *Ber.*, 1920, 53, [B], 2096.

[5] Schone, *Annalen*, 1879, 196, 239; Inglis, *Trans. Chem. Soc.*, 1903, 83, 1010, Rothmund, *Eighth Inter. Congr. App. Chem.*, 1912, 26, 611.

[6] Schaum, *Physikal. Zeit.*, 1905, 6, 73.

[7] Jouglet, *Compt. rend.*, 1870, 70, 539.

[8] Leeds, *Chem. News*, 1879, 40, 86; Thénard, *Compt. rend.*, 1872, 75, 458; Erdmann, *J. prakt. Chem.*, 1857, 71, 209; Houzeau, *Compt. rend.*, 1872, 75, 349.

[9] Harries, *Ber.*, 1908, 41, 42.

(*b*) *Reactions involving Reduction.*—One of the best known of these is the reaction between hydrogen peroxide and ozone, both of which undergo mutual reduction. In alkaline solution, or in the presence of excess of peroxide in acid solution, the reaction proceeds in accordance with the equation

$$H_2O_2+O_3=H_2O+2O_2.$$

2. *All three atoms* of ozone may on occasion be used up in oxidising a substance, but this is less usual. A common illustration is afforded by stannous chloride, the oxidation of which proceeds as follows:[3]

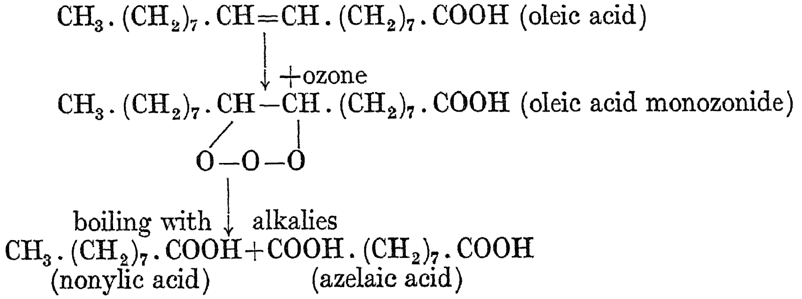
$$3SnCl_2+6HCl+O_3=3SnCl_4+3H_2O.$$

3. *Additive Compounds.*—Under this category the **ozonates** of the alkali metals are frequently considered, but Traube concludes that this is not correct, the oxidation proceeding, in the case of potassium hydroxide for example, as follows:

$$KOH+3O_3=KHO_4+3O_2.$$

The reaction thus falls into our first category and has been considered in that connection (see p. 150).

Addition compounds are frequently formed when ozone acts upon unsaturated organic substances, possessing at least one double bond between two adjacent carbon atoms, and are termed **ozonides.** Benzene, $C_6H_6$, which possesses three such bonds, yields a tri-ozonide, $C_6H_6(O_3)_3$. Oleic acid, $C_{17}H_{33}.COOH$, which possesses one double bond, yields a monozonide, $C_{17}H_{33}(O_3)COOH$, a viscous, transparent, and colourless liquid which decomposes above 90° C. With alkalies it breaks at the double bond, evolving oxygen and yielding nonylic and azelaic acids. Thus



$$CH_3.(CH_2)_7.CH{=}CH.(CH_2)_7.COOH \text{ (oleic acid)}$$

$$\downarrow +\text{ozone}$$

$$\underset{\diagup\qquad\quad\mid\quad}{CH_3.(CH_2)_7.CH{-}CH.(CH_2)_7.COOH} \text{ (oleic acid monozonide)}$$

$$O{-}O{-}O$$

$$\text{boiling with} \downarrow \text{alkalies}$$

$$\underset{\text{(nonylic acid)}}{CH_3.(CH_2)_7.COOH}+\underset{\text{(azelaic acid)}}{COOH.(CH_2)_7.COOH}$$

The formation of ozonides in this manner is of considerable value to the organic chemist in that he is enabled to determine the number and position of double bonds in unsaturated compounds, as indicated above.[1]

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[1] Dorée, *Trans. Chem. Soc.*, 1913, 103, 1347.

[2] Arnold and Mentzel, *Ber.*, 1902, 35, 1324; Fischer and Marx, *Ber.*, 1906, 39, 2555; Würster, *Ber.*, 1888, 21, 921.

[3] Yamauchi, *Amer. Chem. J.*, 1913, 49, 55.

**Oxozonides.**—When ordinary ozone is allowed to react with unsaturated organic compounds, the element is sometimes taken up by the latter in groups of four atoms instead of the usual triatomic groups, whereas if the ozone is previously washed by passage through sodium hydroxide solution and sulphuric acid, the addition occurs only by groups of three oxygen atoms. The formation of oxozonides, as Harries terms the products containing $O_4$ groups, is attributed by Harries to the presence of oxozone $O_4$ in the crude ozone. The evidence as to the possible existence of a tetr-atomic form of oxygen, however, cannot yet be considered as satisfactory.[2] Vapour density determinations reveal no tendency on the part of even pure ozone to associate to higher complexes than that corresponding to $O_3$.[3]

**Physiological Action.**—Owing to its powerful oxidising properties, ozone is both a deodoriser and a bactericide of considerable efficiency. Schönbein [3] found that air, laden with organic matter liberated in the course of one minute from 4 oz. of putrid flesh, may be completely deodorised by its own volume of air containing 1 volume of ozone per 3¼ volumes of air. In 1875 Boillot [4] drew attention to the fact that fresh meat may be preserved for upwards of ten days without going bad, if exposed to ozonised air, whilst, if exposed to ordinary air, the meat will putrefy in half that time. These early observations have received ample confirmation in more recent years,[5] and the bactericidal action of ozone is well established.

It is, however, impossible to make a general statement as to the minimum amount of ozone required to sterilise air, because so many factors are involved. Some organisms are more resistant than others, whilst time, temperature, and the presence of moisture have an important influence upon the results. It is interesting to note, however, that Duphil [6] has drawn attention to the paucity of bacteria in the air of Bordeaux—an air that is characterised by its high percentage of ozone.

Unless the proportion of ozone is exceedingly small, the inhalation of ozonised air by human beings is liable to be accompanied by serious disturbances in the animal organism. The lung tissue is injured, the oxygen intake increased, and the output of carbon dioxide decreased.[7] Exposure for a couple of hours to a concentration of 15 to 20 parts of ozone per million of air is not without risk to life, and even 1 part of ozone per million of air irritates the respiratory tract.[8] This latter dilution, however, may not be harmful; in fact it may be directly beneficial in cases of bad ventilation by stimulating the olfactory nerve and thus relieving the monotony of close air. Air containing not more than 5 parts of ozone per million of air has been breathed by children without any ill effect.

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[1] See Harries and his co-workers, *Ber.*, 1906, 39, 2844, 3732; 1909, 42, 446; *Annalen*, 1906, 343, 318; *Ber.*, 1912, 45, 936; *Zeitsch. Elektrochem.*, 1912, 18, 129; 1911, 17, 629 See also Kailan, *Zeitsch. Elektrochem.*, 1911, 17, 966. Molinari and his co-workers, *Ber.*, 1906, 39, 2735; 1908, 41, 2794. Numerous references to other workers are given in these papers.

[2] Riesenfeld and Schwab, *Zeitsch. Physik*, 1922, 11, 12. *Ber.*, 1922, 55, [B], 2088; Karrer and Wulf, *J. Amer. Chem. Soc.*, 1922 44, 2391.

[3] Schonbein, see *Ozone and Antozone*, by C. Fox (Churchill).

[4] Boillot, *Compt. rend*, 1875, 81, 1258.

[5] See Labbé, *Rev. gén. Chem. Appl.*, 1905, 8, 387; Sigmund, *Centr. Bakt. Par.*, 1905, 14, 400, 494; Arloing and Troude, *Compt. rend. Soc. Biol.*, 1903, 55, 236; Labbé and Oudin, *Compt. rend.*, 1891, 113, 141, and others.

[6] Duphil, *Soc. sci. Stat. Zool. d'Arcachon Univ. Bordeaux, Trav. Lab.*, 1900–1901, p. 51.

[7] Bohr and Maar, *Chem Zentr.*, 1905, i., 945; from *Skand. Arch. Physiol.*, 1905, 16, 41.

[8] Hill and Flack, *Proc. Roy. Soc.*, 1911, [B], 84, 404.

At still greater dilutions than the foregoing, the effect of ozone has been repeatedly proved to be beneficial. In cases of anæmia it appears to stimulate the multiplication of blood corpuscles, to increase the appetite, and to raise the general standard of health of the sufferer. Asthma, bronchitis, pleurisy, and pneumonia have likewise been relieved by inhalation of ozonised air, and it is not impossible that similar treatment may prove beneficial to consumptives.

The odour of ozone is so penetrating that 1 part per $2\frac{1}{2}$ million of air is perceptible to the sense of smell.[1] This is well under the danger limit mentioned above, so that the normal nose may be taken as a pretty safe guide in determining whether or not ozone is present in beneficial or dangerous quantity.

**Applications.**[2]—As mentioned in the previous section, ozone, on account of its powerful oxidising properties, exerts a marked bactericidal effect. It is frequently employed, therefore, for improving the atmosphere of buildings that are liable to be crowded, for underground passages, and for the stations and tunnels of electric tube railways.[3] In these cases great care has to be taken that the concentration of the ozone shall always be well under the danger limit.

As is usual in the case of odoriferous disinfectants, there is always a danger of confusing disinfectant or bactericidal action with the mere masking of an unpleasant smell,[4] and the actual value of the ozone treatment for "stuffy" atmospheres is easily over-estimated.

The bactericidal action of ozone has also been applied to the sterilisation of water[5] and the preservation of foodstuffs.

The oxidising properties of ozone have led to the application of this gas to the bleaching of such substances as starch, flour, oils, and wax, delicate fabrics, etc. It has been used in the production of artificial silk and synthetic camphor. It has also been used to aid the "ageing" or maturing of wines, spirits, and tobacco. The action of ozone on unsaturated organic compounds provides a very convenient general method for the preparation of aldehydes and ketones, which has already been applied to the manufacture of vanillin for flavouring purposes and heliotropin for perfumery.

**Detection.**—Many of the reactions described under the properties of ozone can be used for the detection of this gas in the air. Exposure to an ozone-laden atmosphere causes the formation of a film of oxide on the surface of a globule of clean mercury and so causes this to drag or "tail" when it moves.[6] The formation of a stain of silver peroxide on a clean silver surface[7] supplies a very trustworthy test for ozone, but it lacks somewhat in delicacy and also might give misleading results in the presence of hydrogen sulphide.

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[1] Hartley, *Trans. Chem. Soc.*, 1881, 39, 111.

[2] See *Chem. News*, 1916, 113, 193, 205.

[3] The Central London Tube Railway is ventilated with ozonised air.

[4] Hill and Flack, *loc. cit.*

[5] See Chap. VII.

[6] Volta, *Gazzetta*, 1879, 9, 521.

[7] Frémy, *Compt. rend.*, 1865, 61, 939; Thiele, *Zeit. offentl. Chem.*, 1906, 12, 11; Manchot and Kampschulte, *Ber.*, 1907, 40, 2891; Manchot, *ibid.*, 1909, 42, 3942.

Tetramethyldi-*p*-aminodiphenylmethane provides a satisfactory reagent for the gas (see pp. 151, 178), and the oxidation of iodides with formation of iodine can also be applied. Apart from its historical interest, the last method deserves attention because of its simplicity and the refinements of which it is capable. The liberation of iodine is usually detected by the formation of a blue coloration with starch; if, however, the formation of alkali is concurrently demonstrated by using starch-free paper soaked with potassium iodide and phenolphthalein solution, which becomes reddened by ozone[1] on account of the formation of potassium hydroxide (see p. 178), the possibility of confusion with chlorine or bromine is removed. To render the starch-iodide test absolutely conclusive, however, additional tests are necessary, *e.g.* the success of the test should not be affected if the gas is previously passed through dilute permanganate solution, ozone being unaffected by this reagent whilst hydrogen peroxide vapour is decomposed; passage through a heated tube or through a layer of manganese dioxide causes the decomposition of ozone, and the true ozone reaction with starch-iodide should therefore fail after the gas has been so treated.[2]

Liquid air provides a convenient agent for the detection of ozone and nitrogen dioxide either together or separately, even although only small quantities of the gaseous mixture are available. When the gas is passed into the liquid air the nitrogen dioxide separates as a solid and can be filtered off, whilst the ozone remains dissolved and can be recovered by careful evaporation of the solvent.[3]

**Estimation.**—Ozone in small quantities is usually estimated by the oxidation of potassium iodide, the gas being passed through a neutral or alkaline solution of the salt. With an alkaline solution there is less danger of the loss of iodine, and in any case the solution must not be acidified until after the ozone treatment or the results will be high. The extent of the oxidation is determined by acidifying and then titrating the liberated iodine with thiosulphate in the usual way.[4]

In acid solution, potassium bromide is oxidised quantitatively by ozone yielding an equimolecular proportion of bromine,[5] and this reagent can therefore be used for the estimation of dissolved ozone in the presence of hydrogen peroxide.[6]

Ozone can also be estimated by slowly passing the gaseous mixture through sodium hydrogen sulphite solution and titrating the unchanged sulphite with iodine,[7] or by the gravimetric process of absorbing the gas in oleic acid or linseed oil and measuring the increase in weight.[8]

**Molecular Weight and Constitution.**—Although Schönbein was quite definite in his views of ozone as a distinct substance, the general confusion with hydrogen peroxide vapour retarded the development of the subject. Andrews and Tait, in their formation of ozone by the action of the electric discharge on pure oxygen, demonstrated that ozone was an allotropic form of oxygen of higher molecular weight (see p. 138). Soret then discovered that ozone is completely absorbed by turpentine, and was able to demonstrate that the decrease in volume during the ozonisation of oxygen is approximately one-half the decrease observed when the ozone is subsequently absorbed by turpentine; assuming that the ratio is actually 1 : 2, it is easily seen that the total loss in oxygen is 1½ times the volume of ozone, indicating for ozone a molecular weight 1½ times that of oxygen.[1] The correctness of the assumption as to the ratio of the two volume changes was demonstrated later by Brodie whose experiments yielded the figures 1 : 2·02,[2] and so indicated in a convincing manner that the chemical change in the formation of ozone was to be represented

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[1] Leeds, *Chem. News*, 1878, 38, 224, 227, 235, 249; Arnold and Mentzel, *Ber.*, 1902 35, 1324.

[2] Keiser and M'Master, *Amer. Chem. J.*, 1908, 39, 96. For a summary of tests distinguishing ozone from hydrogen peroxide and nitrous fumes see Vaubel, *J. prakt. Chem.*, 1913, ii., 88, 61.

[3] Fischer and Braehmar, *Ber.*, 1906, 39, 940.

[4] See Ladenburg, *Ber.*, 1901, 34, 1184; Treadwell and Anneler, *Zeitsch anorg. Chem.*, 1905, 48, 86; Lechner, *Zeitsch. Elektrochem.*, 1911, 17, 412; Baskerville and Crozier, *J. Amer. Chem. Soc.*, 1912, 34, 1332.

[5] Inglis, *Trans. Chem. Soc.*, 1903, 83, 1010.

[6] Rothmund and Burgstaller, *Monatsh.*, 1913, 34, 693. Compare, however, Treadwell and Anneler, *loc. cit.*

[7] Ladenburg, *Ber.*, 1903, 36, 115.

[8] Fenaroli, *Gazzetta*, 1906, 36, ii., 292.

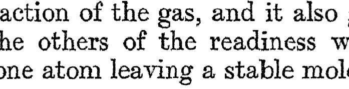
$$3O_2=2O_3.$$

Soret also confirmed his earlier result by an independent investigation [3] based on the relative velocity of diffusion of mixtures of oxygen with ozone, carbon dioxide, and chlorine respectively, in which he was able to show that the vapour density of ozone was a little higher than that of carbon dioxide, but distinctly lower than that of chlorine. This experiment has been repeated with greater accuracy by Ladenburg who used a gas containing 84·4 per cent. of ozone obtained by evaporation of liquefied ozone, and, from the velocity of diffusion, was able to calculate a density 1·3698 referred to oxygen which leads to the value 1·469 instead of the theoretical 1·5 for pure ozone of molecular formula $O_3$.[4]

Recent determinations [5] of the vapour density of pure ozone confirm the value 48 for the molecular weight. No tendency to associate to higher molecules has been observed either in the pure liquid or the gas.

The greater molecular complexity of ozone relative to oxygen is also distinctly discernible in the ratio of the specific heat at constant pressure and constant volume. For ozone this ratio has the value [6] 1·29 which approximates closely to that expected of a triatomic gas, whilst for oxygen the value is 1·404.

Various suggestions have been made as to the structure of the ozone molecule, the most favoured being



According to Brühl, the last representation is in closest agreement with the specific refraction of the gas, and it also gives at least as easy an explanation as the others of the readiness with which the ozone molecule eliminates one atom leaving a stable molecule of oxygen.

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[1] Soret, *Compt. rend.*, 1863, 57, 604; *Ann. Chim. Phys.*, 1866, 7, 113. *Phil. Mag.*, 1866, 31, 82; 1867, 34, 26.

[2] Brodie, *Proc. Roy. Soc.*, 1872, 21, 472.

[3] Soret, *Ann. Chim. Phys.*, 1868, 13, 257.

[4] Ladenburg, *Ber.*, 1898, 31, 2508, 2830; 1899, 32, 321; 1901, 34, 1834; Stoedel, *ibid.*, 1898, 31, 3143; Groger, *ibid.*, 1898, 31, 3174.

[5] Riesenfeld and Schwab, *Ber.*, 1922, 55, B, 2088. *Zeitsch. Physik.*, 1922, 11, 12 Karrer and Wulf, *J. Amer. Chem. Soc.*, 1922, 44, 2391.

[6] Richarz, *Sitzungsber. Ges. Beförd. ges. Naturew.*, 1904, p. 57.

# CHAPTER VI.

## THE ATMOSPHERE.

**Historical.**—The fact that the world is surrounded by an atmosphere[1] must have been realised by man at a very early stage in his development. A knowledge of the chemical composition of air and its influence upon living organisms, however, has only been recently acquired. At first air was regarded as a simple substance, and in the Aristotelean philosophy ranked as an element, along with fire, earth, and water.

Galileo (1564–1642) drew attention to the material nature of air by demonstrating the apparent increase in the weight of a metal globe when air is compressed into it.

The development of the chemistry of the atmosphere was somewhat delayed by the early lack of realisation that there exist various kinds of gases. At first the term " air " was applied to all gaseous substances, and not until the commencement of the seventeenth century was the difference in the nature of various gases recognised; at this time van Helmont, who introduced the term " gas," observed the divergence in the properties of gases from different sources, and as an almost immediate result carbon dioxide was accepted as a minor constituent of the atmosphere.

In the sixteenth century it was already known to alchemists that the calcination of metals is accompanied by an increase in weight, and in the seventeenth it had been noted that the air, from its behaviour, must contain a " principle " analogous to that in nitre.

The correct conception of the main constituents of the atmosphere immediately preceded the fall of the phlogiston theory, when Lavoisier (1775–1776), who first recognised the true nature of the two main constituents also effected a rough analysis. At the same period Priestley determined the amount of oxygen in the air by causing it to combine with nitric oxide, a gas which he had himself discovered[2]; whilst Scheele, with a similar purpose, absorbed the oxygen from a measured volume of air by a solution of potassium sulphide (" liver of sulphur "). Cavendish, the first chemist to bring pneumatic chemistry to a state of accurate measurement, estimated the amount of the active constituent in air by removing it with nitric oxide and also by exploding it with hydrogen, and followed up this work by a demonstration that the inactive constituent was almost entirely homogeneous, observing that the portion of atmospheric nitrogen which could not be made to combine with additional oxygen under the influence of electric sparks did not exceed $\frac{1}{120}$th part of the original air.[1]

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[1] Greek ἀτμός, vapour, and σφαῖρα, sphere.

[2] Priestley, *Experiments on Air*, 1774, i., 110; *Experiments and Observations*, 1779, p. xxx.

As was indicated by the earliest experiments, the atmosphere shows but little variation in chemical composition. Priestley could detect no difference between the composition of country air and air in a Birmingham workshop, and Cavendish, in 1783, obtained the ratio 20·84 : 79·16 as a surprisingly constant value for the relative volumes of oxygen and nitrogen. These results led several chemists to the conclusion that air is a definite compound of oxygen and nitrogen. Dalton,[2] however, maintained that air is simply a mechanical mixture of its constituent gases; and this view was confirmed some years later when, as the result of more accurate analyses, small though decided differences were detected in compositions of air obtained from different sources.[3] Thus, in 1846, Bunsen detected slight variations in the air at Marburg, and since that date many similar observations have been made.

For more than a century no explanation was forthcoming for Cavendish's observation that a small portion of the nitrogen obtained from air exhibits a peculiar inertness, in that it refuses to unite with oxygen under the influence of electric sparks. Indeed, the fact appears to have been entirely overlooked until Lord Rayleigh drew attention to it in 1894. The air was regarded as consisting of a mixture of oxygen and nitrogen with more or less moisture, and containing traces of carbon dioxide, ozone, and several other minor constituents. In 1893 Rayleigh[4] published the results of a series of very accurate determinations of the densities of nitrogen obtained from various sources, and drew attention to the fact that atmospheric nitrogen invariably yielded a higher density than nitrogen obtained from chemical sources, such, for example, as by the decomposition of oxides of nitrogen, of ammonia, or of urea. His results were as follow:

| | |
|---|---|
| Mean weight of atmospheric nitrogen contained in large globe . | 2 31016 grams. |
| Mean weight of "chemical" nitrogen contained in large globe . | 2·29927 ,, |

Rayleigh satisfied himself that the density of none of his samples of nitrogen was affected by the action of the silent electric discharge; he also proved that the lightness of the nitrogen from chemical sources was not due to admixture with any known gas such as hydrogen, ammonia, or water-vapour, possessing less density than itself. From this it was evident that either the "chemical" nitrogen contained an unknown and less dense gas, or, what was more probable, that the atmospheric nitrogen was contaminated with a heavier, but likewise unknown gas.

Cavendish's experiments were therefore repeated in a more modern and refined manner, and it was found that, after sparking atmospheric nitrogen with an excess of oxygen, and absorbing the resulting oxides of nitrogen and any unattacked oxygen by suitable reagents, a residue of an inert gas was always obtained, the volume of which was proportional to the original volume of air used. In conjunction with Ramsay, Rayleigh[1] isolated this new gas in sufficient quantity to determine many of its properties Spectroscopic examination proved that it was not nitrogen, and as all attempts to make it combine chemically with any other known elements proved futile, the new gas was christened *argon*.[2]

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[1] Cavendish, *Phil. Trans.*, 1785, 75, 372. See also *Alembic Club Reprints III.*, and this series, Vol. I., p. 330.

[2] Dalton, *Manchester Memoirs*, 2nd series, 1, 244.

[3] Bunsen, *Gasometrische Methoden* (Braunschweig), 1857; also Regnault, *Compt. rend.*, 1848, 26, 4, 155; 1852, 34, 863; *Ann. Chim Phys*, 1852, 36, 385.

[4] Rayleigh, *Proc. Roy. Soc.*, 1893, 53, 146, 1894, 55, 340.

Soon after the discovery of argon, namely, towards the close of 1894, Ramsay was able to obtain helium in sufficient quantities to render an examination of the gas possible, by heating powdered clèveite. Up to that time helium had never been isolated ; indeed, its existence was only known through its spectrum. When this gas was found to resemble argon in its remarkable chemical inertness it was thought that possibly other similar gases might exist, and liquid air was therefore subjected to careful fractional distillation whereby three new gases were found, namely,[3] Neon,[4] Krypton,[5] and Xenon.[6] The presence of helium in the atmosphere was also established. All of these latter gases, however, are only present in the air in very minute quantities.

### COMPOSITION OF THE ATMOSPHERE.

The chemical composition of dry air varies slightly at different places and, indeed, at one and the same place at different times. The following may be regarded as a fair average :

| Gas | Per cent. by Volume | Per cent. by Weight |
|---|---|---|
| Nitrogen[7] . . . . . | 78·06 | 75·50 |
| Oxygen[7] . . . . . | 21·00 | 23·20 |
| Argon[7] . . . . . | 0·94 | 1·30 |
| Carbon dioxide[8] . . . . | 0·03 | 0·09 |
| Krypton[9] . . . . . | 0·000005 | . . |
| Xenon[9] . . . . . | 0·0000006 | . . |
| Neon[9] . . . . . . | 0·00123 | 0·00086 |
| Helium[9] . . . . . | 0·00040 | 0·000056 |
| Ammonia . . . . . | 0·0004 to 0·0009 | . . |
| Hydrogen[10] . . . . . | <0·0001 | . . |
| Ozone and hydrogen peroxide . | 0·0025[11] | . . |

In addition to the foregoing, the following gases are usually present in variable but minute proportions—carbon monoxide, hydrocarbons, nitric acid, sulphur dioxide, sulphuric acid, hydrogen sulphide, mineral salts, organic matter. The amount of water-vapour in the air is extremely variable.

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[1] Rayleigh and Ramsay, *Phil. Trans.*, 1895, 186, 187.

[2] Greek ἀργον, inactive.

[3] Ramsay and Travers, *Proc Roy. Soc.*, 1898, 62, 316 ; 63, 405, 437 , *Phil Trans.*, 1901, 197, 47 ; Ramsay, *The Gases of the Atmosphere* (Macmillan, 1902) ; Moore, *Chem. News*, 1911, 103, 242.

[4] Greek νεον, new.

[5] Greek κρυπτόν, hidden.

[6] Greek, ξένος, stranger.

[7] Leduc, *Compt. rend.*, 1896, 123 805.

[8] See p. 179.

[9] Ramsay, *Proc. Roy. Soc.*, 1908, 80, [A], 599.

[10] Claude, *Compt. rend.*, 1909, 148, 1454.

[11] See p. 175.

The mean composition of Paris air, freed from carbon dioxide and water-vapour, is given by Leduc[1] as follows :

| Gas. | Per cent by Volume. | Per cent by Weight. |
|---|---|---|
| Nitrogen . . . . . | 78·06 | 75·49 |
| Oxygen . . . . . | 21·00 | 23·21 |
| Argon . . . . . . | 0·94 | 1·30 |
| Neon . . . . . . | $15\times10^{-6}$ | $8{\cdot}4\times10^{-6}$ |
| Helium . . . . . | $5\times10^{-6}$ | $0{\cdot}7\times10^{-6}$ |
| Hydrogen . . . . . | $1\times10^{-6}$ | $0{\cdot}07\times10^{-6}$ |
| Krypton . . . . . | $5\times10^{-8}$ | $14\times10^{-10}$ |
| Xenon . . . . . . | $6\times10^{-9}$ | $3\times10^{-10}$ |

**Physiological Action of the Air.**—As a general rule any harmful effect produced on man by air must be due to some foreign impurity in the air ; the mixture of nitrogen and oxygen is an absolute necessity for prolonged existence. The fat of mammals, however, dissolves more than five times as much nitrogen as does an equal volume of water, and this fact may give rise to serious results with men working under conditions, for example, in caissons, in which the external atmospheric pressure undergoes sudden and considerable variations. If the reduction in pressure is too sudden the fat-containing tissues of the workers are liable to injury on account of the formation of gas bubbles.[2]

**The Percentage of Oxygen in the Air.**—Oxygen and nitrogen (with argon and the other inert gases) are the most constant constituents of the atmosphere, and an estimation of their relative quantities in air which, if necessary, has been previously freed from carbon dioxide and moisture, may be made either by gravimetric or volumetric methods. In 1841 Dumas and Boussingault[3] published the results of their classical experiments in which air, freed from moisture and carbon dioxide by passage over sulphuric acid and caustic potash respectively, was drawn through a tube of heated metallic copper into an evacuated metal globe of several litres capacity. From the increases in weight of the globe and tube containing the copper, the relative weights of nitrogen and oxygen were ascertained, the mean results of six experiments being as follows :

| | |
|---|---|
| Weight of nitrogen[4] . . . . . | 76·995 |
| Weight of oxygen . . . . . | 23·005 |
| | 100·000 |

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[1] Leduc, *Engineering*, 1919, 108, 569. See also Krogh, *Math. fysiske Meddelelser*, 1919, i., No. 12. For a discussion of the chemical and geological history of the atmosphere, see Stevenson, *Phil. Mag.*, 1900, [5], 50, 312, 399; 1902, [6], 4, 435, 1905, [6], 9, 88; 1906, [6], 11, 226. On the origin of the oxygen of the air, see Phipson, *Compt. rend.*, 1895, 121, 719.

[2] Vernon, *Proc. Roy. Soc*, 1907, 79, [B], 366. Twort and Hill, *Proc physiol. Soc.*, 1910, v–vi.

[3] Dumas and Boussingault, *Compt. rend.*, 1841, 12, 1005; *Ann. Chim. Phys.*, 1841, 3, 257.

[4] Including, of course argon and the other inert gases, which were unknown at the time.

Other investigators obtained closely similar results, the most important researches being those of—

| Authority. | Locality. | Mean Weight of Oxygen. | Mean Weight of Nitrogen.[1] |
|---|---|---|---|
| Lewy (1841) . | Copenhagen | 22 998 | 77·002 |
| Stas (1842) . | Brussels | 23 100 | 76·900 |
| Marignac (1842) . | Geneva | 22 990 | 77·010 |

The gravimetric analysis of air can only be carried out with the aid of considerable laboratory apparatus, and necessitates a large supply of air. A more convenient method of analysing air consists in determining the relative *volumes* of oxygen and nitrogen. This is readily effected by mixing a known volume of air with excess of hydrogen, noting the combined volume, and sparking. The volume is again noted, one-third of the contraction being due to the oxygen which has combined with two-thirds of its volume of hydrogen to yield water. Before admitting the hydrogen, or at any rate before sparking the mixture, the gases must be carefully freed from carbon dioxide, ammonia, and similar impurities, as their presence would introduce an appreciable error into the results obtained. This method was largely used by Bunsen.

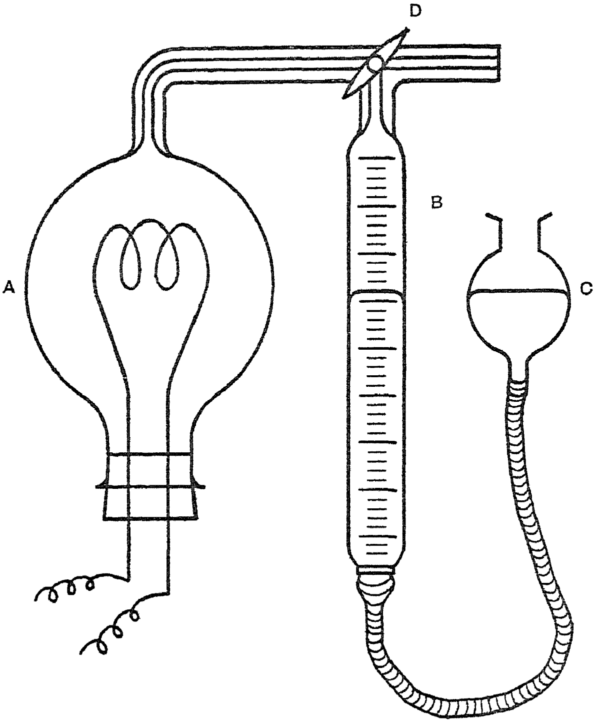

Fig. 32.—Joly's apparatus.

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[1] Including, of course, argon and the other inert gases, which were unknown at the time.

Joly's method consists in heating a spiral of copper wire to redness, by means of an electric current, in a known volume of air. Copper oxide is formed, and from the diminution in volume the relative proportions of oxygen and nitrogen (including the inert gases) are readily obtained. A convenient form of the apparatus is shown diagrammatically in fig. 32. The glass globe A, of approximately 100 c.c. capacity, is filled with pure, dry air, free from carbon dioxide, and connected by means of a capillary tube to the graduated tube B containing a mercury seal. After the volume at atmospheric pressure has been noted, C is raised until the air in B has been forced into A as indicated by the rise of the mercury in B to the stop-cock D. The spiral of copper wire in A is now heated electrically in order to "fix" the oxygen, after which the apparatus is allowed to cool and the residual volume of nitrogen measured.

Other methods consist in absorbing the oxygen by means of an alkaline solution of pyrogallol[1]; by means of phosphorus; or some other suitable reagent. In 1846 Bunsen, using his volumetric or *eudiometric*[2] method, confirmed the observation of Cavendish, that the air has not always the same composition. This was further illustrated by Regnault,[3] who analysed air from a number of localities, with the following results:[4]

| Locality | No of Samples. | Extreme Percentages of Oxygen by Volume. |
|---|---|---|
| Lyons . . . . . | 9 | 20·918–20·966 |
| Berlin. . . . . . . | 30 | 20·908–20·998 |
| Madrid . . . . . . | 10 | 20·916–20·982 |
| Geneva and Chamounix . . | 23 | 20 909–20·993 |
| Toulon Roads and Mediterranean . | 17 | 20·912–20·982 |
| Atlantic Ocean . . . . . | 5 | 20·918–20·965 |
| Ecuador . . . . . . | 2 | 20·96 |
| Summit of Pichincha . . . | 2 | 20·949–20·988 |
| Antarctic Seas . . . . | 2 | 20·86 –20·94 |

Dalton,[5] who always maintained that air was not a compound but a mixture, suggested that, since nitrogen is the lighter gas, the proportion of this gas to oxygen ought to increase with the altitude. This expectation was borne out some eighty years later by the researches of Morley,[6] extending from January 1880 to April 1881, at Hudson, Ohio, U.S.A. It was observed that severe depressions of temperature were connected with the descent of cold air from very high altitudes, and that the proportion of oxygen was usually slightly less than normal.

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[1] Henrich, *Ber.*, 1915, 48, 2006; Henrich and Kuhn, *Zeitsch. angew. Chem.*, 1916, 29, 149.

[2] Greek *eu*, well, and *metron*, measure.

[3] Regnault, *Ann. Chim. Phys.*, 1852, 36, 385.

[4] Taken from Roscoe and Schorlemmer, *Treatise on Chemistry*, vol. i, p. 585 (Macmillan, 1905).

[5] Dalton, *Manchester Memoirs*, 2nd series, vol. i., p. 244.

[6] Morley, *Amer. J. Sci.*, 1881, 22, 417; *Chem. News*, 1882, 45, 283.

Owing to the intermixing of volumes of air by the winds it is extremely unlikely that any appreciable difference can exist in the proportions of oxygen and nitrogen due to elevation alone,[1] although indications are not wanting that at the highest altitudes the percentage of oxygen is slightly reduced. This is evident from the accompanying table in which are given the results obtained by Leduc.[2] At an altitude of 2060 metres on the Alps descending currents of air contained nearly 0·2 per cent. less of oxygen than did ascending currents the following day. The same table shows a slight increase of oxygen in summer over that of winter and spring.

## PERCENTAGE OF OXYGEN IN THE AIR.

| Locality. | Oxygen per cent. by Weight. |
|---|---|
| Sorbonne . . . | 23·14 to 23·20 |
| Paris . . . | 23·20 |
| Nice, Nîmes, Algiers . | 23·23 |
| Dieppe . . . | 23·16 (July)<br>23·07 (April) |
| Belgian Frontier . | 23·17 (summer)<br>23·09 (winter) |
| Alps (2060 metres) . | 23·05 (descending air currents)<br>23·23 (ascending air currents) |

The proportion of oxygen appears to vary somewhat with the latitude, there being—if Hempel's analyses may be regarded as typical—rather less oxygen in the tropics and more in northern latitudes than in temperate regions.[3]

## VARIATION IN OXYGEN PERCENTAGE WITH LATITUDE.

| Locality. | Latitude. | Mean Percentage of Oxygen by Volume. |
|---|---|---|
| Trömsoe (Norway) . . | 69° 40′ N. | 20·92 |
| Dresden (Saxony) . . . | 51° 30′ N. | 20·90 |
| Para (Brazil) . . . | 1° 27′ S. | 20·89 |

Not merely does the proportion of oxygen vary from place to place, it also varies at one and the same place from time to time. Thus Levy[4] found that after great forest conflagrations the air of New Granada underwent remarkable changes, the oxygen-content falling from about 21·01 to 20·33 per cent. Such a variation is decidedly abnormal, but in volcanic districts is perhaps more frequent than is generally known.

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[1] Gay-Lussac, Thénard, Brunner, Frankland (*Trans Chem. Soc.*, 1861, 13, 22), and Watson (*ibid.*, 1911, 99, 1460) could detect no appreciable difference at elevations ranging up to 7000 metres above sea-level.

[2] Leduc, *Compt. rend.*, 1893, 117, 1072.

[3] Hempel, *Ber.*, 1885, 18, 267, 1800; 1887, 20, 1864.

[4] Levy, *J. prakt. Chem.*, 1851, 54, 253; *Phil. Mag.*, 1851, [4], 2, 500.

The following data, compiled from the researches of a variety of investigators in different localities, will serve to indicate the results usually obtained.

## OXYGEN PERCENTAGE AT VARIOUS LOCALITIES.

| Locality. | Authority. | No. of Analyses. | Volume Percentage of Oxygen |
|---|---|---|---|
| Heidelberg . | Bunsen . . . . | 28 | 20·84 –20·97 |
| Manchester . | Angus Smith *On Air and Rain* (Longmans, 1872) | 32 | 20·78 –21·02 |
| Bonn . . | Kreusler (*Ber.*, 1887, **20**, 991) . . . . | 45 | 20·901–20·939 |
| Cape Horn . | Muntz and Aubin (*Compt. rend.*, 1886, **102**, 422) . | 20 | 20·72 –20·97 |
| Cleveland, Ohio . | Morley (*loc. cit.*) . . | 15 | 20·90 –20·95 |
| Geneva . | Watson (*Trans. Chem. Soc.*, 1911, **99**, 1460) . | 4 | 20·93 –20·98 |

The mean percentage of oxygen in the air may be taken as 21·00 by volume and 23·20 by weight.[1]

**Physiological Importance of Oxygen in Air.**—It has already been mentioned (see p. 134) that the chief physiological function of oxygen is to aerate the system and thereby ensure the removal of waste material in the form of carbon dioxide, which escapes into the air through the lungs. The oxidation processes involved cause considerable heat evolution, and it is through this means that the body temperature is maintained. Berthelot concluded [2] that six-sevenths of the heat developed by respiration is liberated in various parts of the body other than the lungs, one-seventh only being liberated in the lungs. This pulmonary heat was found to be almost completely compensated by the absorption of heat due to liberation of carbon dioxide and water. It would appear, therefore, that upon the temperature of the inspired air would depend whether or not the lung temperature rises. In any case the variation would be small.

*Respired air* is saturated with moisture, after removal of which it contains normally some 4 per cent. of carbon dioxide and 16 to 17 per cent. of oxygen. These amounts vary both with the individual and with circumstances. Thus Thomson [3] found that the expired air of the average Manchester citizen contained 4 per cent. of carbon dioxide, whereas an average of 5 per cent. was observed in country districts, reaching to 5·4 per cent. on high ground near Buxton. Under normal conditions the rate of breathing is subconsciously regulated so that the proportion of carbon dioxide in the arterial blood leaving the lungs contains a definite equilibrium pressure of carbon dioxide. A very slight increase in the amount of carbon dioxide excites the nervous centre controlling the breathing and stimulates respiration. Hence, during physical exercise or in cold weather,[1] when more carbon dioxide is being produced, the proportion of this gas in expired air remains substantially the same, but the volume of air passing through the lungs increases proportionately, the breathing being deeper and more rapid.

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[1] Leduc, *Compt rend*, 1896, 123, 805.

[2] Berthelot, *ibid.*, 1890, 109, 776.

[3] W. Thomson, *VII. Inter. Congr. Appl. Chem.*, 1909, sec. VIII., [A], 154.

During sleep, when both mental and physical activity are at a minimum, the amount of carbon dioxide produced is less than normal, and the rate of breathing is proportionately reduced.[2]

When at rest, the average man consumes some 18 litres of oxygen per hour, an amount which may increase to 60 litres when walking at about three miles per hour, whilst in cases of more violent exercise such as running or jumping even 100 litres may not be quite sufficient.

*The Physiological Influence of Excess of Oxygen.*—This has been made the subject of a considerable number of researches, and the conclusions arrived at by different investigators are reasonably concordant. It would appear[3] from experiments on the cat and on man that the inhalation of pure oxygen does not materially augment the quantity of that gas in the blood, nor affect its average carbon dioxide content. Again,[4] in a series of experiments on men at rest, performed some twelve hours after the last meal, no noticeable difference could be detected, either in the gaseous metabolism or in the character, depth, or frequency of respiration when the men breathed air containing 40, 60, and 90 per cent. of oxygen. The only difference that could be detected lay in the pulse rate which fell as the percentage of oxygen rose. It is very important to remember, however, that these experiments were only conducted for relatively short periods of time, and it has yet to be discovered whether or not a permanent increase in the percentage of oxygen in inspired air would have an influence upon the system in the long run. Thus J. L. Smith,[5] in 1899, drew attention to the fact that oxygen, at the tension of the normal atmosphere, stimulates the lung cells to active absorption; but his experiments on mice indicated that at higher tensions inflammation might be produced.

*The Physiological Influence of Reduced Oxygen Tension.*—The effect upon respiration of a reduced oxygen tension is one of much greater importance from a practical point of view than the problem just considered, inasmuch as the main difficulty in practice lies not in reducing the amount of oxygen in buildings, but in raising it to the normal. It is thus of the greatest importance to determine whether or not 21 per cent. of oxygen is essential to vigorous human life, and if not, what is the minimum amount of oxygen that may be safely permitted. A moment's consideration will show that no perfectly exact answer, at any rate to the second of these problems, can be arrived at, for not only do the needs of different persons vary, but those of the same individual are likewise influenced by the state of health and extent of physical and mental activity at the time of experiment. Further, after prolonged exposure to certain abnormal conditions, unless these latter are too severe, the body adapts itself to meet the new requirements. Thus persons who habitually live in ill-ventilated buildings are much less affected on any particular occasion than those who enter such buildings after a life in the open. This adaptive tendency is extremely well illustrated by the researches of Douglas, Haldane, Henderson, and Schneider,[1] who stayed at Pike's Peak, Colorado, for five weeks at an altitude of 14,000 feet, the barometer standing at 45·7 cm. A careful study of their persons showed that they gradually became accustomed to the altered conditions, except that hyperpnœa upon exertion lasted longer than usual.

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[1] Falloise (*Trav lab. de L. Fredericq*, Liége, 1901, 6, 183) found that a fall of temperature from 21° C. to 0° C. results in the production of an increased amount of carbon dioxide. Above 21° C there is also an increase, but it is not so marked.

[2] According to L de St. Martin (*Compt rend*, 1887, 105, 1124) sleep reduces the carbon dioxide output by one-fifth and the oxygen intake by one-tenth

[3] G A Buckmaster and J. A. Gardner, *Proc Roy. Soc.*, 1912, [B], 85, 56.

[4] F G Benedict and H. L. Higgins, *Amer. J. Physiol.*, 1911, 28, 1. See also J. Loeb and H Wasteneys, *Biochem. Zeitsch*, 1912, 40, 277; L. E Hill and J. R. Macleod, *Proc. Roy. Soc.*, 1902, 70, 455; L. E. Hill and M. Flack, *Proc. Physiol Soc.*, 1909, xxviii. to xxxvi., W. Thomson, *loc. cit.*; A. Falloise, *Trav. lab. de L. Fredericq*, Liége, 1901, 6, 135; P. von Terray, *Pflugers Archiv.*, 1896, 65, 293.

[5] J. L. Smith, *J. Physiol.*, 1899, 24, 19.

The reduced tension of the oxygen was counteracted—

1. By increased lung ventilation.

2. A considerable increase in the red corpuscles and hæmoglobin of the blood, the extent of which, however, varied with the individual. The volume of the blood likewise increased slightly, except during the first week.

3. Finally, an increased secretory activity of the pulmonary epithelium was observed.

Inasmuch as all these adaptations take considerable time to develop, they would not occur in rapid balloon or aeroplane ascents. On coming down from Pike's Peak, the normal state of the body began to assert itself, and in the course of four weeks all traces of the change had disappeared.

There is abundant evidence to show that the percentage of oxygen in the air may be reduced very considerably without producing any unpleasant symptoms. Dr. Whalley, in his report on the ventilation of Scottish coal mines, alludes to one in which considerable quantities of black-damp were evolved. "A light," he writes, "would not burn 1½ feet from the floor . . . but the men had no fault to find with the atmosphere, and the foreman told me it was better than usual." Upon analysis, the air on the pavement was found to contain only 13·13 per cent. of oxygen, and that at the coal face 18·97 per cent. Valenzuela [2] caused his consumptive patients to breathe an artificial atmosphere, containing only 17 per cent. of oxygen, and noted that this exerted a marked stimulating action upon respiration, increasing the chest expansion, and liberation of carbon dioxide, whilst the nutrition was not adversely affected. This apparently indicates that in a normal atmosphere we consume more oxygen than we need, just as we ordinarily partake of more food than is really necessary. In the case of a person at rest, the percentage of oxygen may be reduced to 11 without anything very unusual being experienced,[1] and the respiratory exchange remains the same.[2] Below 10·5 per cent. the body loses its compensatory power, and the amount of carbon dioxide increases.[3] The breathing now becomes deeper and slightly laboured. By reducing the supply to 7 per cent., the face becomes leaden in hue, and the senses deadened, and a further slight reduction results in sudden loss of consciousness.[4]

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[1] C. G. Douglas, J. S. Haldane, Y. Henderson, and E. Schneider, *Proc. Roy. Soc.*, 1912, [B], 85, 65; E. C. Schneider, *Amer. J. Physiol.*, 1913, 32, 295, has recently published further data on similar lines.

[2] Quoted by J. Harger, *Coal and the Prevention of Explosions, etc.*, (Longmans & Co., 1913), p. 41.

Closely connected but not absolutely identical with this problem of the minimum partial pressure of oxygen in the atmosphere is that of the effect of reducing the total pressure of the air.[5] This, for example, is experienced in balloon ascents and in mountaineering. The average individual does not feel himself inconvenienced at an altitude of 9000 feet, in which circumstances the barometer stands at approximately 50 cm., and the pressure of oxygen is correspondingly reduced to about 14 per cent. of an ordinary atmosphere. Above this altitude the average European begins to observe something peculiar during periods of physical exertion, and at 14,000 feet the effect is very marked, the amount of oxygen being equivalent to that of about 12 per cent. in an ordinary atmosphere at sea-level.

In view of the foregoing, it would appear that 11 *per cent. of oxygen is the lowest limit to which it is safe to go. Below this the air is dangerous, and at 7 per cent. may prove fatal.*

When taking physical exercise, however, these limits are probably too low for the average person, and 14 per cent. of oxygen may then be taken as the lowest that can be breathed with safety.

The greatest height ever reached by an investigator in a balloon is probably that attained by Berson and Suring in July 1901, namely, 35,400 feet (10,789 metres), although in 1862 Glaisher and Coxwell ascended over Wolverhampton to about 29,000 feet, when they became unconscious and are believed to have risen to nearly 36,000 feet for a short time. The two greatest heights recorded for aeroplanes are those of Rohlfs, who, in September 1919, ascended to about 32,418 feet (9880·5 metres), and of Schroeder, in February 1920, who reached approximately 31,184 feet (9505 metres).[6]

**Carbon Dioxide in the Air.**—It is to Dr. Black that we owe the first proof of the existence of carbon dioxide in the air, during the years 1752–1754.[7] He termed it *fixed air.* Lavoisier, however, showed that it was a compound of oxygen and carbon.

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[1] Haldane and his co-workers, *J. Physiol.*, 1905, 32, 225, 486.

[2] J. Tissot, *Compt. rend.*, 1904, 138, 1454.

[3] P. von Terray, *Pflugers Archiv*, 1896, 65, 393.

[4] The rapidity with which loss of consciousness sets in constitutes one of the perils that the diver has to face when working under water in an artificial atmosphere. When Lieutenant Damant was testing the Fleuss apparatus for the Admiralty Committee, and was deep under water, he suddenly swooned, owing to the fact that he had unwittingly allowed the oxygen percentage to fall too low. Only the prompt application of artificial respiration saved his life. See Martin, *Triumphs and Wonders of Modern Chemistry* (Sampson Low), p. 177.

[5] Many writers regard these two phenomena as identical, and from the point of view of respiration this is probably sufficiently near the truth. The personal equation of persons experimented upon varies so much that such exact results cannot be obtained, as is possible with analogous combustion experiments like the burning of a candle, etc.

[6] M'Adie, *Nature*, 1920, 105, 437.

[7] And not to M'Bride as Thorpe (*J. Chem. Soc.*, 1867, 20, 189) and Symons and Stephens (*Trans. Chem. Soc.*, 1896, 69, 869), stated. See preface to *Lectures on the Elements of Chemistry*, by Jos. Black (Edinbro. 1803), p. xxiii.

The actual proportion of carbon dioxide in the air varies very considerably according to circumstances. Whalley reported that in a Scottish mine the carbon dioxide in the air near the coal face reached 1·21 per cent., whilst on the pavement it was no less than 4·56 per cent. Lewy,[1] in discussing the abnormal air of New Granada, points out that owing to forest fires the percentage of carbon dioxide in the air would often rise to 0·49 per cent. These cases, however, are abnormal.

The average amount of carbon dioxide in pure, fresh air may be taken as 3 parts per 10,000 by volume. This is subject, however, to alteration by a variety of factors. Thus over land it increases slightly during the night,[2] and it is somewhat greater over land than over sea.[3] In Antarctic regions it is less than in more temperate climes.[4] Fog and mist likewise play an important part. Angus Smith,[5] in his summary of the then available data, showed that the average carbon dioxide content of Manchester air in times of fog amounted to 6·79 parts per 10,000, the normal amount for Manchester being 4·03. Similarly, Russell[6] observed as much as 14·1 parts of carbon dioxide in 10,000 of air in thick, white London fog. Indeed, his average for twenty-nine fogs was 7·2, whilst for ordinary clear London air he found only 4·0 parts. Rain is accompanied by a diminution of carbon dioxide, but with snow the gas is in excess. Its variation with altitude is apparently inappreciable,[7] but the evidence of the effect of latitude is conflicting.

Considerable variation may be due to local circumstances. Thus Reiset found that the presence of a flock of 300 sheep on a fine, calm day in Dieppe induced a notable rise in the proportion of carbon dioxide in the immediate neighbourhood, which registered 3·18 parts per 10,000 instead of 2·96—the normal value for Dieppe. The influence of vegetation upon the carbon dioxide content of the air has not received the consideration it deserves, although a few isolated experiments have been carried out. Ebermayer,[8] for example, found an excess of the gas in the forest, a result that confirmed the earlier observation of Truchot.[9] In confined spaces, such as dwellings, the carbon dioxide shows a marked increase owing to its being a product of human metabolism, and may reach 0·5 per cent.

A connection has been traced between the relative amounts of carbon dioxide and ozone in the atmosphere, the amount of the former varying inversely with that of the latter for values below the normal.[10]

In the following table are listed a few of the more important and recent determinations of the amount of carbon dioxide in the atmosphere.

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[1] Lewy, *J. prakt. Chem.*, 1851, 54, 253; *Phil. Mag.*, 1851, [4], 2, 500.

[2] This diurnal variation is negligibly small or non-existent over the sea, Thorpe, *J. Chem. Soc.*, 1867, 20, 189. Reiset, *Annales Agronom*, 1879, 5, 199. *Compt. rend.*, 1879, 88, 1007; 1880, 90, 1144, 1457.

[3] See the excellent summary with full references by Letts and Blake, *Proc. Roy. Dublin Soc.*, 1899–1902, ix., 107–270.

[4] Müntz and Lainé, *Compt. rend.*, 1911, 153, 1116. Müntz and Aubin, *Compt. rend.*, 1881, 92, 247, 1229; 1881, 93, 797; 1882, 94, 1651; 1883, 96, 1793; 1884, 98, 487.

[5] Angus Smith, *Air and Rain*, (Longmans, 1872).

[6] See Russell's work in the *Monthly Weather Reports of the Met. Council*, 1884

[7] M. de Thierry, *Compt. rend*, 1899, 129, 315.

[8] Ebermayer, *Die Beschaffenheit der Waldluft*, Stuttgart, 1885.

[9] Truchot, *Annales Agronom.*, 1877, 3, 69.

[10] Henriet and Bonyssy, *Compt. rend.*, 1908, 146, 977.

## CARBON DIOXIDE IN THE ATMOSPHERE.

| Locality | Observation. Parts of Carbon Dioxide by Volume in 10,000 Parts of Air | Authority |
|---|---|---|
| Near Dieppe | 2·942 (mean of 92 determinations) | J. Reiset. *Compt rend*, 1879, 88, 1007, 1880, 90, 1144, 1157 |
| Luttich | 3·3526 (mean of 266 analyses) | Spring and Roland, *Chem Zentr*, 1886, p 81. |
| Country air (Belgium) | 2·944 (mean) | A. Peterman and J Graftian, *Chem Zentr*, 1892, ii, 201. |
| In town of Gembloux, Belgium | 3·70 (mean) | A Peterman and J Graftian, *Chem Zentr*, 1892, ii, 201 |
| Sheffield | 3·9 (mean of numerous determinations in centre of city) | W C Williams, *Ber.*, 1897, 30, 1450 |
| 1½ miles west from centre of Sheffield | 3·27 (mean) | W C. Williams, *Ber*, 1897, 30, 1450. |
| Mt Blanc. | | |
| Altitude, 1080 m. | 2·62 | M de Thierry, *Compt. rend*, 1899, 129, 315 |
| Altitude, 3050 m. | 2·69 | |
| Belfast | 2·91 (mean of 16 determinations) | Letts and Blake, *Sci Proc Roy Dub. Soc*, 1900, 9, part 2, pp 107–270 |
| Kew | 2·43 to 3·60 (minimum and maximum of numerous determinations during 1898 to 1901) | H. T. Brown and F. Escombe, *Proc Roy. Soc*, 1905, [B], 76, 118. |
| Monte Video | 2·70 to 3·30 (mean value, 2·98) | Schroder, *Chem Zeitung*. 1911, 35, 1211. |
| Antarctic air over sea, lat 64°–67° | 2·05. | Muntz and Lainé, *Compt rend*, 1911, 153. 1116 |
| Bucharest | 3·02 (in the city)<br>2·81 (surrounding plain) | St. Minovici and Grozea, *Sci Roumanie*, 1914, 2, 275 |

*The Source of Atmospheric Carbon Dioxide.*– It is not generally realised that 3 parts of carbon dioxide in 10,000 of air amount to a total weight of 3 billion tons of gas in the whole atmosphere surrounding the globe, and correspond to the presence of 0·8 billion tons of carbon.[1] Enormous quantities are evolved from volcanoes[2] and mineral springs.[3] Boussingault[4] calculated in 1844 that Cotopaxi alone emitted more carbon dioxide than the whole of Paris, which at that time gave up daily some 3 million cubic metres of the gas. The persistent respiration of human beings,[5] of animals, and of plants, the combustion of ever-increasing quantities of fuel,[6] and the decay of vegetation and carbonaceous material are constantly adding to the carbon dioxide content of the air.

---

[1] See p. 192 A. Krogh (*Meddelelser om Groenland*, 1904, 26, 419) gives $2 \cdot 4 \times 10^{12}$ tons of carbon dioxide; van Hise (*Mon. U.S. Geol. Survey*, 1904, 47, 967) and Dittmar (*Challenger Report*, vol. i., part 2, p. 954) give figures of the same order; Chamberlin (*J. Geol.*, 1899, 7, 682) gives a somewhat higher estimate.

[2] See Meunier, *Compt. rend.*, 1878, 87, 541, etc

[3] See Varigny, *Air and Life*, Smithsonian Miscellaneous Collections.

[4] Boussingault, *Ann. Chim. Phys.*, series iii., 1844, 10, 456.

[5] It has been calculated that the human race breathes about one million tons of carbon dioxide into the air daily.

[6] The estimated world's consumption of coal in 1912 was 1200 million tons This mostly finds its way into the air as carbon dioxide.

The soil is continually evolving carbon dioxide; part of this is no doubt of volcanic origin, and part is due to chemical processes of a more superficial character. As an instance of the former, it is interesting to note that after eruptions of Vesuvius the soil has breathed out such vast quantities of carbon dioxide that game have been poisoned wholesale. The famous Valley of Death in Java, the Death Gulch of Western America, the Grotto del Cane near Naples, and others, owe their poisonous atmospheres to carbon dioxide exhaled by the soil.

It has been calculated that each square mile of fertile garden soil evolves some 4000 tons of carbon dioxide during the summer months This is due to the decay of vegetation and organic matter, as well as to the continued respiration of small creatures. Thus, for example,[1] earth-worms breathe out as much carbon dioxide as a human being, weight for weight.

Nevertheless, the carbon dioxide content of fresh air remains fairly constant at 0·03 per cent., a fact which suggests that some reactions must be proceeding on a grand scale, tending to absorb or destroy the gas. Three such have been discovered. First there is the action of plants,[2] the green parts of which under the influence of sunlight inhale carbon dioxide and exhale pure oxygen. As illustrating this it may be mentioned that one square metre of leaf surface of *Catalpa bignonoides* in full sunlight is capable of assimilating 344·8 c.c. of carbon dioxide in a single hour.[3] When the vast amount of foliage in tropical and temperate climes is considered, it can readily be imagined that this plays no small part in the reoxygenation of the atmosphere; indeed it has been calculated[4] that leaf action alone would suffice for the purpose. There can be no doubt that the amount and luxuriance of vegetation does respond within certain limits to the amount of carbon dioxide in the atmosphere,[5] and existing coalfields probably represent Nature's attempt to reduce the percentage of this gas by locking it up as carbon beneath the crust of the earth.[6]

A second important regulator of the atmospheric carbon dioxide is to be found in the rocks of the earth's crust. T. C. Chamberlin[7] calculates that the carbon locked up in the sedimentary rocks of the earth's crust is 30,000 times as much as is now existing in the air, and he further estimates that 1620 million tons of carbon dioxide are being annually withdrawn from the air in the course of building up new sedimentary rocks.

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[1] Friend, *Science Progress*, 1912, 6, 393. See also von Fodor, *Hygienische Untersuchungen uber Luft, Boden und Wasser* (Viewig, 1882).

[2] We owe the discovery of this fact to Priestley in 1771, but Ingen-Housz was the first to show that light was essential to the process. See Ingen-Housz, *Annales de Physique*, 1784, 24, 44.

[3] H. T. Brown, *Nature*, 1899, 60, 479

[4] E. H. Cook, *Phil. Mag*, 5th series, 1882, 14, 387.

[5] See the researches of Dehérin and Maquerine; E. C. Teodoresco, *Rev. Gen. Bot.*, 1899, 2; J. B Farmer and S. E. Chandles, *Proc. Roy. Soc.*, 1902, 70, 413; H. T. Brown and F. Escombe, *ibid.*, 1902, 70, 397; 1905, 76, 118, E. Demoussy, *Compt rend.*, 1903, 136, 346; from which it appears the rate by assimilation of plants is within small limits proportional to the partial pressure of carbon dioxide; but if the latter gas is present in very great excess the leaves curl as if to avoid assimilating too much. According to Godlewski, the Polish botanist, assimilation reaches a maximum in the case of *Glyceria Spectabilia* with 9 per cent. of carbon dioxide. A further increase of the gas decreased the assimilation again. The maximum varies for different plants.

[6] Letts and Blake, *Proc. Roy. Dublin Soc*, 1899–1902, 9. 162

[7] T. C. Chamberlin, *J. Geol.*, 1899, 7, 682

Finally, the ocean serves as a vast regulator, as was first pointed out by Peligot [1] in 1855. Rain-water dissolves carbon dioxide from the air,[2] and on reaching the soil absorbs yet more, both in the free state and in combination as carbonates. The streams and rivers carry this away and discharge it into the sea.[3] There can be no doubt that each of these factors plays an important part in regulating the composition of the air, but the actual share borne by each will vary according to circumstances.

*Estimation of Atmospheric Carbon Dioxide.*—A convenient method is that of Pettenkofer,[4] which consists in introducing a standard solution of barium hydroxide into a large bottle containing several litres of the air to be examined. The bottle is shaken from time to time to keep the sides moistened with the solution, and after 5 or 6 hours the absorption of carbon dioxide may be regarded as complete. The baryta solution is decanted into a small stoppered bottle and allowed to stand until any suspended barium carbonate has settled. A portion of the clear liquid is then removed and titrated with dilute sulphuric acid, using phenolphthalein as indicator. The diminution in alkalinity due to combination with carbonic acid is thus measured, and from the data obtained the percentage of carbon dioxide in the atmosphere may easily be calculated.

The results obtained are frequently irregular and invariably indicate too high a percentage of carbon dioxide in consequence of the absorption of expired air from the operator during the titration. To obtain accurate results many precautions must be observed.[5]

Carbon dioxide may also be estimated volumetrically by absorption in concentrated potassium hydroxide solution from a volume of air. The diminution in volume is noted by direct measuring, and results of considerable accuracy can be obtained in this manner within a very few minutes.[6]

Gravimetric methods are, in general, more accurate, but require a considerable amount of apparatus, and take a longer time to execute. The simplest method [7] consists in slowly aspirating some 40 litres of air over caustic potash contained in U-tubes and noting the increase in weight. The air must first be dried by passage over concentrated sulphuric acid, which simultaneously removes any ammonia.

*The Physiological Significance of Carbon Dioxide.*—Carbon dioxide is a colourless, almost tasteless, and odourless gas, and it is consequently impossible by the unaided senses alone to detect its presence in the air. The odour of respired air is not due to carbon dioxide, but to other gases accompanying it, and the close, stuffy effect of ill-ventilated buildings is due to the same cause. From a physiological point of view, carbon dioxide is of as much direct importance to us as to our complementary organisms, the plants. " A certain percentage of carbon dioxide in the atmosphere is essential to our very existence from minute to minute; not only is it the normal stimulus to the respiratory centre, but it assists in the splitting up of oxyhæmoglobin in the tissues. If an animal is made to breathe a carbon dioxide free atmosphere, the normal circulating carbon dioxide in its blood is reduced, and there arises after a time a condition known as *acapnia*, in which the respiratory centre[1]—missing its customary fillip—goes on strike, stops breathing, and the result may be fatal; restore, however, the due proportion of carbon dioxide and the breathing is resumed."[2] In other words, the animal organism is so accustomed to breathe air containing traces of carbon dioxide that it cannot do without it.

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[1] Peligot, *Ann. Chim. Phys.*, 1855, [3], 44, 257.

[2] Both Levy and Fodor in their extensive researches found that after rain the carbon dioxide content of the air was reduced temporarily, showing it had dissolved in the rain.

[3] Schloesing, *Compt. rend.*, 1880, 90, 1410. See also *ibid*, 1872, 74, 1552; 1872, 75, 70; Müntz and Lainé, *ibid.*, 1911, 153, 1116.

[4] Pettenkofer, *J. Chem. Soc.*, 1858, 11, 292.

[5] See Blochmann, *Annalen*, 1887, 237, 39; Letts and Blake, *loc. cit.*; Walker, *Trans. Chem. Soc.*, 1900, 77, 1110.

[6] See Haldane, *J. Hygiene*, 1901, 1, 109.

[7] Saussure, *Pogg. Annalen*, 1830, 19, 391.

It is equally true that an excess of carbon dioxide is fatal to human life, although it is difficult to determine the exact amount that is so, inasmuch as it varies with a number of factors, such as the health and individuality of the person, and the time during which the gas is inspired.[3] In breweries and mineral-water factories large quantities of the gas are regularly inhaled by the men. Beadnell mentions that 20 per cent. of pure carbon dioxide has been inhaled for three hours without fatal results.[4] On the other hand, carbon dioxide from a candle or gas flame is harmful at much smaller concentrations.[5] Possibly this is due to the relatively large amount of moisture simultaneously produced, for Grandis,[6] in a series of experiments made upon the venous blood taken from the jugular vein of a dog, shows that dry air is capable of taking up more carbon dioxide from blood than damp air. Consequently, the lungs are less easily relieved in moist air, and the presence of carbon dioxide in the inspired air must have a proportionately more baneful influence. In 1893 Kronecker and Jordi[7] published an account of an interesting series of experiments performed on themselves with the direct object of determining how much carbon dioxide can be breathed with impunity in inspired air. The gaseous mixture was contained in a gas-holder of 40 litres capacity. It was observed that a mixture of equal parts of air and carbon dioxide rendered breathing impossible by causing spasms of the glottis. Thirty per cent. of carbon dioxide on being breathed for a minute changed the appearance of the person experimented upon, dyspnœa resulting. A 22 per cent. mixture caused less inconvenience. With an 8 per cent. mixture the breathing was ample, being slightly more than normal. This latter observation is in complete harmony with the recent work of Hough,[8] who shows that by breathing in a confined space of some 30 litres, healthy individuals attempt to secure an increased ventilation of their lungs by increasing the rate or depth or both of the respiratory efforts. In 1895, two years after the publication of Kronecker and Jordi's paper, J. S. Haldane[9] gave the results of some valuable experiments carried out upon his own person. From these he concluded that carbon dioxide is a cumulative poison, and that the symptoms depend upon the extent of saturation of hæmoglobin with it. During rest it is not until the corpuscles are about one-third saturated that the symptoms become sensible; headache and respiratory distress become pronounced on reaching half saturation. Haldane further concluded that when air containing carbon dioxide is breathed some 50 per cent. of that actually inhaled is absorbed. The maximum amount of carbon dioxide that the blood can absorb from an atmosphere containing a small but fixed percentage of it, depends upon two factors, viz. the relative affinities of hæmoglobin for oxygen and carbon dioxide, and the relative tension of these two gases in arterial blood. Upon breathing fresh air the disappearance of carbon dioxide from the blood is slower than its absorption was, and is due to the dissociation of carbonated hæmoglobin by the mass influence of the oxygen in the pulmonary capillaries and the consequent outward diffusion of the gas through the aveolar epithelium.

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[1] That carbon dioxide is an excitant to the respiratory centre was confirmed by Zuntz and Loewy (*Arch. Physiol.*, 1897, p. 379) and Rulot and Cuvelier (*Trav. lab. de L. Fredericq*, Liége, 1901, 6, 1).

[2] Beadnell, *J. Roy. Inst. Public Health*, 1913, 21, 3.

[3] This was emphasised by L. de Saint Martin, *Compt rend.*, 1893, 116, 260.

[4] Beadnell, *loc. cit.* See also p. 186.

[5] About 0·2 per cent. for a gas flame.

[6] V. Grandis, *Atti R. Accad. Lincei*, 1900, [5], 9, i., 224. See also W. Thomson (*VII. Inter. Congr. Appl. Science*, 1909, sec. viii., p. 154), who confirms this.

[7] Kronecker and Jordi, *Proc. Physiol. Soc.*, 1893, 21.

[8] T. Hough, *Amer. J. Physiol.*, 1911, 28, 369.

[9] J. S. Haldane, *J. Physiol.*, 1895, 18, 430.

From the foregoing it is clear that the effect of breathing air containing relatively large quantities of carbon dioxide is very similar to that produced by diminution of oxygen and by high altitudes, and it is no doubt due partly to the deficiency of the oxygen, but partly also to the direct influence of the carbon dioxide itself; in fact Haldane and Smith [1] regard this latter as the more potent cause of the hyperpnœa and headache which result.

The actual proportion of carbon dioxide that can be supported without inconvenience is seen to be much higher than is generally believed. It is impossible to fix with definiteness the limiting amount for safety, as this again depends upon the personal equation of the subject and upon the moisture and temperature obtaining at the time. It would appear, however, that from 8 to 10 per cent. of pure carbon dioxide may be inspired with impunity for many hours, and a slightly higher percentage for short periods. Above 10 per cent. the gas begins to have a narcotic effect, and at about 25 per cent. death may occur after several hours, although 50 per cent. may be breathed for a short time without fatal effects.[2]

**Water-Vapour.**[3]—The amount of moisture in the air is an exceedingly variable factor, and is usually expressed in terms of *relative humidity*, that is the ratio, expressed as a per cent., of the amount actually present to that which the air could hold if saturated at the same temperature. The *absolute humidity*, on the other hand, is the weight, in grams, of moisture contained in 1 c.cm. of air.

In the following table (p. 173) are given the numbers of grams of water-vapour contained in 1 cubic metre, saturated at various temperatures, under a normal pressure of 76 cms.[4]

It is seldom that the atmosphere is actually saturated with moisture, and the temperature to which it must be cooled, on any given occasion, in order that its contained moisture may effect its saturation, is termed the *dew-point.* This is an important point in meteorological studies, for our sensations as to the dryness or moistness of the air are influenced more by the relative than by the absolute humidity. Thus, for example, on a hot summer's day the air may feel very dry and yet contain more water-vapour than would be required for saturation on a cold winter's morning, under which latter conditions we should experience an acute sense of dampness.

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[1] J. Haldane and J. L. Smith, *J. Path. Bact.*, 1892, I, 168. See also H Rulot and L Cuvelier, *Trav. lab. de L. Fredericq*, Liége, 1901, 6, 1.

[2] Foster and Haldane, *Investigation of Mine Air*, p. 144.

[3] An interesting account of the subject is given by Simpson, *Nature*, 1923, III, Supplement to April 14, pp. v.–xii.

[4] As corrected by Dibbits (*Zeitsch. anal. Chem.*, 1876, 15, 121) from the results of Magnus (*Ann. Phys. Chem.*, 1843, 61, 247) and Regnault (*ibid.*, 1845, 65, 322).

| Temperature, ° C. | Magnus. | Regnault. |
|---|---|---|
| —20 | 1·046 | 1·058 |
| —10 | 2·317 | 2·299 |
| 0 | 4·788 | 4 868 |
| 5 | 6·725 | 6·789 |
| 10 | 9·310 | 9 356 |
| 15 | 12·716 | 12·738 |
| 20 | 17·152 | 17·147 |
| 30 | 30·131 | 30·079 |
| 40 | 50·735 | 50·677 |

The water-vapour of the atmosphere is an important factor in preserving equability of temperature, inasmuch as it absorbs a large portion of the heat radiated from the earth. Water-vapour has a density of 9 ($H=1$), whilst that of dry air is 14·4. In consequence of this the humidity of the air affects its pressure and is thus an important factor in connection with fluctuations in the height of the barometer. The presence of water-vapour in air exerts a pronounced retarding action on the rate of aeration of natural waters. For this reason metals corrode much more rapidly when submerged in water exposed to a dry atmosphere than when the air above is humid.

*Determination of Atmospheric Moisture.*—The amount of moisture in the atmosphere may be estimated gravimetrically by aspirating air through U-tubes containing some desiccating agent such as sulphuric acid or, better, phosphorus pentoxide, and noting the increase in weight. Calcium chloride may be used for approximate estimations, but for accurate work it is not efficient.[1]

A more rapid and convenient method consists in a determination of the dew-point by means of a hygrometer. One commonly used is that devised by Regnault,[2] and consists of a glass tube, the lower end of which is encased in a silver thimble. The tube contains ether, into which dips the bulb of a sensitive thermometer. Air is aspirated through the ether causing evaporation and cooling. The temperature is noted at which a film of moisture collects on the thimble, and again when it disappears after stopping the aspiration. The mean of these two data is taken as the dew-point.[3]

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[1] For the efficiency of the above drying agents, see Pettenkofer, *Annalen Suppl.*, 1863, 2, 29; Dibbits, *Zeitsch. anal. Chem.*, 1876, 15, 145; Morley, *ibid.*, 1885, 24, 533.

[2] Regnault, *Ann. Chim. Phys.*, 1845, 15, 129.

[3] For details of other types of hygrometers, including the wet and dry bulb thermometer, the reader is referred to text-books of Physics and Meteorology.

**Desiccation of Air.**—It is frequently necessary to dry the air for chemical and metallurgical processes. For example, air required to be ozonised for ventilating or sterilising purposes must first be dried; and the efficiency of a blast furnace in the production of pig-iron is greatly enhanced by the desiccation of the blast.[1] One convenient method [2] consists in cooling the air by passage through chambers fitted with pipes through which cooled brine from a refrigerator is passed. The moisture is deposited as ice on the tubes, the escaping air having been cooled to about −5° C. (23° F.), and its moisture content reduced to approximately 2·6 grams per kilogram of dry air.

In the Daubiné-Roy process [3] air is made to ascend a tower and during the process to pass through trays of calcium chloride, the temperature of which is kept low (namely, 4° to 5° C.) by means of water coolers. The limits of hydration range from the monohydrate to the octahydrate; thus

$$CaCl_2 . H_2O + 7H_2O \rightleftharpoons CaCl_2 . 8H_2O,$$

the monohydrate being periodically regenerated by passing hot gases through the tower at a temperature not exceeding 200° C.[4] Experience shows that 240 kilograms of the monohydrate spread out in a layer 24 cm. deep and cooled by tubes containing water to 4° or 5° C. will per hour desiccate 300 cubic metres of air percolating it from above downwards; it will continue to do this for 4 hours, reducing the humidity of the air from an average of about 15 grams of moisture per cubic metre to one of about 1·5 grams. To desiccate a gas to this extent by refrigeration would require a temperature of about −15° C.

For laboratory purposes small quantities of air are frequently dried by passage over anhydrous calcium chloride—which is a slightly more powerful desiccator than the monohydrate. A better reagent is sulphuric acid. Gases may be led directly through the concentrated acid or, better, through tubes or towers containing pumice, glass beads, or other suitable substances moistened with the acid. The concentrated acid reduces the moisture content to about 1 milligram in 4000 litres.[5]

The most powerful desiccator available to the chemist is phosphorus pentoxide. Prolonged exposure of a gas to this reagent, conveniently scattered over glass-wool, reduces the moisture content to about 1 milligram in 40,000 litres.[5]

**Atmospheric Ozone, Hydrogen Peroxide, and Organic Peroxides.**—For many years traces of oxidising substances have been known to exist in the atmosphere,[6] and have been variously characterised as ozone, hydrogen peroxide, and organic peroxides. Unfortunately early investigators failed to appreciate the fact that it is extremely difficult to distinguish between and severally estimate such minute traces of these substances as occur in the air, although but little difficulty occurs when they are present in larger amounts. It is also now known that oxides of nitrogen would vitiate the earlier tests, and as traces of these gases are likewise frequently present in the atmosphere, no little uncertainty has arisen as to the correct interpretation to be placed upon the majority of the results obtained by early workers.

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[1] See this series, Vol. IX., Part III.

[2] Gayley, *J. Iron Steel Inst.*, 1904, ii., 274; 1905, i., 256; *Trans. Amer. Inst Mining Eng.*, 1904, 35, 746; 1905, 36, 315.

[3] Daubiné and Roy, *Bull. Soc. Ind. Min.*, 1910, 11, 397, 479; *J. Iron Steel Inst.*, 1911, 83, 28.

[4] For further details, see this series, Vol. IX., Part III.

[5] Morley, *Amer. J. Sci.*, 1887, 34, 200.

[6] Struve, in 1869, appears to have been the first to detect what he believed to be hydrogen peroxide in the air, and Schone (*Ber.*, 1874, 7, 1695; 1893, 23, 3011; 1894, 27, 1233; *Zeitsch. anal. Chem.*, 1894, 33, 137) proved the occurrence of some oxidising material in dew, rain, and snow. Ilosvay (*Ber.*, 1894, 27, 920) regarded Schone's evidence as incomplete.

This confusion is further enhanced by the fact, which has only recently been ascertained with certainty, that hydrogen peroxide sometimes decomposes, yielding ozone and water (*vide infra*).

In the following table are given a few of the more important results of the so-called determinations of ozone in the atmosphere. The data prior to 1917 should be interpreted as representing the amounts of oxidising substances expressed as milligrams of ozone per cubic metre of air.

### PERCENTAGE OF OXIDISING MATERIAL IN THE ATMOSPHERE.

| Oxidising Material expressed as Milligrams of Ozone in one Cubic Metre of Air. | Authority. |
|---|---|
| About 2 8 milligrams . . | Houzeau (*Ann. Chim. Phys.*, 1872, (4), **27**, 5; *Compt. rend.*, 1872, **74**, 712). |
| 10–100 milligrams . . . | Schöne (*Brochure*, Moscow, 1897). |
| At an altitude of 1050 metres, 0·035 to 0·039 milligram, rising to 0·094 milligram at 3020 metres. | Thierry (*Compt. rend.*, 1897, **124**, 460). |
| 0·01–0·03 milligram . . . | H. de Varigny (*Smithsonian and Miscell. Coll.*, **39**, 27). |
| By one method 31·6 to 158 milligrams; by a second method, 8·0 to 34 milligrams. | Hatcher and Arny (*Amer. J. Pharm.*, 1900, **72**, 9). |
| 4·5 milligrams in 100 kilograms of air (equivalent to 0·06 milligram in one cubic metre), the proportion being independent of of the altitude. | R. Lespieau (*Bull. Soc. Chim.*, 1906, [3], **35**, 616). |
| Up to an altitude of 8000 feet, the ozone was less than 0 003 milligram. Above this and up to 10 miles the ozone lay between 0·1 and 0·4 milligram. | W. Hayhurst and J. N. Pring (*Trans. Chem. Soc.*, 1910, **97**, 868). |
| 2·5 volumes per million volumes of air over Britain. In the Alps a mean value of 2·5 volumes was found at an altitude of 2100 metres and 4 7 at 3580 metres. | Pring, *Proc. Roy. Soc.*, 1914, A, **90**, 204. |
| No ozone found in 14 tests between July 1916 and January 1917. | Usher and Rao (*Trans. Chem. Soc.*, 1917, **111**, 799). |

Hayhurst and Pring were careful to introduce a correction for oxides of nitrogen, but did not distinguish between ozone and hydrogen peroxide. Usher and Rao appear to have eliminated all oxidisers except ozone, and it is remarkable that they should have discovered no ozone whatever in their series of experiments. In the neighbourhood of London, Reynolds[1] finds one volume of ozone in about 20 million of air. This amount is greatly increased after a thunderstorm. From a study of the absorption of ultra-violet light by ozone, combined with measurements of the sun's light transmitted by the atmosphere, the conclusion has been reached[2] that, if the ozone were equally distributed throughout the air, its amount would equal 0·6 c.c. per cubic metre, or 6 parts of ozone per 10 million of air.

*Hydrogen peroxide* is produced in nature in a variety of ways. According to Dixon[3] it occurs as a product of evaporation of water, and it has recently been shown that moist oxygen, when exposed to ultra-violet light, yields distinct traces of hydrogen peroxide in the course of seven or eight days, according to the temperature.[4]

In 1909 Kernbaum[5] produced hydrogen peroxide by exposing water to the action of penetrating rays from radium salts, and two years later Kailan[6] confirmed this result. How much of the atmospheric peroxide is due to the above causes it is difficult to say. Undoubtedly most of the peroxide, and certainly the bulk of the organic peroxides of the air, originate from the direct action of air, moisture, and sunlight upon the essential oils and other organic emanations of plants.[7]

*Ozone* may be produced in nature in a variety of ways. When water evaporates into the air, particularly when thrown up in the form of spray, traces of ozone are produced, and this accounts for its presence in the fresh sea breeze and in the neighbourhood of waterfalls.[8] The refreshing odour after a shower of rain or the passing of a water-cart over the road is probably due to ozone. The gas is also produced by silent electric discharges from thunder-clouds and accompanies the flash discharge of lightning. In 1886 Wurster[9] called attention to the fact that ozone may result from the action of sunlight upon the clouds, and since then the results of numerous researches have pointed to the fact that the bulk of the atmospheric ozone is yielded by the action of ultra-violet rays from the sun's light upon the oxygen in the upper reaches of the air.[1] This would account for the observation of Thierry [2] and of W. Hayhurst and Pring [3] that the amount of oxidising material increases with the altitude. In clear weather ozone is probably produced also by the direct action of the sun's rays upon the lower layers of the atmosphere.[4] These observations probably explain why R. Lespieau [5] found that in his experiments the proportion of atmospheric ozone was independent of the altitude.

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[1] Reynolds, *Nature*, 1923, 112, 396.

[2] C. Fabry and H Buisson, *Compt. rend.*, 1913, 156, 782. See also F. Krüger and M. Moeller, *Physikal. Zeitsch.*, 1912, 13, 729; *Festschrift, W. Nernst*, 1912, 240, 251; Holmes, *Amer. Chem. J.*, 1912, 47, 497; W. Hallwachs, *Ann Physik*, 1909, [4], 30, 602; E. Meyer, *ibid.*, 1903, [4], 12. 849; and Hartley, *Trans. Chem. Soc.*, 1881, 39, 60, 111.

[3] Dixon, *Trans. Chem. Soc.*, 1886, 49, 108; Ramsay (*Proc. Chem. Soc.*, 1886, 2, 225) found a substance capable of reducing potassium permanganate to be present in water that had evaporated into the air. N. Smith (*Trans. Chem Soc.*, 1909, 89, 481) has been unable to confirm Dixon's result.

[4] Bieber, *Ann. Physik*, 1912, 39, 1313.

[5] Kernbaum. *Compt. rend.*, 1909, 148, 705; 1909, 149, 116, 273.

[6] Kailan, *Monatsh.*, 1911, 32, 1019. In this connection it is interesting to note that H. J. M. Creighton (*Trans. Nova Scotia Inst. Sci.*, 1908, 12, 34) found that hydrogen peroxide was decomposed by radium rays in the dark, yielding traces of ozone. This emphasises the close connection existing between peroxides and ozone.

[7] See the numerous researches of Kingzett, summarised in his work *Nature's Hygiene*, 5th ed., 1907 (Baillière & Co.).

[8] See Bellucci (*Gazzetta*, 1876, 6, 88), who summarises the data available up to his time; also H. Duphil, *Soc. sci. Stat. Zool. d'Arcachon Univ. Bordeaux, Trav. Lab.*, 1900–1901, p. 51, on the sea air of Arcachon.

[9] Wurster, *Ber.*, 1886, 19, 3208.

Ozone has recently been shown [6] to result from the action of rays from radio-active substances upon oxygen, but to what extent atmospheric ozone is attributable to this cause is uncertain. Probably a small quantity of ozone is produced by the slow oxidation of the essential oils and other organic exhalations of plants,[7] and Duphil [8] has recently observed an excess of ozone in the air of the maritime pine forests in the neighbourhood of Bordeaux.

From the point of view of ventilation, ozone and peroxides are of interest inasmuch as they impart a crispness or freshness to the air, and the fact that they are readily decomposed by heat is probably one of the causes of the "flatness" of heated air. The well-known Sanitas preparations are essentially solutions of hydrogen peroxide and of different organic peroxides. There can be no doubt that in nature the presence of hydrogen peroxide is an important factor in removing fœtid and putrid matter from the atmosphere. Bosisto [9] has calculated that 96,877,440,000 gallons of eucalyptus oil "are held continually at one and the same moment in the leaves of trees massed together and occupying a belt of country over which the hot winds blow" in New South Wales and South Australia alone. Kingzett concludes that this amount of eucalyptus oil "can and must produce in the atmosphere surrounding the forests no less than 92,785,023 tons of peroxide of hydrogen, and about 507,587,945 tons of the soluble camphor, not to mention the other products of oxidation."

*Detection of Atmospheric Ozone.*—Schönbein's method hinges on the fact that since ozone liberates iodine from potassium iodide, starch-iodide papers [10] are readily turned blue in its presence. But inasmuch as peroxides of hydrogen and nitrogen have a like effect, the test is valueless unless the absence of these other substances can be proved.[1] Houzeau[2] therefore recommended a litmus-iodide paper.[3] Nitrogen peroxide liberates iodine but, unlike ozone, will not simultaneously liberate free alkali, so that the litmus either remains unchanged or is slightly reddened. Ozone, on the other hand, not only liberates iodine but alkali which turns the litmus blue. The main disadvantage of this method lies in the tendency of the iodine to mask the colour of the litmus, and thus render any change in the latter difficult to detect. It is true that hydrogen peroxide likewise liberates iodine, but by first passing the air over chromic acid,[4] hydrogen peroxide may be effectively removed[5] whilst the ozone is not affected.[6] Filter paper soaked in an alcoholic solution of tetramethyl base[7] has been recommended, since the paper becomes violet with ozone, yellow with nitrous fumes, but remains unaltered in contact with hydrogen peroxide. The reaction, however, does not appear to be sufficiently sensitive[8] for the tests under discussion.

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[1] F. Fischer and F. Braehmer, *Ber.*, 1905, 38, 2633 ; F. Russ, *Zeitsch. Elektrochem.*, 1906, 12, 409 ; Henriet and Bonyssy, *Compt. rend.*, 1908, 147, 977 ; F. Fischer, *ibid*, 1909, 42, 2228 ; *Physikal. Zeitsch*, 1909, 10, 453 ; E. van Aubel, *Compt. rend.*, 1909, 149, 983 ; 1909, 150, 96 ; M. G. Johnson and D. M'Intosh, *J Amer. Chem. Soc.*, 1909, 31, 146 ; W. J. Humphreys, *Astrophys. J.*, 1910, 32, 97 ; W. G. Chlopin, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 554. It is interesting to note that the same rays accelerate the decomposition of ozone when once it has been formed. Eva von Bahr, *Ann. Physik*, 1910, [4], 33, 598.

[2] Thierry, *Compt. rend*, 1897, 124, 460.

[3] Hayhurst and Pring, *Trans. Chem Soc.*, 1910, 97, 868. See also Holmes, *Amer. Chem. J.*, 1912, 47, 497.

[4] W. Henriet and Bonyssy, *Compt. rend*, 1908, 146, 977 ; H. N. Holmes, *Amer. Chem J.*, 1912, 47, 497. Contrast Bayeux, *Compt. rend*, 1919, 169, 957.

[5] Lespieau, *Bull Soc. Chim*, 1906, [3], 35, 616.

[6] Curie (*Compt. rend.*, 1899, 129, 823) confirmed by R. Nasini and M. G. Levi, *Atti. R. Accad. Lincei*, 1908, [5], 17, ii, 46. See also Richarz and Schenck, *Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 12, 1,102 ; 1904, 13, 490.

[7] Cloëz (*Compt. rend.*, 1856, 43, 38 ; 1861, 52, 527) found that starch iodide papers are coloured by the exhalations of certain trees indicating the presence of some oxidiser, though not necessarily of ozone.

[8] Duphil, *loc. cit.*

[9] Bosisto, quoted by Kingzett, *Nature's Hygiene* (Baillière, 1907), p. 488.

[10] Unglazed (filter) paper soaked in a solution containing starch and potassium iodide.

*Estimation of Atmospheric Ozone.*—The majority of investigators in the past have relied upon the liberation of iodine from potassium iodide solution as a convenient method of estimating ozone. Thus Hatcher and Arny[9] aspirated air through potassium iodide solution, whereby first iodine and subsequently potassium iodate are formed, as indicated in the following equations:

$$2KI+H_2O+O_3=2KOH+O_2+I_2;$$
$$2KOH+I_2=KIO+KI+H_2O;$$
$$3KIO=KIO_3+2KI.$$

On acidifying, free iodine is again liberated according to the equation

$$KIO_3+5KI+3H_2SO_4=3K_2SO_4+3I_2+3H_2O,$$

and is estimated by titration with thiosulphate. This method does not distinguish between ozone and hydrogen peroxide, neither does it guard against the disturbing influence of nitrogen peroxide. This difficulty was surmounted by Hayhurst and Pring,[10] who estimated the free alkali in addition to the iodine and were thus able to introduce a correction for the peroxide of nitrogen, although they were unable to distinguish between hydrogen peroxide and ozone.

If, however, the air is first freed from peroxides of nitrogen and hydrogen, the liberated iodine owes its presence entirely to ozone. Keiser and M'Master,[11] therefore, recommend the passage of air through a solution of potassium permanganate prior to testing for ozone, as this gas is not affected by the permanganate whereas the two peroxides are destroyed.

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[1] In consequence of this Moffatt's results (*Brit. Assoc. Reports*, 1870, p. 61) are inconclusive.

[2] Houzeau, *Ann. Chim. Phys.*, 1872, [4], 27, 5; *Compt. rend.*, 1872, 74, 712.

[3] Unglazed (filter) paper containing litmus and potassium iodide.

[4] Or over solid chromic anhydride crystals.

[5] Engler and Wild, *Ber.*, 1896, 29, 1940.

[6] Usher and Rao, *Trans. Chem. Soc.*, 1917, 111, 799.

[7] Wurster, *Ber.*, 1888, 21, 921; Arnold and Mentzel, *Ber.*, 1902, 35, 1324, 2902.

[8] Hayhurst and Pring, *Trans. Chem. Soc.*, 1910, 97, 868; also Pring, *Chem News*, 1914, 109, 73.

[9] Hatcher and Arny, *Amer. J. Pharm.*, 1900, 72, 9.

[10] Hayhurst and Pring, *loc. cit.*

[11] Keiser and M'Master, *Amer. Chem. J.*, 1908, 39, 98.

Potassium arsenite is oxidised by ozone to arsenate, and may be substituted for potassium iodide in the previous method[1]; although here again it is necessary to first remove the peroxides of hydrogen and nitrogen from the air prior to testing.

A method that appears capable of greater accuracy and less open to criticism than any of the foregoing is that devised by Usher and Rao.[2] It hinges on the fact that ozone oxidises aqueous solutions of alkali nitrites to nitrates, the reaction proceeding quantitatively according to the equation

$$NaNO_2+O_3=NaNO_3+O_2.$$

Two samples of air are taken and collected in large stoppered bottles of some 7-litres capacity. One sample is admitted through two tubes containing respectively chromic anhydride and powdered manganese dioxide, the second sample through a tube containing chromic anhydride only. They are then shaken with a dilute standard solution of sodium nitrite rendered slightly alkaline, and the nitrite content subsequently determined colorimetrically.[3]

The first sample of air contains only nitrogen peroxide, the hydrogen peroxide and ozone having been destroyed by the chromic acid and manganese dioxide respectively. The increase in the amount of nitrite in the bottle thus gives the measure of the nitrogen peroxide absorbed.

The second sample contains ozone and nitrogen peroxide and the difference between the nitrite contents of the two bottles is equivalent to the ozone present. The presence in the air of ammonia, sulphur dioxide, and hydrogen sulphide does not interfere with the estimation of ozone and nitrogen peroxide by this method as all three gases are completely absorbed during passage through the chromic anhydride tube.

**Nitrogen and the Inert Gases** function mainly as diluents in the atmosphere, exerting a restraining influence upon the chemical activity of the oxygen. They exist in approximately the following proportions by volume:

| | |
|---|---|
| Nitrogen[4] . . . . | 78·06 per cent. |
| Argon[5] . . . . | 0 941 ,, |
| Helium[5] . . . . | 1 part in 185,000 |
| Neon[5] . . . . . | 1 ,, 55,000 |
| Krypton[5] . . . . | 1 ,, 20,000,000 |
| Xenon[5] . . . . | 1 ,, 170,000,000 |

The nitrogen is not entirely inert, however. During thunderstorms it can unite with the oxygen yielding, in the presence of the moisture, both nitrous and nitric acids.[6] Again, certain plants, such as the *leguminosæ*, owing to the presence of bacteria in their root-tubercles, are liable to assimilate nitrogen direct from the atmosphere, and certain bacteria in the soil act similarly. These reactions, however, are relatively of minor importance. The inert gases, on the other hand, appear to be absolutely inert and to enter into no atmospheric chemical reactions whatever.

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[1] Hatcher and Arny, *loc. cit.*

[2] Usher and Rao, *Trans. Chem. Soc.*, 1917, 111, 799.

[3] The Griess-Ilosvay method is recommended. See Sutton, *Volumetric Analysis*, 9th ed., p. 449.

[4] Leduc, *Compt. rend.*, 1896, 123, 805.

[5] See also this series, Vol. I., Part II. This Vol., p. 158.

[6] See pp. 52 and 217.

To the presence of krypton in the atmosphere is due the phenomenon known as the *aurora borealis* or northern lights. The inert gases find their way into the atmosphere through escape from mineral springs, and, in the case of helium, through the disintegration of radium.

**Hydrogen.**—The proportion of hydrogen in the air varies considerably, although it is always minute.[1] The hydrogen content, however, is believed [2] to increase with the altitude. In the spectrum of the aurora the intensity of the nitrogen lines diminishes and that of the hydrogen lines increases with increasing height. The hydrogen originates from volcanic emanations as well as from bacterial activity.

**Carbon Monoxide** is scarcely a normal constituent of fresh air, although it occurs in the minutest traces in the air of towns and of volcanic districts. It also occurs in railway tunnels [3] and even in well-ventilated coal mines to the extent of 0·002 to 0·004 per cent.[4] It is a most dangerous gas, 0·43 per cent. being fatal to man [5] in a short time. Even 0·2 per cent. may prove fatal if breathed for a long time. Headaches and other unpleasant symptoms are produced by concentrations ranging from 0·03 upwards.

Carbon monoxide is produced by the incomplete combustion of fuel, and since it readily diffuses through heated iron, it frequently happens that iron stoves, used for heating purposes in large buildings, constitute a source of this gas in the air, the carbon monoxide diffusing into the building, instead of being carried up the chimney or burned.

Ordinary coal-gas may contain anything up to 20 per cent. of carbon monoxide, and an escape of coal-gas into the air produces a proportionate vitiation of the same.

**Miscellaneous Substances in the Air.**—That oxidisable organic compounds are present in the air has been known for many years, the Swedish chemist Berzelius [6] being one of the first to refer to the fact. This explains the observation of Levy and Henriet [7] that air freed from carbon dioxide by treatment with caustic potash generates it again on standing, owing to the oxidation of the organic matter. The exact nature of the organic compounds present in the air is uncertain. Gautier [8] finds 1·21 parts of marsh gas or methane in 10,000 of Parisian air, and 0·17 of benzene and its analogues. Formaldehyde and other organic derivatives have been detected in minute quantities.[9] The unhealthy air of marshes is usually attributed to the volatile organic substances produced by the decomposition of the vegetation. Analyses of the gases evolved from marsh land show that methane constitutes in general more than half the total volume of gases,[1] the remainder consisting of carbon dioxide, nitrogen, and in some cases of oxygen and hydrogen.

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[1] Gautier (*Compt. rend.*, 1902, 131, 86, 535, 647, 1276) found 0·02 per cent. by volume, but Rayleigh (*Phil. Mag.*, 1901, [6], 1, 100; 1902, 3, 416) found only 0·003 per cent., and Dewar (*Proc. Roy. Soc.*, 1901, 68, 360) 0·001 per cent. Claude (*Compt. rend.*, 1909, 148, 1454) found less than 0·0001 per cent.; Ramsay (*Proc. Roy. Soc.*, 1905, [A], 76, 111) gives an equally low figure. See also Coates, *ibid.*, 1906, [A], 78, 479.

[2] Wegener, *Zeitsch. anorg. Chem.*, 1912, 75, 107; *Physikal. Zeitsch.*, 1911, 12, 170, 214.

[3] See p. 183.

[4] Mahler and Denet, *Compt. rend.*, 1910, 151, 645.

[5] Mosso, *J. Gaslighting*, 1902, 80, 1334.

[6] Berzelius, *Jahrbuch*, 1835, 22, 47.

[7] Levy and Henriet, *Compt. rend.*, 1889, 126, 1651; 1898, 127, 353.

[8] Gautier, *Compt. rend.*, 1900, 131, 535.

[9] Henriet, *ibid.*, 1904, 138, 203, 1272; 1904, 139, 67; 1903, 136, 1465. Frillat, *Bull. Soc. chim.*, 1905, 33, 386, 393.

Oxides of nitrogen and free nitric acid occur in traces in the air, the former owing their existence [2] to the combination of oxygen and nitrogen under the influence of lightning flashes, and possibly also to a much smaller degree to the oxidation of ammonia. These oxides unite with water, yielding nitric acid.

During thundery weather accompanied by very little rain 1 part of oxides of nitrogen in 4 or 5 million of air has been found.[3]

Ammonia, mainly as carbonate but also as nitrate, is present in the air, and originates in the decomposition of organic nitrogenous substances. H. T. Brown [4] found the air at Burton-on-Trent, during the years 1869 to 1870, to contain from 0·04 to 0 09 parts of ammonium carbonate in 10,000 of air. The analysis of rain-water [5] shows the presence of ammonium nitrate in appreciable quantities.

Sulphur compounds are detectable in the neighbourhood of active volcanoes and in towns and cities where much coal is burned. Thus at Lille, Ladureau [6] found 1·8 c.c. of sulphur dioxide in 1 cubic metre of air, which corresponds to 0·018 parts per 10,000 of air. Sulphuretted hydrogen is present in traces in coal-gas, and in the neighbourhood of decaying organic matter containing sulphur. It would appear that as much as 2·0 parts of this gas per 10,000 of air have no deleterious action upon the system, even if breathed for protracted periods.[7] All of these sulphur compounds are rapidly oxidised to sulphuric acid, which may or may not be neutralised by the ammonia of the air yielding ammonium sulphate. Warington [8] found the equivalent of 17·26 lb. of sulphur trioxide fell annually on each acre of land at Rothamsted, and this may be taken as a fair average, for Miller [9] gives 20·89 lb. for Sicily, and Gray [10] 15·2 lb. as the mean for four and a half years of observation in New Zealand.

**Soil Atmosphere.**[11]—By soil atmosphere is understood the air filling the pores between the particles of the soil mass. Although part of the ordinary atmosphere, its composition is influenced by two opposing forces. On the one hand the various organisms of the soil abstract the oxygen and evolve carbon dioxide; on the other hand gaseous interchange with the outside air, brought about by diffusion and other processes, tends to restore the normal oxygen content of the atmosphere. The net result, therefore, is determined by the difference in velocity between these two processes.[12]

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[1] Hoppe-Seyler, *Zeitsch. physiol Chem.*, 1886, 10, 201.

[2] Hayhurst and Pring, *Trans Chem. Soc.*, 1910, 97, 968.

[3] Usher and Rao, *Trans. Chem. Soc.*, 1917, 111, 799.

[4] H. T. Brown, *Proc. Roy. Soc.*, 1870, 18, 286.

[5] Warington, *Trans. Chem. Soc.*, 1889, 55, 537. See also p. 217.

[6] Ladureau, *Ann. Chim. Phys.*, 5 series, 1883, 29, 427. See also Witz, *Compt. rend.*, 1885, 100, 1358.

[7] J. Habermann, W. Kulka, and E. Homma, *Zeit. Anal. Chem.*, 1911, 50, 1.

[8] R. Warington, *Trans. Chem. Soc*, 1887, 51, 500. See also data given by Rideal, *Proc. Paint and Varnish Soc.*, 1914, No. 3 [9] N H. J. Miller, *J. Agric. Sci.*, 1905, 1, 292.

[10] G. Gray, *Rept. Australasian Assoc. Adv. Science*, 1881, 1, 138

[11] For early researches on this subject, see Boussingault and Lewy, *Ann. Chim. Phys.*, 1853, [3], 37, 1; Schloesing, *Compt. rend*, 1889, 109, 618, 620, 673; Kissling and Fleischer, *Landw. Jahrbücher*, 1891, 20, 876.

[12] The subject has been studied by a considerable number of investigators since the middle of last century. A useful summary is given by Russell and Appleyard, *J. Agric. Sci.*, 1915, 7, part i., p. 1.

Analyses of the soil atmosphere show that it suffers greater fluctuations in composition than ordinary air. As a rule it contains less oxygen, but nearly ten times as much carbon dioxide as the air, as shown by the following data:[1]

| | Soil atmosphere. | Ordinary air. | |
|---|---|---|---|
| Carbon dioxide . . . . | 0·25 | 0·03 | by volume |
| Oxygen . . . . . | 20·60 | 21·00 | ,, |
| | 20·85 | 21·03 | |

Usually the sum of these two gases in the soil atmosphere is only slightly less than that in the air although at periods when nitrates rapidly increase, and in water-logged soils, there is a perceptible reduction in oxygen.

In addition to this free atmosphere there is a second soil atmosphere, consisting mainly of carbon dioxide and nitrogen, with practically no oxygen, which is dissolved in the water and colloids of the soil. The existence of this second atmosphere is important, in that it renders possible the existence of anærobic organisms in the soil.[2]

**Mine Air.**—The air in mines has been made the subject of considerable investigation. Freshly hewn coal evolves methane and other gases, and absorbs or occludes gases from the air, oxygen being taken up rather more rapidly than nitrogen. This is well exemplified by the following table which gives the relative proportions of oxygen, nitrogen, carbon dioxide, and methane contained in samples of freshly hewn coal, and in other samples of the same coal after prolonged exposure to air.[3]

| | Freshly hewn Coal | Coal exposed to Air. |
|---|---|---|
| Oxygen . . . . | 8·8 | 23·8 |
| Nitrogen . . . | 44·7 | 71·4 |
| Carbon dioxide . . | 1·6 | 1·18 |
| Methane . . . | 44·6 | 3·5 |

It is not surprising, therefore, that the air of mines should exhibit a deficiency in oxygen and an increase in the percentage of carbon compounds. Analyses of air[4] taken at different levels in a Scottish mine, are given by Whalley as follows:

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[1] Russell and Appleyard, *loc cit.* See also Wollny, *Forschungen auf dem Gebiete der Agrikulturphysik*, 1880 3, 1; 1881, 4, 1; 1886, 9, 165; 1889, 12, 396; 1890, 13, 231. Ebermayer, *ibid.*, 1878, 1, 158; 1890, 13, 15. Hannen, *ibid.*, 1892, 15, 6, Moller, *ibid.*, 1879, 2, 329.

[2] The radio-activity of subsoil air is discussed by Castello and Fernández, *Anal. Fis. Quim*, 1913, 11, 167, 294; Satterly, *Proc. Camb. Phil. Soc.*, 1911, 16, 336; Joly and Smyth, *Sci. Proc. Roy. Dublin Soc.*, 1911, 13, 148; Sanderson, *Amer. J. Sci.*, 1911, 32, 69; Gockel, *Physikal. Zeitsch*, 1908, 9, 304.

[3] Bedson, *Trans. Fed. Inst. Min. Eng.*, Aug. 1902.

[4] See also Moureu and Lepape, *Compt. rend.*, 1911, 153, 849, 1043.

| | Oxygen. | Nitrogen. | Carbon Dioxide. |
|---|---|---|---|
| Near the floor . . | 13·13 | 82·28 | 4 56 |
| Near the roof . . | 20·08 | 79·2 | 0 69 |
| Near the coal face . . | 18·97 | 79·8 | 1·21 |

**Tunnel Air.**—The air in tunnels, through which coal-fired locomotives pass, contains many impurities in exceptional quantities, chief amongst which are sulphur dioxide, carbon monoxide and dioxide.[1]

In the following table are given the average amounts of sulphur dioxide and carbon monoxide in 10,000 parts of air as found in tunnels in Baltimore, U.S.A., through which steam and electric locomotives, respectively, pass.[2]

| | Steam Locos. | Electric Locos. |
|---|---|---|
| $SO_2$ . . | 0·151 | 0·029 |
| CO . . | 2·67 | 0·25 |

**Dust.**—Another important constituent is the so-called dust, the presence of which must have been noticed for ages. It is a highly complex mixture of inorganic, lifeless organic, and living organic matter. The first named originates partly from natural causes, such as wind and volcanic activity. Thus the writers have in their possession sand found at Las Palmas, which had been blown over 100 miles of sea from the Great Sahara Desert. During the great eruption of Krakatoa in 1883 vast quantities of dust were hurled into the air, and for several years afterwards the sunsets were remarkable for their glow, indicating that the particles of dust continued to float in the atmosphere for a proportionately long time. In a spectroscopic analysis of dust Hartley [3] has found a large number of inorganic substances that must have travelled from many parts of the earth very wide distances apart. Among the inorganic particles are minute crystals, for example, of sodium chloride [4] which owe their origin to sea spray, and may be carried inland for hundreds of miles; sodium sulphate particles, probably formed by the interaction of the sodium chloride with sulphurous acid vapour and subsequent oxidation, are also present, and cause the ready crystallisation of supersaturated solutions of sodium sulphate when exposed to the air. A good deal of atmospheric dust is of artificial production, due to the combustion of coal, to factories, etc., thus a massive bank of smoke in London has been seen to rise to a height of several thousand feet and be carried away in a sunlight-obscuring trail fifty miles in length.[1] Knecht has examined Manchester soot and finds in it some 50 per cent. of substances that are not carbon, such as salts of ammonium, calcium sulphate, and the like. Even the purest atmospheres contain particles of dust, and Aitken doubts if a perfectly dust-free atmosphere can exist. It is rare to find air with fewer than 100 particles of dust per c.c. In London it may rise to 100,000 or even 150,000 particles per c.c. Fridlander [2] found 2000 particles per c.c. of air on crossing the Atlantic Ocean, on the Mediterranean Sea 875, the lowest results being obtained on the Pacific and Indian Oceans, the particles numbering 245 and 243 respectively. Similarly, Melander [3] has studied the dust of Swiss air, but never found fewer than 300 particles per c.c.

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[1] See analyses by Longmuir, *J. Iron Steel Inst.*, 1911, i., 147.

[2] Seidell and Meserve, *U.S. Public Health Service, Hygienic Lab. Bull.*, No. 92, 1914, pp. 1–47.

[3] Kingzett, *opus cit.*, p. 490; W. N. Hartley and Ramage, *Proc. Roy. Soc.*, 1901, 68, 97; W. N. Hartley, *Proc. Roy. Dub. Soc.*, 1899–1902, 9, 457; *Proc. Roy. Soc.*, 1911, [A], 85, 271.

[4] Gautier, *Compt. rend.*, 1899, 128, 715. See also Hartley, *Proc. Roy. Soc.*, 1911, [A], 85, 271.

In the following table are given some of the data obtained by Owens [4] on the Norfolk Coast in a series of tests during August 1921 :—

### EXAMINATION OF AIR AT HOLME, NORFOLK.

(Owens, 1922.)

| Date August 1921. | Number of Particles per c.c. of Air. | Average Diameter (Microns). | Remarks. |
|---|---|---|---|
| 13 | 150 | 0·5 | Fine dark-coloured dust. No crystals. |
| 18 | 310 | 0·5 to 0·7 | Very uniform in size. No crystals. |
| 20 | 145 | 0 5 | Some crystals. |
| 25 | 304 | 0·5 | All rounded. Some perfect spheres. |
| 28 | 17 | 0·5 | Irregular. |

It is interesting in this connection to recall the experiments of Lehmann and his colleagues [5] who demonstrated quite recently that when a dust-laden air is breathed through the nose, approximately 40 per cent. of the dust remains in the system, either in the lungs or stomach, the remaining 60 per cent. being either respired or retained by the nose and mouth. If, however, the subject breathes through the mouth some 80 per cent. is retained by the body. This illustrates the importance of breathing through the nose, but it also illustrates the necessity of reducing the dust in the atmospheres of public rooms and dwellings to the smallest possible amount, as no matter how careful the subject is, some of the dust finds its way into the system.

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[1] See Coles Finch, *Water* (Alston Rivers, Ltd., 1908), p. 61 ; Rideal, *Proc. Paint and Varnish Soc.*, 1914, No. 3 ; Ruston, *J. Roy. Sanitary Inst.*, 1912, 33, 433.

[2] E. D. Fridlander, *Quart. J. Roy. Met. Soc.*, July, 1896.

[3] G. Melander, *La Condensation de la Vapeur d'Eau dans l'Atmosphere* (Helsingfors, 1897). See also Owens, *J Soc. Chem. Ind.*, 1922, 41, 438 R.

[4] Owens, *Proc. Roy. Soc.*, 1922, [A], 101, 18. See also Whipple, *Amer. J. Public Health*, 1913, 3, 1139. Bill, *J. Ind. Hygiene*, 1919, 1, 7.

[5] K. B. Lehmann, Y. Saito, and W. Gfiorer (*Archiv. Hygiene*, 1912, 75, 152–159).

**Bacteriology of Air.**—Fresh air contains a number of micro-organisms, Uffelmann[1] finding some 250 per cubic metre of air in the open fields near Rostock, and 450 in the University yard. Most of these, however, are probably spores of moulds and yeasts, and of the bacteria proper in the air the majority are saprophytic and not disease producing.[2] Kijanitznan[3] found that by supplying sterilised air to rabbits the metabolic functions were reduced and the animals wasted away. It seems reasonable to conclude, therefore, that the atmospheric micro-organisms play a useful part in metabolism. Possibly their special function is to provide the blood with ferments for oxidation purposes, since in their absence the oxidation changes in the organism appear to be diminished, and an accumulation of waste products or leucomaines occurs. Sterilisation of perfectly fresh air supplied to buildings is not therefore to be recommended, and herein no doubt lies a potent cause of the depressing effect produced by air that has been artificially heated—the consequent sterilisation, coupled with the destruction of ozone and peroxides, producing a lack of crispness Whilst the spores of moulds are light and can remain floating in the air, the bacteria are heavy and are usually found adhering to particles of dust. Consequently the air over the sea and high mountains is poorer in bacteria than that in towns.

The dust of public buildings contains vast numbers of micro-organisms, and many of these are not merely detrimental but positively dangerous. Thus Cornet[4] found the tubercle bacillus in the dust of dwellings, and showed that this may easily prove a source of infection. Chour[5] examined dust from infected barracks and found no fewer than 14 million typhoid bacilli per gram of dust. Clearly, therefore, either all dust should be removed, or else all operations tending to raise the dust should be avoided during occupancy of inhabited buildings.

Buchan mentions that[6] "in an experiment in the High School at Dundee with one of the classes in a room, under ordinary conditions the organisms amounted to 11 per litre. Upon the boys being told to stamp with their feet upon the floor, a cloud of dust was raised, when upon being tested the atmosphere of the room showed 160 organisms per litre."

**Respired Air.**—It has long been known that respired air is unsuitable to support human or animal life, and the question is—why?

Assuming respired air to have the composition—

| | | |
|---|---|---|
| Carbon dioxide | 4–5 | per cent. |
| Oxygen | 15 | „ |
| Nitrogen | 76 | „ |
| Water-vapour | 5 | „ |

it is not at first sight easy to understand why it should be unwholesome. The oxygen content is sufficiently high, for we have already seen that even 14 per cent. of this gas is ample for normal respirative purposes.[7] We cannot therefore complain of oxygen shortage. Neither can we argue that the carbon dioxide is excessive, for 8 to 10 per cent. of the pure gas may be breathed for protracted periods without any injury.[1]

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[1] Uffelmann, *Archiv. Hygiene*, 1888, 8, 262.

[2] Andrews, *Trans. Path. Soc.*, 1902, 54, 43.

[3] J. J. Kijanitznan, *Virchow's Archiv.*, 1900, 162, 515.

[4] Cornet, *Zeitsch. Hygiene*, 1889, 5, 98.

[5] Quoted by Buchan, *Ventilation* (Crosby, Lockwood & Son, 1902), p. 120

[6] Buchan, *opus cit.*, p. 119.

[7] See p. 166.

Brown-Sequard and d'Arsonval[2] in 1889 concluded, from a series of experiments, that respired air contains small quantities of a powerful organic poison, and that the unsuitableness of it for further respiration lies, not so much in its carbon dioxide content, as in the presence of this organic toxin. This view was supported by Merkel[3] in 1892, but since then a large number of physiologists[4] have brought forward a formidable array of arguments, indicating that the unwholesome properties of respired air may be more readily explained in other ways. Let us briefly consider these.

There are at least three important factors to consider.

1. *The Influence of Moisture on Respiration.*—The presence of moisture in air has a two-fold action upon respiration.

First, there is the very obvious fact that if warm air saturated with moisture enters the lungs, the latter will have great difficulty in discharging their superfluous moisture, and a sense of oppression must result. This explains the heavy feeling produced upon entering hot-houses, in which the air, apart from its moisture content, is perfectly good, and very free from carbon dioxide. Cold air, even if saturated with moisture, will not have anything like the same effect, for upon entering the lungs the temperature rises proportionately higher, and the air is thus able to take up much more moisture before becoming saturated, thereby allowing the lungs full opportunity to relieve themselves. Secondly, air containing moisture cannot take up carbon dioxide from the blood as easily as dry air,[5] consequently the ventilation of the lungs is retarded by inhaling moist air.

These two factors working together are sufficient to show that respired air, being saturated with moisture at a warm temperature, cannot be wholesome, and L. E. Hill[6] and his co-workers regard the moisture content as the main cause of the discomfort of ill-ventilated buildings.

2. *The Influence of Carbon Dioxide on Respiration.*—Mention has been made of the fact that relatively dry air containing 8 to 10 per cent. of pure carbon dioxide can be breathed for a long time with impunity. For the reason given in the preceding paragraph, however, it follows that breathing warm air both saturated with moisture and containing some carbon dioxide must be attended by a greater difficulty in ventilating the lungs, and that a proportionately smaller quantity of carbon dioxide will be capable of being breathed with impunity. Since respired air may contain anything from 4 to 5·4 per cent. of this gas, it is easy to understand how this may be the potent cause of the hyperpnœa and

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[1] See p. 172.

[2] Brown-Sequard, *Compt. rend*, 1889, 108, 267. The supposed toxin is termed "Anthropo-Toxin."

[3] Merkel, *Archiv. Hygiene*, 1892, 15

[4] Seegen and Nowadi, *Pflugers Archiv.*, 1879, xix ; Hermans, *Archiv. Hygiene*, 1883, i. ; Dastre and Loye, *Soc. Biologie*, 1888 ; von Hofmann Wellenhof, *Wien. klin. Wochenschrift*, 1888 ; J. Geyer, *Jahresber. Thierchem.*, 1889, xix. ; Lehmann and Jessen, *Archiv. Hygiene*, 1890, x. ; Beu, *Z. Hygiene Infektionskrankheiten*, 1893, xiv. ; Rauer, *Z. Hygiene*, 1893, xv. ; Lubbert and Peters, *Hygien. Rundshau*, 1894 ; Billings, *ibid.*, 1897 ; Růžička, *Rospravyčěské akademie Věd*, 1899 ; Formanek, *Archiv. Hygiene*, 1900, 38, 1 ; Haldane, etc.

[5] See references, p. 171.

[6] L. E. Hill, etc., *Proc. Physiol. Soc.*, 1910, iii. to viii.

headache, resulting from inhabiting ill-ventilated rooms. Haldane and Smith[1] are evidently of this opinion.

3. *The Influence of Organic Material on Respiration.*—There can be no reasonable doubt that expired air contains, in addition to moisture and carbon dioxide, some organic bodies of more complex composition. Thus Weichardt[2] finds that by breathing into distilled water, or better still, into glycerine,[3] a ponderable residue is obtained upon evaporation, which contains organic products of high molecular weight; and numerous other investigators have found evidence of organic matter in respired air. It is no doubt this, together with exhalations from the mouth (consequent upon bad teeth), and secretions from the skin, such as perspiration, etc., which give an unpleasant odour to the air of ill-ventilated rooms, tending to produce sickness and faintness.

The above three factors are quite sufficient to account for the unwholesomeness of respired air without assuming the presence of any particularly toxic organic poisons; and when it is remembered that, in addition to these, micro-organisms of a harmful nature are hurled into the air by people sneezing, coughing, spitting, and even talking, the need for very thorough and systematic ventilation becomes evident.

**How much Fresh Air must each Individual have?**—In very warm weather the windows may be thrown wide open and the air of rooms made almost as pure as that outside. But on cooler days when artificial heating is essential and draughts must be avoided, a certain amount of vitiation of the air is unavoidable. The question which now arises is—To what extent may that vitiation be permitted without harmful effects? It is reasonable to assume that if the air of a room is so pure as not to affect the sense of smell, when a person enters it direct from breathing the fresh air outside, there cannot be much wrong with it—provided, of course, the only impurity likely to be present is respired air, and not inodorous gases such as pure carbon dioxide obtained from chemical sources, or carbon monoxide from heated stoves, etc., which gases have no action upon the olfactory nerve. De Chaumont investigated this limit very carefully in 1875, and concluded that, on the average, air containing 0·02 per cent. or more of respired carbon dioxide possesses a detectable odour. This, of course, depends upon a variety of factors, such as the humidity, temperature, sensitiveness of the nasal organ, and last, but by no means least, the personal cleanliness of the persons who have been breathing the air. This must be evident when we remember that it is not the pure carbon dioxide that we smell, but the organic impurities respired with it. Let us, however, take 0·02 per cent. of carbon dioxide as the maximum amount of respired carbon dioxide that ought to be permitted in the atmosphere of inhabited rooms.

In order to determine the amount of fresh air to be supplied to each individual on this basis we require to know the amount of carbon dioxide exhaled per hour. This may be stated roughly as in table on p. 188.

As an average for a mixed community we may take 0·6 cubic feet. If now we divide this by the permissible respired impurity, namely,

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[1] Haldane and Smith, *J. Path., Bact.*, 1892, I, 168.

[2] Weichardt, *Archiv. Hygiene,* 1911, 74, 185.

[3] Weichardt and Stotter, *ibid.*, 1912, 75, 265.

0·02 per cent., we have the amount of air required per hour per person, namely—

$$\frac{0\cdot 6}{0\cdot 0002}=3000 \text{ cubic feet per hour;}$$

and this is the standard generally adopted.

For general purposes the equation may be expressed as

$$\frac{C}{R}=F,$$

where C=Amount of carbon dioxide exhaled by each person per hour;
R=Respired impurity that may be allowed;
F=Amount of fresh air required, in cubic feet per hour.

For children we have

$$\frac{0\cdot 4}{0\cdot 0002}=2000 \text{ cubic feet per hour.}$$

The U.S. Book on School Architecture allows only half this amount, namely, 1000 cubic feet per hour for children.

| Individual. | Cubic Feet of Carbon Dioxide exhaled per Hour |
|---|---|
| Adult males in heavy work . | 1·84 |
| Adult males in light work . . | 0·95 |
| Adult males at rest . . . | 0·72 |
| Adult females at rest . . | 0·6 |
| Children . . . . . | 0·4 |

**The Influence of Artificial Light.**—The chemical changes induced by the combustion of coal-gas, as a source of artificial illumination, may be enumerated as follows :

1. Oxygen is consumed, each cubic foot of coal-gas using up almost exactly its own volume of oxygen during combustion.[1]
2. Carbon dioxide is produced, 1 cubic foot of coal-gas yielding 0·4 to 0·5 cubic feet.[1]
3. Water-vapour is evolved, 1 cubic foot of gas yielding at normal pressure and room temperature approximately 26 grams of water.[1]
4. Small quantities of sulphur dioxide result by the oxidation of traces of sulphuretted hydrogen etc., normally present in coal-gas.
5. Organic impurities are incinerated by the flame.

From (4) and (5) above, we gather that if sufficient air is forthcoming to supply the necessary oxygen and to dilute down the carbon dioxide, a coal-gas flame should be more healthy than electric incandescent lamps. This has, in practice, proved to be the case. The sulphur dioxide is present in too minute a quantity to injure human beings, but, according to Rideal,[1] it can and does tend to purify the air, and in conjunction with the incinerating action of the flame it reduces very sensibly the micro-organism content. Haldane [2] draws attention to the small vitiation of air produced when incandescent gas mantles are used, as compared with any other form of gas burner. This is attributed to the very complete combustion of the gas on the surface of the mantle and to the incinerating activity.

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[1] The mean of many experiments carried out by the writer on Worcester City coal-gas. Rideal (next reference) gives 0·6 c. ft. carbon dioxide and 295 grains, *i.e.* 19·1 grams, of water for London coal-gas.

In addition to these chemical effects, we have two important physical factors to consider, namely—

(1) The rise in temperature of the air ; and

(2) The consequently increased rapidity in the circulation of the air.

By having artificial gas lights above the heads of the inhabitants of a room the warm air is impelled upwards, and if suitable ceiling ventilation is provided there is considerably less danger of the bad air cooling and sinking, and thus vitiating the purer air below. In the absence of good ceiling ventilation, the air cools near the walls and slowly creeps down them.

It is customary to regard, from the ventilation point of view, the presence of a gas flame as equivalent to that of a definite number of persons. As we have already learned, however, it is the organic impurities as well as the moisture and carbon dioxide content which renders respired air injurious. Consequently we ought not *strictly speaking* to express gas flames in terms of people. For the sake of convenience, however, and for want of a better method, we must continue to do so. It is usually agreed that 0·1 per cent. of carbon dioxide produced by combustion of coal-gas, and hence accompanied by water-vapour, is as much as ought to be permitted in the air of a room. Such being the case, an average burner, consuming 5 or 6 cubic feet of gas per hour yields from 2·5 to 3 cubic feet of carbon dioxide, and thus requires from 2500 to 3000 cubic feet of fresh air per hour. In other words, in calculating the air required, a gas flame may be taken as numerically equivalent to a human being.

**Air a Mixture.**—As has already been mentioned, the apparent constancy of composition of the atmosphere led many early chemists to believe that it was a definite compound of oxygen and nitrogen and not a mechanical mixture of these two gases. When later and more accurate analyses of air were made, however, small but decided variations in the relative proportions of its oxygen and nitrogen were found—a discovery that disposed entirely of the suggestion that air is a compound.

Several other lines of argument point to the same conclusion however. For example, when air is shaken with water each constituent dissolves to an extent dependent upon its own solubility and partial pressure. Since oxygen is approximately twice as soluble in water as nitrogen, the dissolved air is slightly richer in oxygen.[3] If air were a compound, on the other hand, the gases would dissolve in the water in the same proportions as they exist in the free air.

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[1] An excellent memoir on the " Relative Hygienic Values of Gas and Electric Lighting," Rideal, *J. Roy. San. Inst*, 1908–1909, 29, 51–132.

[2] Haldane, *J. Hygiene*, 1902, 2, 414.

[3] Advantage has been taken of these properties to separate oxygen from nitrogen commercially, see p. 13.

When oxygen and nitrogen gases are intermixed in the relative proportions necessary to form air, no heat is set free, yet the resulting mixture possesses the properties of pure air, and its constituents admit of separation again by means of diffusion. It seems highly improbable, therefore, that a compound can have been formed.

When air is liquefied and subsequently boiled, a vapour rich in nitrogen gas is the first to escape, leaving a liquid proportionately richer in oxygen.[1] If the air were a compound, however, the escaping gas would have the same composition as the liquid.

Finally, the properties of air, whether in the gaseous or liquid phase, are intermediate between those of oxygen and nitrogen respectively, thereby suggesting a mixture, for, as a general rule, compounds do not resemble their components either physically or chemically.

## GENERAL PROPERTIES OF THE ATMOSPHERE.

**Physical Properties of Air.**—Pure air is a tasteless and inodorous gas which appears colourless, except in very deep layers when a faint blue colour is visible, which has been attributed to its ozone content. Under normal conditions of 760 mm. pressure and 0° C., the weight of a litre of air varies, as a rule, between 1·2927 and 1·2933 grams,[2] the variation being attributable to the fact that the air has not a perfectly constant chemical composition. For this reason it is useless to determine with great accuracy the density of a gas relatively to air unless the composition of the latter is simultaneously ascertained.[3] For most purposes a mean value of 1·2930 at 0° C. and 760 mm. will be a sufficiently accurate figure to adopt. One gram of air under the above conditions will occupy 773 c.c., and its density with reference to hydrogen is 14·44. At 15° C. 1000 cubic feet of air weigh 76·5 lb., whilst 1 lb. of air occupies 13·07 cubic feet.

The more important determinations of the weight of 1 litre of air are given in table p. 191.

With a knowledge of the density of each constituent of the air it is possible to calculate the relative proportions of nitrogen and oxygen in the atmosphere; but such calculations at first indicated more oxygen than could be found by direct analysis, and not until the discovery of argon was the cause of the discrepancy realised. Knowing the density of oxygen, nitrogen, and argon, the proportion of these gases in the atmosphere can now be calculated to be as follows:[4]

### CALCULATION OF COMPOSITION OF AIR FROM DENSITY DETERMINATIONS.

| | Weight per cent. | Volume per cent. |
|---|---|---|
| Oxygen . . | 23·2 | 21·00 |
| Nitrogen . . | 75·5 | 78·06 |
| Argon . . | 1·3 | 0·94 |

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[1] Advantage has been taken of these properties to separate oxygen from nitrogen commercially, see p. 31.

[2] See Guye, *J. Chim. phys.*, 1917, 15, 561.

[3] See Leduc, *Compt. rend.*, 1893, 117, 1072.

[4] Leduc, *Compt. rend.*, 1896, 123, 805.

## WEIGHT OF 1 LITRE OF AIR.

| Weight of 1 litre of Air at N T.P (Grams ) | Remarks. | Authority. |
|---|---|---|
| 1·2928 | Paris, g.=980·665 | Leduc, *Engineering*, 1919, **108**, 569. |
| 1·2927<br>1·2932 | .. | Germann, *Compt. rend.*, 1913, **157**, 926; *J. Chim. phys.*, 1914, **12**, 66. |
| 1·2930 | Mean of 30 determinations . | Guye, Kovacs, and Wourtzel, *Compt. rend.*, 1912, **154**, 1424, 1584. |
| 1·29315<br>1·29330 | Paris . . .<br>,, | Leduc, *Compt. rend.*, 1893, **117**, 1072; 1891, **113**, 186. |
| 1·29327 | ,, . . . | Rayleigh, *Proc. Roy. Soc.*, 1893, **53**, 134. |
| 1·29351 | ,, . . . | Jolly, 1880 (given by Rayleigh, *loc. cit.*). |
| 1·29361<br>1·29343 | At Berlin . .<br>Over sea, lat. 51° | Kohlrausch, *Pogg. Annalen*, 1856, **98**, 178. |
| 1·29364<br>1·29320 | Berlin . .<br>Paris | Lasch, *Chem. Zentr.*, 1852, p. 148. |
| 1·29317<br>1·29349 | ,, . . .<br>,, . . . | Regnault (1847).<br>Regnault, corrected by Crafts, *Compt. rend.*, 1888, **106**, 1662. |

That the air possesses weight was apparently first recognised by Jean Rey,[1] *c.* 1630, an observation that was confirmed by Torricelli in 1643 and by Pascal in 1648. Rey made his discovery by observing that tin, on calcination in air, increases in weight, and thus anticipated the results of Lavoisier by nearly a century and a half. Torricelli tackled the problem in an entirely different manner. He filled with mercury a glass tube, closed at one end and measuring some 3 feet in length. When the tube was inverted with its open end dipping under mercury in a trough, the tube no longer remained filled with the liquid. It held a column of mercury some 30 inches in height, but above this the tube was empty. This space came to be known as the Torricellian vacuum, and its discoverer correctly attributed its formation to the fact that the open air acting on the surface of the mercury in the trough is able to support by its pressure a column of mercury of definite length, and no more. Pascal extended Torricelli's experiments by employing tubes filled with other liquids such as oil, alcohol, and water. In every case he found that the height of the column of liquid supported by the air was inversely proportional to the liquid density; in other words, the pressure supported was constant, irrespective of the chemical composition of the liquid. Pascal also surmised that if air is a ponderable fluid, it will exert a greater pressure at sea level than on the top of a mountain, and that this difference should be capable of measurement by observing the relative heights of mercurial columns in such situations. Experiment proved this to be the case. Boyle christened Torricelli's tube, containing mercury, a *barometer*,[1] and it is customary to express the pressure of the air in terms of the height of a column of mercury which it is capable of supporting at any moment.

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[1] See Maurice Petit, *Essais de Jean Rey*, Paris, 1907.

The pressure of the air, as already mentioned, varies with altitude; indeed, at one and the same place it does not remain constant in consequence of variation in composition, the influence of wind, etc. A standard pressure, known as an *atmosphere*, has been chosen. The British unit is a column of mercury 29·905 inches in height, measured at 32° F. in London, and is equivalent to a pressure of 14·73 lb. per square inch.

The metric unit is a column of mercury 760 mm. (29·922 inches) in height measured at 0° C. at sea level at latitude 45°. The density of mercury at 0° C. is 13·596, and the acceleration due to gravity at sea level and at latitude 45° is 980·60 cm. per sec$^2$. Hence the value of the metric standard of pressure is

$$76{\cdot}0 \times 13{\cdot}596 \times 980{\cdot}60 = 1013250 \text{ dynes per sq. cm.}$$

which is equivalent to a weight of 1033·3 grams per sq. cm. The British atmosphere is 0·99968 that of the metric unit.

The total weight of the atmosphere is approximately as follows:

| | Tons. |
|---|---|
| Nitrogen (including argon, etc.) . | 4,041,200,000,000,000 |
| Oxygen . . . . . | 1,218,040,000,000,000 |
| Carbon dioxide . . . . | 3,156,000,000,000 |

Except at pressures but little removed from atmospheric, air does not obey Boyle's Law. Regnault,[2] who was the first investigator to obtain trustworthy results, found that air deviated appreciably from the Law between pressures of 1 and 27 atmospheres—the range used—the gas being more compressible than the Law demands. Several other investigators then took up the work, the most important experiments being those of Amagat,[3] whose results are given in the following table, (p. 194) together with the data obtained by him for oxygen and nitrogen.

The results for oxygen and nitrogen are shown diagrammatically in fig. 33 together with curves for hydrogen and carbon dioxide for the sake of comparison.

It will be observed that air gives results intermediate between those of nitrogen and oxygen, as is to be expected from a mixture of the two.

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[1] See *New Experiments on Cold*, 1664–1665; Boyle's *Works*, 1772, vol 2, p 487.

[2] Regnault, *Relations des Expériences*, 1847; *Mém. de l'Acad.*, 1847, 21, 329.

[3] Amagat, *Ann. Chim. Phys.*, 1880, 19, 345; 1881, 22, 353, 1883, 28, 456, 464, 480. His results are summarised, *ibid.*, 1893, 29, 68.

At first the values for PV fall, the attraction between the molecules causing the gases to be more compressible than Boyle's Law demands. As, however, the pressure increases, the volume ceases to contract in strict proportionality, since the dimensions of the molecules themselves begin to make themselves felt. The gas thus becomes less compressible than the law demands.

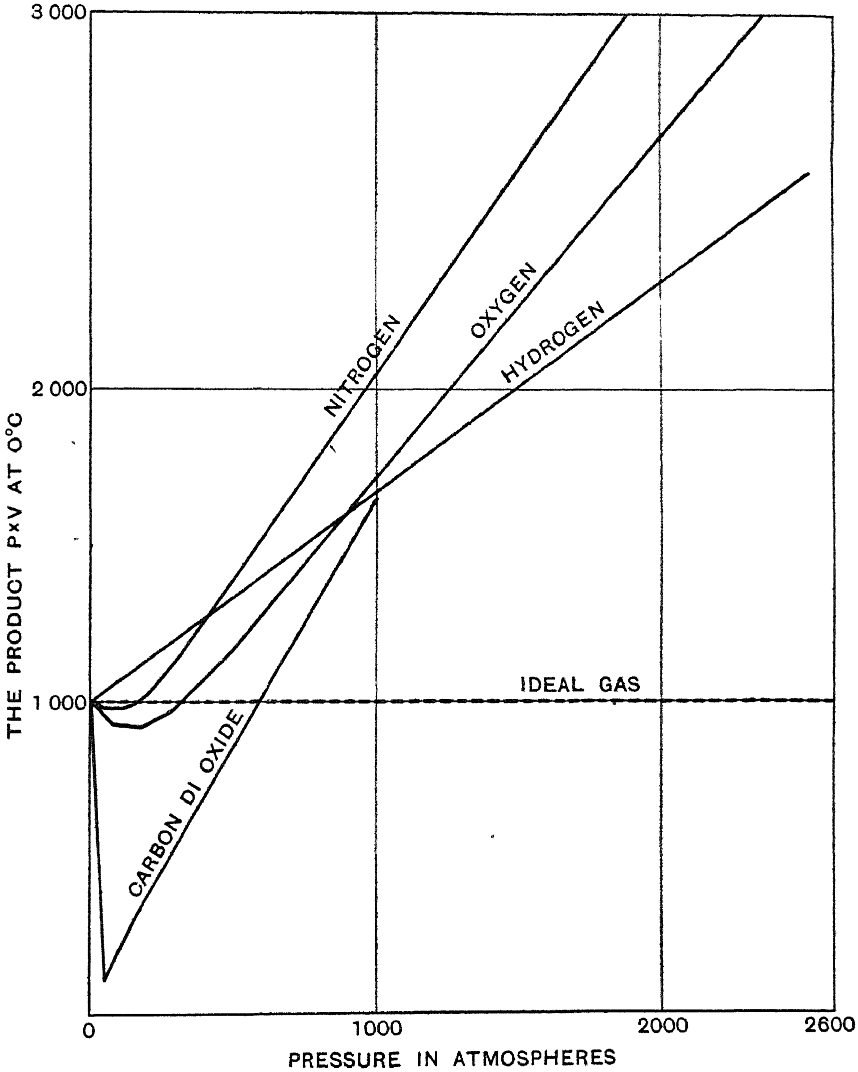

Fig. 33.—The compressibilities of oxygen and nitrogen (Amagat, 1893).

As the temperature falls, air shows an ever increasing tendency to deviate from Boyle's Law. This is well demonstrated by the results of Witkowski[1] given in the table on p. 195 and shown diagrammatically in Fig. 34.

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[1] Witkowski, *Phil. Mag.*, 1896, 41, 288. Further data are given by Holborn and Schultze, *Ann. Physik*, 1915, 47, 1089; 1910, 31, 945.

## RELATION BETWEEN PRESSURE AND VOLUME OF OXYGEN, NITROGEN, AND AIR.

(Amagat, 1893.)

| Pressure in Atm. | PV at 0° C. (Oxygen). | PV at 0° C (Nitrogen). | PV at 0° C. (Air) |
|---|---|---|---|
| 1 | 1·0000 | 1·0000 | 1·0000 |
| 100 | 0·9265 | 0·9910 | 0·9730 |
| 200 | 0·9140 | 1·0390 | 1·0100 |
| 300 | 0·9625 | 1·1360 | 1·0975 |
| 400 | 1·0515 | 1·2570 | 1·2145 |
| 500 | 1·1570 | 1·3900 | 1·3400 |
| 1000 | 1·7360 | 2·0700 | 1·9990 |
| 1500 | 2·2890 | 2·72025 | 2·6310 |
| 2000 | 2·8160 | 3·3270 | 3·2260 |
| 2500 | 3·32375 | 3·9200 | 3·79125 |
| 3000 | 3·7120 | 4·4970 | 4·3230 |

The *mean specific heat* of air at constant pressure rises with the temperature. The most reliable data are those given in the table on p. 195.

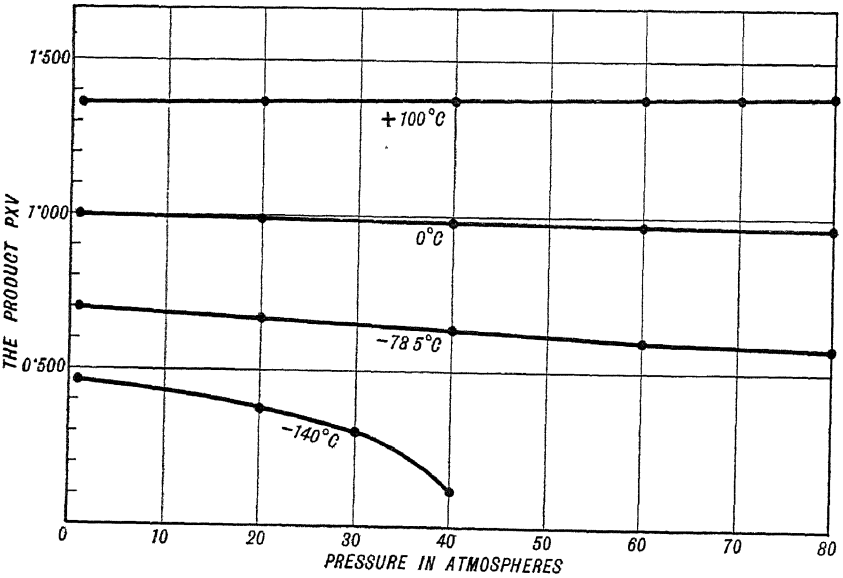

Fig. 34.—The compressibility of air (Witkowski, 1896).

The variation of the specific heat at constant pressure over a range of 1 to 300 atmospheres is readily calculated[1] for a mean temperature of 60° C. from the formula

$$10^4c_p=2414+2{\cdot}86p+0{\cdot}0005p^2-0{\cdot}0000106p^3,$$

where $p$ represents the pressure in atmospheres.

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[1] Holborn and Jakob, *Zeitsch. Verein deut. Ing.*, 1917, 61, 146; 1914, 58, 1429; *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, p. 213. The high values found by Lussana (*Nuovo Cim.*, 1894, 36, 5, 70, 130) appear to be incorrect.

## THE COMPRESSIBILITY OF AIR.

(Witkowski, 1896.)

| Pressure. (Atm.) | Values for PV at | | | | | |
|---|---|---|---|---|---|---|
| | −140° C | −130° C. | −78 5° C. | 0° C. | +16° C. | +100° C. |
| 1 | 0·4862 | 0·5229 | 0·7119 | **1·0000** | 1·0587 | 1·3670 |
| 10 | .. | .. | .. | 0·9951 | 1·0550 | 1·3678 |
| 20 | 0·3808 | 0·4410 | 0·6778 | 0·9897 | 1·0509 | 1·3691 |
| 30 | 0·3063 | 0·3936 | 0·6599 | 0·9842 | 1·0468 | 1·3704 |
| 40 | 0·1128 | 0·3329 | 0·6423 | 0·9793 | 1·0433 | 1·3725 |
| 50 | .. | 0·2544 | 0·6252 | 0·9754 | 1·0408 | 1·3754 |
| 60 | .. | 0·2013 | 0·6089 | 0·9723 | 1·0390 | 1·3784 |
| 70 | .. | 0·1989 | 0·5937 | 0·9701 | 1·0381 | 1·3821 |
| 80 | .. | 0·2043 | 0·5796 | 0·9688 | 1·0379 | 1·3866 |
| 90 | .. | .. | 0·5680 | 0·9681 | 1·0382 | 1·3908 |
| 100 | .. | .. | .. | 0·9681 | 1 0390 | 1·3951 |
| 110 | .. | .. | .. | 0·9690 | 1·0406 | 1·4004 |
| 120 | .. | .. | .. | 0·9710 | 1·0432 | 1·4065 |
| 130 | .. | .. | .. | 0·9738 | 1·0467 | .. |

## SPECIFIC HEAT OF AIR AT CONSTANT PRESSURE.

| Temperature Interval, ° C | Mean Specific Heat at Constant Pressure. | Authority. |
|---|---|---|
| −183 | 0 2525 | Scheel and Heuse, *Ber. deut. physikal. Ges.*, 1911, **13**, 870. |
| −78 | 0·2432 | |
| −102 to +17 | 0·2372 | Witkowski, *Phil. Mag.*, 1896, **41**, (5), 288. |
| +20 | 0·2417 (extreme values 0·2418 and 0·2427). | Swann, *Proc. Roy. Soc.*, 1909, **82**, **A**, 147. |
| +20 | 0·2408 | Scheel and Heuse, *loc. cit.* |
| +20 | 0·2403 | Scheel and Heuse, *Ann. Physik*, 1912, **37**, 79 ; 1913, **40**, 473 ; *Chem. Zentr.*, 1919, iii., 148. |
| 100 | 0·2430 | Swann, *loc. cit.* |
| 20 to 440 | 0·2366 | Holborn and Austin, *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, p. 175. |
| 20 to 630 | 0·2429 | |
| 20 to 800 | 0·2430 | |
| 59 | 0·2415 | Holborn and Jacob, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, p. 213. |
| 17 | 0·2387 | Partington, *Proc. Roy. Soc.*, 1921, **A, 100**, 27. |

The variation of the molecular heat at constant volume with rise of temperature between 0° C. and 700° C. is given by the expression

$$C_v = 4{\cdot}8 + 0{\cdot}0004T,$$

where T is the absolute temperature.[1]

Partington[2] gives the following results at 17° C.:

| | |
|---|---|
| Specific heat at constant volume . . . | 0·1701 |
| „ „ „ pressure . . . | 0·2387 |
| Molecular heat at constant volume . . . | 4·931 |
| „ „ „ pressure . . . | 6·920 |

The ratio of the specific heat at constant pressure to that at constant volume is given by the expression

$$\gamma = c_p/c_v = 0{\cdot}2387/0{\cdot}1701 = 1{\cdot}4027.$$

Other recent values for $\gamma$, as determined by different investigators, are as follow:

## RATIO OF THE SPECIFIC HEATS OF AIR.

| $\gamma$. | Authority. |
|---|---|
| 1·401 | Moody, *Physikal. Zeitsch.*, 1912, **13**, 383. |
| 1·401 | Scheel and Heuse, *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, p. 44. |
| 1·400 | Mercer, *Proc. Phys. Soc. London*, 1914, **26**, 155. |
| 1·4034 | Grüneisen and Merkel, *Ann. Physik*, 1921, **66**, 244. |

These values agree well with that required theoretically for a diatomic gas.

The value for $\gamma$ is stated to remain constant to within 1 per cent. between 0° and 500° C.,[3] although most observers[4] agree that $\gamma$ tends to fall with rise of temperature.

Increase of pressure, however, raises the value from 1·404 at 0·5 atm. to 1·411 at 3·5 atm.,[5] 1·460 at 20 atm.,[6] and 1·533 at 50 atm.[6]

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[1] Dixon, Campbell, and Parker, *Proc. Roy. Soc.*, 1921, [A], 100, 1.

[2] Partington, *Proc. Roy. Soc.*, 1921, [A], 100, 27. See also Womersley, *ibid*, 1922, [A], 100, 483.

[3] Fürstenau, *Ann. Physik*, 1908, [4], 27, 735; *Ber. deut. physikal. Ges.*, 1909, 11, 137.

[4] See Lussana, *Nuovo Cim.*, 1894, 36, 5, 70, 130; Witkowski, *J. Phys.*, 1896, 5, 123; Holborn and Austin, *Abh. Physik. Tech. Reichsanstalt*, 4, 131: Holborn and Henning, *Ann. Physik*, 1905, 18, 739; 1907, 23, 809; Langen, *Mitt. Forschungsarbeiten*, 8; Swann, *Phil. Trans.*, 1910, [A], 210, 199, 238; Moody, *Physikal. Zeitsch.*, 1912, 13, 383.

[5] Schöler, *Ann. Physik*, 1914, 45, 913. See also Joly, *Proc. Roy. Soc.*, 1894, 55, 390, 392; 1890, 48, 441; Valentiner, *Sitzungsber. K. Akad. München*, 1903, p. 691; Holborn and Jacob, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, p. 213; Koch (*Abh. Bayer. Akad. Wiss.*, 1907, 23, 377) at high pressures found $\gamma$ to fall.

[6] Worthing, *Physical Review*, 1911, 33, 217.

The *coefficient of expansion* of dry air, with rise of temperature per 1° C. and at normal pressure, has been variously determined as follows :

### COEFFICIENT OF EXPANSION OF AIR WITH RISE OF TEMPERATURE.

| Co-efficient of Expansion. | Authority. |
|---|---|
| 0·003671 | Regnault. |
| 0·00367 | Amagat, *Compt. rend.*, 1872, **74**, 1299. |
| 0·0036677 | Jolly, *Pogg. Annalen, Jubelb.*, 1874, p. 82. |
| 0·0036843 | Mendeléef and Kagander, *Compt. rend.*, 1876, **82**, 450. |
| 0·0036728 | Chappuis. |

For a gas that obeys Boyle's Law, the coefficient of expansion at constant pressure is the same numerically as the *coefficient of pressure increase* with rise of temperature at constant volume. The more important results obtained for this latter coefficient are as follow :

### PRESSURE COEFFICIENT OF AIR.

| Pressure. cm. Hg. | Temperature, Range, ° C. | Co-efficient of Pressure. | Authority. |
|---|---|---|---|
| 0·58 | .. | 0·0037666 | Melander (1892). |
| 1·32 | .. | 0·0037172 | ,, |
| 10·0 | .. | 0·0036630 | ,, |
| 17–24 | .. | 0·0036513 | Regnault (1847). |
| 23 | 0–1067 | 0·0036643 | Jaquerod and Perrot [1] (1905). |
| 76 | .. | 0·0036650 | Regnault (1847). |
| 100·1 | 0–100 | 0·0036744 | Chappuis (1903). |
| 200 | .. | 0 003690 | Regnault (1847). |
| 2000 | .. | 0·003887 | .. |

The coefficient of *viscosity* of air is given [2] as 0·000180 at 11·75° C.

The *thermal conductivity* [3] of air at the mean temperature of 55° C. is 0·0000571, a value intermediate between that of oxygen (0·0000593) and nitrogen (0·0000569) [4]

The velocity of sound in free air at various temperatures has been determined as follows : [5]

| Temp., ° C. . . | 0 | 100 | 200 | 300 | 400 | 500 | 600 | 700 |
|---|---|---|---|---|---|---|---|---|
| Velocity, m. per sec. | 331·8 | 387·5 | 435 8 | 479·0 | 518·6 | 555·2 | 589·3 | 621·6 |

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[1] Jaquerod and Perrot, *Compt. rend.*, 1905, 140, 1542.

[2] Roberts, *Phil. Mag.*, 1912, 23, 250.

[3] See p. 43.

[4] Todd, *Proc. Roy. Soc.*, 1909, [A], 83, 19. See also Stefan, *Sitzungsber. K. Akad. Wiss. Wien*, 1872, [2], 65, 45.

[5] Dixon, Campbell, and Parker, *Proc. Roy. Soc.*, 1921, [A], 100, 1.

The velocity of sound in free air as determined by the Bureau des Longitudes is 331·2 metres per second, whilst Hebb[1] found the value 331·44, and Gruneisen and Merkel[2] 331·57 at 0° C. and 760 mm.

The *refractive index* of dry air is 1·0002918 at 0° C.[3] and 760 mm. for the sodium D line ($\lambda=5893\times10^{-8}$ cm.); the indices for other wave-lengths not widely removed may be calculated from Cauchy's equation

$$n-1=A(1+B/\lambda^2).$$

where $n$ and $\lambda$ represent the refractive index and wave-length respectively, whilst A and B are constants of values $28{\cdot}71\times10^{-5}$ and $5{\cdot}67\times10^{-11}$ respectively. The latter constant B is the coefficient of dispersion. According to Cuthbertson[4] the refractive index $n$ of air for any incident light of frequency $f$ is given by the expression

$$n-1=\frac{4{\cdot}6463\times10^{27}}{16125\times10^{27}-f^2}.$$

For the sake of comparison, the refractive indices of the more important individual gases present in the atmosphere are given in the following table:

| Gas or Vapour. | $n$ for D line. | Authority. |
|---|---|---|
| Air . . | 1·0002918 | Scheel, *loc. cit.* |
| Argon . . | 1·0002837 | Burton, *Proc. Roy. Soc.*, 1908, A, **80**, 390. |
| Nitrogen . | 1·000297 | Scheel, *loc. cit.* |
| Oxygen . | 1·000272 | Rentschler, *Astrophys. J.*, 1908, **28**, 345. |
| Water-vapour | 1·000257<br>1·000250 | Mascart, 1878.<br>Lorenz, 1874. |

When entirely free from dust, dry air possesses a high degree of transparency to light, which the presence of moisture and dust tends to decrease. This is evident from the following table:[5]

| | Coefficient of Transparency. |
|---|---|
| Dry, dust free air . . . | 0·99718 |
| Moist, dust free air . . . | 0·99388 |
| Air in a dusty dwelling-house room | 0·9952 |

---

[1] Hebb, *Phys. Review*, 1905, 20, 89; *Trans. Roy. Soc. Canada*, 1919, 13, [3], 101.

[2] Grüneisen and Merkel, *Ann. Physik*, 1921, 66, 344.

[3] Scheel, *Ber. deut. physikal Ges.*, 1907, 5, 24. See also Statescu, *Bull. Acad. Sci Roumanie*, 1914–1915, 3, 211; Ramsay and Travers, *Proc. Roy. Soc.*, 1897, 62, 225. For an investigation of the ultra-violet spark spectrum of air, see Wagner, *Zeitsch. wiss. Photochem.*, 1911, 10, 69. The absorption spectrum of air has been studied by Egoroff, *Compt. rend.*, 1881, 93, 788; 1882, 95, 447; Becquerel, *ibid.*, 1883, 96, 1215; Janssen, *ibid.*, 1885, 101, 649. The band spectrum by Wüllner, *Pogg. Annalen*, 1872, 147, 321.

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

[5] Wild, taken from Dammer, *Anorganische Chemie*, 1892, iii., p. 442. The reference quoted for Wild (*Pogg. Annalen*, 1868, 40, 568) does not give the data.

Dry air is highly diathermanous, that is to say, it absorbs but little of the sun's heat.[1]

Owing to its oxygen content, air is magnetic, its magnetic susceptibility being about $0{\cdot}25 \times 10^{-7}$ at 10° C.

Its *specific inductive capacity* or *dielectric constant* referred to a vacuum is 1·000586 at 0° C., and 1·000576 at 20° C.[2]

The **solubility** of air in water has been made the subject of considerable research, and possesses several points of interest. The independence of the two main constituents (argon being included with the nitrogen) is clearly observable from the table given below; further, owing to the fact that the coefficients of solubility of the individual gases are affected differently with rise of temperature the composition of the dissolved mixture is not constant.

Since oxygen is practically twice as soluble in water as nitrogen, it follows that the dissolved gas is proportionately richer in oxygen. By expelling the gas into a vacuum and reabsorbing it in water, the concentration of the oxygen is still further increased. By repeating these processes several times, a fairly pure oxygen can be obtained, and this has been made the basis of a patent for the commercial separation of oxygen from the air (see p. 13).

The number of cubic centimetres of oxygen and nitrogen (containing argon) dissolved in a litre of water saturated with air from a dry atmosphere at 760 mm. pressure at various temperatures are given in the following table: [3]

## SOLUBILITY OF AIR IN WATER AT VARIOUS TEMPERATURES.

| Temperature, ° C. | Winkler [4] (1904). $1000\beta'$. | | Fox [5] (1909). $1000\beta$. | |
|---|---|---|---|---|
| | Oxygen. | Nitrogen.[6] | Oxygen. | Nitrogen [6] |
| 0 | 10·19 | 18·99 | 10·29 | 18·64 |
| 4 | 9·14 | 17·18 | 9·26 | 17·02 |
| 8 | 8·26 | 15·64 | 8·40 | 15·63 |
| 12 | 7·52 | 14·35 | 7·86 | 14·45 |
| 16 | 6·89 | 13·25 | 7·08 | 13·45 |
| 20 | 6·36 | 12·32 | 6·57 | 12·59 |
| 24 | 5·89 | 11·49 | 6·14 | 11·86 |
| 28 | 5·46 | 10·75 | 5·75 | 11·25 |

Measurement has also been made of the solubility of air in sulphuric acid of varying concentration.[1] At 18° C. the coefficient of solubility in 98 per cent. acid is 0·0173, and in 70 per cent. acid attains a minimum value of 0·0055.

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[1] Tyndall, *Proc. Roy. Soc.*, 1863, 30, 10; Buff, *Jahresber.*, 1876, p. 79; Gregor, *Pogg. Annalen*, 1884, 8, 304.

[2] Tangl, *Ann. Physik*, 1908, 26, 59; Siertsema, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 925.

[3] For definitions of $\beta$ and $\beta'$ see p. 36

[4] Winkler, *Physikalisch-Chemische Tabellen*, Landolt-Bornstein, 1912.

[5] Fox, *Trans. Farad. Soc.*, 1909, 5, 68.

[6] Including argon.

**Radio-activity of the Atmosphere.**—In 1887 Linss[2] drew attention to the fact that a charged conductor, thoroughly well insulated in so far as its supports are concerned, loses its charge in the air. This was confirmed in 1899 by Elster and Geitel[3] who, two years later,[4] discovered the cause by finding that a negatively charged wire exposed to air becomes coated with a radioactive deposit which can be removed either mechanically by rubbing with felt, or chemically by solution in ammonia.[5]

Observations on the rate of decay of the radioactivity of this deposit indicate that it is due to the presence in the atmosphere of the emanations of thorium and radium.[6]

Since air drawn from the soil exhibits radioactivity, it seems probable that ground air is the source of the atmospheric emanations;[7] and this theory receives support from the fact that atmospheric radioactivity rises with a falling barometer.[8] This would account for the fact that near and over the sea very low values have obtained.[9] The problem of the relative proportions of radium and thorium emanations in the air has been made the subject of considerable research. Balloon observations made at a height of 3000 metres above the earth's surface indicate the existence of radium emanation even at that elevation.[10] In a series of tests in the Apennines, 1090 metres above sea level, the proportion of the total atmospheric activity due to thorium emanation was found to vary from 29 to 73 per cent.[11] On the other hand, a wire charged negatively in Manchester gathered an active deposit containing on an average 62 per cent. of thorium emanation,[12] whilst in Rome under analogous conditions results indicated 60 to 70 per cent. of thorium emanation,[13] the remainder consisting of the radium product. As a general rule, it appears that, in the lower regions of the atmosphere, thorium emanation preponderates, whilst at higher altitudes radium emanation is in excess. It would appear also that American air contains a lower relative percentage of thorium emanation than European air.[14]

Determination of the actual amount of radium emanation in the air indicates that on the average the quantity contained per cubic metre of air is equal to that which would be in radioactive equilibrium with $1 \times 10^{-10}$ gram of radium.[1] There can be no doubt that the presence of these emanations is the main cause of the atmospheric ionisation which manifests itself in permitting electricity to escape from a charged conductor. Whether or not they exert any physiological influence has yet to be discovered.[2]

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[1] Tower, *Zeitsch. anorg. Chem.*, 1906, 50, 382.

[2] Linss, *Meteorolog. Zeitsch.*, 1887, 4, 352.

[3] Elster and Geitel, *Terrestrial Magnetism*, 1899, 4, 213

[4] Elster and Geitel, *Physikal. Zeitsch.*, 1901, 76, 590.

[5] Allan, *Phil. Mag.*, 1904, [6], 7, 140.

[6] Rutherford and Allan, *Phil. Mag.*, 1902, [6], 4, 704; Bumstead, *Amer. J. Sci.*, 1904, 18, 1. For data concerning the radioactivity of radium and thorium respectively, see this series, Vols. III. and V.

[7] Elster and Geitel, *Terrestrial Magnetism*, 1904, 9, 49; Mache and Rimmer, *Chem. Zentr.*, 1906, ii., 1237; *Physikal. Zeitsch*, 1906, 7, 617.

[8] Simpson, *Phil. Trans.*, 1905, [A], 205, 61; Gockel, *Physikal. Zeitsch*, 1908, 9, 304.

[9] Compare Runge, *Chem. Zentr.*, 1907, ii., 1353; 1911, ii., 786.

[10] Flemming, *Physikal. Zeitsch*, 1908, 9, 801

[11] Pacini, *Physikal. Zeitsch.*, 1910, 11, 227. Compare Gockel, *Arch. sci. phys. nat*, 1909, 27, 248; Gockel and Wulf, *Physikal Zeitsch.*, 1908, 9, 907.

[12] Wilson, *Phil. Mag.*, 1909, [6], 17, 321.

[13] Blanc, *Phil. Mag.*, 1907, [6], 13, 378; *Atti R. Accad. Lincei*, 1908, [5], 17, i., 101.

[14] Wilson, *loc. cit.*

## LIQUID AIR.

When air, cooled below the critical temperatures of its constituents, is subjected to compression, liquefaction may occur, but the constituents will not separate out in strict proportionality [3] because oxygen is more easily condensed than nitrogen. For a similar reason liquid air, when kept, loses nitrogen more rapidly than oxygen, so that the boiling-point gradually approaches that of the latter element and the gas evolved at first extinguishes a lighted match whereas the last portions increase its combustion.[4]

On account of the uncertainty introduced by this behaviour of liquid air, it is important to bear in mind that statements of the physical properties are of relatively little value unless accompanied by figures giving the composition of the liquid air examined. Freshly prepared liquid air usually has a boiling-point near −193° C. at 760 mm.,[5] a temperature as low as −220° C. being attainable by rapid evaporation under a pressure of a few millimetres of mercury; under constant pressure the boiling-point gradually rises, approaching that of liquid oxygen. The compositions of the gaseous mixture in equilibrium with liquid air of varying oxygen content are given numerically in the accompanying table (p. 203) and shown diagrammatically in Fig. 35.[6]

---

[1] Satterley, *Phil. Mag.*, 1908, [6], 16, 584; 1910, [6], 20, 1, for Cambridge air; Ashman *Amer. J. Sci.*, 1908, [4], 26, 119) obtained the same mean result in Chicago. Eve (*Phil. Mag.*, 1908, [6], 16, 622) in Montreal found $0\ 6 \times 10^{-10}$.

[2] For further details the reader is referred to text-books on Physics and Radioactivity. The following references may also prove useful: Geitel, *Physikal. Zeitsch*, 1900, 2, 116; Wilson, *Proc. Roy Soc*, 1901, 68, 151; M'Clelland, *Sci. Trans. Roy. Dub. Soc.*, 1903, 8, ii., 57; Elster and Geitel, *Physikal. Zeitsch.*, 1904, 5, 11, 321; 1905, 6, 733; Gockel, *ibid.*, 1904, 5, 591: Conrad and Topolansky, *ibid.*, 1904, 5, 749; Zolss, *ibid*, 1904, 5, 106, 260; Schenk, *Jahrb. Radioaktiv. Elektronik.*, 1905, 2, 19; Langevin, *Compt. rend.*, 1905, 140, 232; Geitel, *Chem. Zentr.*, 1906, i., 1080, 1772; Runge, *ibid.*, 1907, ii., 1353; Ashman, *Amer. J. Sci.*, 1908, 26, 119; Satterley, *Phil. Mag.*, 1908, 16, 584; Lusby and Ewing, *J. Roy. Soc. New South Wales*, 1906, 40, 158; Blanc, *Physikal. Zeitsch.*, 1908, 9, 294; Dadourian, *ibid.*, 1908, 9, 333; *Amer. J. Sci.*, 1908, 25, 335; Gockel and Wulf, *Physikal. Zeitsch.*, 1908, 9, 907; Gockel, *Arch. sci. phys nat.*, 1909, 27, 248; Crowther, *Proc. Roy. Soc.*, 1909, [A], 82, 351; Harvey, *Physikal. Zeitsch.*, 1909, 10, 46; Wulf, *ibid.*, 1909, 10, 152; Eve, *Le Radium*, 1909, 6, 88; *Phil. Mag.*, 1910, 19, 657; 1907, 14, 724; 1908, 16, 222; Kurz, *Abhandl. K. Akad. wiss. Munchen*, 1909, 25, 5; Pacini. *Atti R. Accad Lincei*, 1909, [5], 18, i., 123; *Physikal. Zeitsch.*, 1910, 11, 227; Kinoshita, Nishikawa, and Ono, *Phil. Mag*, 1911, [6], 22, 821; Eve, *ibid.*, 1911, 21, 26; Runge, *Chem. Zentr.*, 1911, ii., 786; Kohlrausch, *Physikal. Zeitsch*, 1912, 13, 1193; Knoche, *ibid.*, 1912, 13, 112, 152; Laube, *ibid.*, 1913, 14, 81; Satô, *Sci. Reports Tôhoku Univ.*, 1913, 2, 171; Wright and Smith, *Physikal. Zeitsch.*, 1914, 15, 31; Bongards, *ibid.*, 1920, 21, 141; Olujić, *Jahrb. Radioaktiv Elektronik*, 1918, 15, 158.

[3] See Erdmann, *Ber*, 1904, 37, 1193.

[4] Stock and Nielsen, *ibid.*, 1906, 39, 3393

[5] Olszewski, *Compt. rend*, 1884, 99, 184; 1885, 101, 238, von Wroblewski, *ibid.*, 1884, 98, 982; 1885, 101, 635; 1886, 102, 1010; *Ann. Phys. Chem.*, 1885, 25, 402; 26, 134.

[6] Baly, *Phil. Mag.*, 1900, [5], 49, 517.

Liquid oxygen and nitrogen mix without appreciable change in volume; hence the approximate composition of the liquid mixture can be calculated from its density at any particular temperature.[1] Measurements which have been made lead to the expression

$$d=0{\cdot}86+0{\cdot}00289x$$

for the value at the boiling-point under ordinary pressure, when $x$ represents the percentage of oxygen[2] and $d$ the density required.

Measurement has also been made of the heat of evaporation,[3] the refractive index,[4] and the absorption spectrum of liquid air,[5] these properties again being almost entirely the resultant of the properties of the constituents.

The critical constants of liquid air have been estimated as having the following values: temperature −140° C., pressure 39 atmospheres, and volume 0·00257.[6]

A distinction is sometimes made[7] between the point at which the two co-existing phases, namely, vapour and liquid, become identical—the *plait point*—and the point representing the limiting condition for the separation into two phases—the *critical point of contact.* The difference between the two is very small, as is evident from the following estimation:[7]

| | Temperature, ° C. | Pressure, Atm. | Density of Liquid |
|---|---|---|---|
| Plait point . . . . . | −140·73 | 37·25 | 0·35 |
| Critical point of contact . . | −140·63 | 37 17 | 0·31 |

The critical density of air, as calculated from the critical densities of oxygen and nitrogen by the simple rule of mixtures, is 0·34. This lies within the range given above.

The specific heat of liquid air is about half that of water, whilst the latent heat of evaporation is approximately 50 calories.

The viscosity of liquid air of boiling-point 79·6° absolute is given[8] as 0·001678.

Liquid air is of relatively small value as a source of energy; its conversion into gas at the ordinary temperature is capable of yielding only as much energy as the combustion of one-tenth its weight of petrol, and the heat absorbed from the surroundings during the change is only sufficient to melt 1¼ times its weight of ice.

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[1] Inglis and Coates, *Trans. Chem. Soc.*, 1906, 89, 886.

[2] Ladenburg and Krügel, *Ber.*, 1899, 32, 46, 1415. See also von Wroblewski, *Compt. rend.*, 1886, 102, 1010; and Behn, *Ann Physik*, 1903, IV., 12, 669.

[3] Estreicher, *Zeitsch. physikal. Chem*, 1904, 49, 597.

[4] Liveing and Dewar, *Compt. rend.*, 1895, 121, 162.

[5] Liveing and Dewar, *Phil. Mag.*, 1893, [5], 36, 328

[6] Olszewski, *loc. cit.*

[7] Kuenen and Clark, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, 19, 1088.

[8] Verschaffelt and Nicaise, *ibid.*, 1916, 18, 1659.

## PERCENTAGES OF OXYGEN IN EQUILIBRIUM IN GASEOUS AND LIQUID PHASES OF AIR AT VARIOUS TEMPERATURES UNDER ATMOSPHERIC PRESSURE.

(Baly, 1900.)

| Temperature. ° C | Oxygen in Liquid. Per cent. | Oxygen in Vapour. Per cent |
|---|---|---|
| —182 | 100 | 100 |
| —184 | 91·98 | 79·45 |
| —186 | 82·95 | 60·53 |
| —188 | 72·27 | 44·25 |
| —190 | 59 55 | 29·93 |
| —192 | 43·38 | 17·66 |
| —194 | 21·60 | 6·80 |
| —195 | 8·10 | 2·10 |
| —195·46 | 0·00 | 0·00 |

**Applications.**—Although it evaporates rapidly in ordinary vessels, liquid air can be preserved for a considerable time with relatively little loss in glass vessels, the hollow, silvered walls of which enclose an

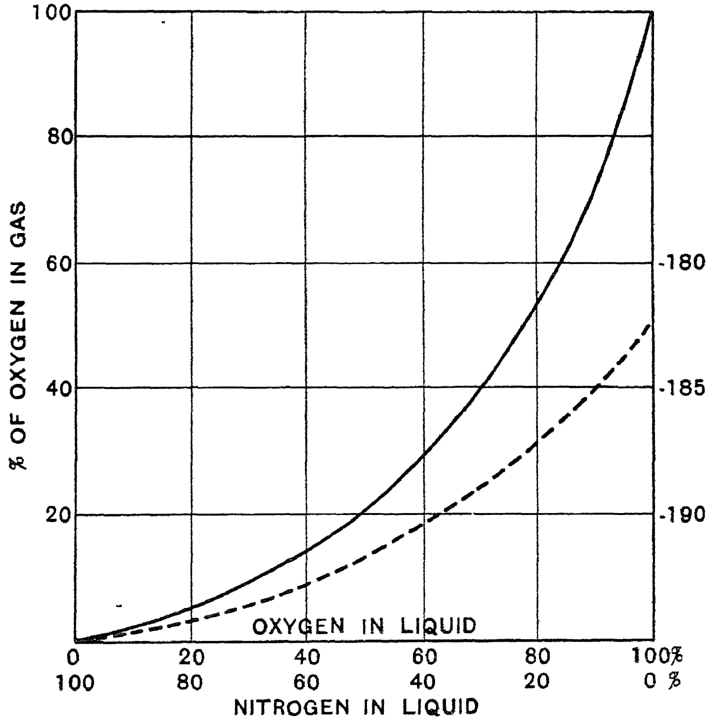

FIG. 35.—Curves showing composition of liquid and gaseous air in equilibrium at various temperatures under atmospheric pressure (Baly, 1900).

evacuated space;[1] these are manufactured in various shapes and sizes.

Liquid air is now a common commercial product and can be applied to various useful purposes. An obvious application is to the production of low temperatures for experimentation work,[2] and a valuable extension is to the production of high vacua by filling with carbon dioxide the apparatus which has already been attached by hermetically sealing to a bulb of coconut charcoal; when this bulb is immersed in liquid air, the carbon dioxide is absorbed so rapidly and completely that the pressure may be almost immediately reduced to a fraction of a millionth of an atmosphere.

Mention has already been made[3] of the employment of liquid air as a blasting agent. It also finds application as a convenient source of pure nitrogen and oxygen.[4]

By the rapid evaporation of liquid air under reduced pressure sufficient further cooling can be effected to cause the air to solidify, when it yields a colourless, transparent mass.[5] The fact that nitrogen has a higher melting-point (namely −210° C.) than oxygen (−219° C.) tends to the predominance of the former element in the solid mixture.

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[1] Dewar, *Chem. News*, 1894, 69, 29, 39; 1895, 71, 192, 199. See also Berry, *Proc. Roy. Soc.*, 1906, [A], 78, 458; and Beckmann, *Zeitsch. angew. Chem.*, 1909, 22, 673.

[2] Dewar, *loc. cit.*; Ladenburg, *Ber.*, 1898, 31, 1968; Stock and Hofmann, *ibid.*, 1903, 36, 895.

[3] See p. 136.

[4] See p. 33.

[5] Dewar, *loc. cit.*

# CHAPTER VII.

## WATER.

**Occurrence.**—Of all compound substances occurring on the earth in a fairly pure condition, water is by far the most abundant. Not only does it exist in immense quantities in seas, rivers, glaciers, and lakes, but it is also remarkably widespread as a necessary constituent of the tissue of all living organisms whether animal or vegetable. It is also present as vapour in the atmosphere, whence it separates as clouds and rain. Some minerals, for example clay, also contain very appreciable quantities of this substance in combination.[1]

Although there is a possibility that the compound nature of water was realised by the Chinese at a very early date,[2] in Europe the substance was regarded as an elementary substance, Aristotle grouping it with fire, air, and earth, as one of the basic or fundamental elementary bodies composing the universe. And so it remained until the latter portion of the eighteenth century when Cavendish, *c.* 1781, demonstrated its formation by the combination of hydrogen and oxygen either by burning or explosion when the gases disappeared in the approximate ratio of 2 : 1 by volume.[3] A year or so later, Lavoisier effected the synthesis from oxygen and hydrogen, the latter of which he learned to obtain from steam by the action of heated iron.[4] Almost simultaneously an investigation was made by Monge, who demonstrated the combination of two volumes of hydrogen with one volume of oxygen when a mixture was exploded, and from this result, together with a knowledge of the density of the gases, calculated the relative proportions by weight.[5] On account of the presence of moisture in the gases the latter result was inaccurate, but the method is of interest as anticipating the procedure adopted later by Scott and Morley in their well-known experiments.[6] In 1800 Nicholson and Carlisle effected the quantitative analysis of water by the passage of an electric current,[7] an experiment which, as a proof of the composition, is not as satisfactory as might be wished because it is not possible with pure water, but requires the presence of small quantities of an electrolyte. Hence the decomposition is actually a secondary result dependent on the interaction of the water with the discharged ions of the electrolytic impurity.

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[1] For an attempt to detect the rôle of water in various minerals by the absorption spectra, see Coblentz, *J. Franklin Inst.*, 1911, 172, 309.

[2] See p. 10.

[3] *Alembic Club Reprints*, iii., 13–16.

[4] *Œuvres de Lavoisier*, ii., 335–373.

[5] Monge, *Mém. Acad. Sci. Paris*, 1783, 78. See also Humboldt and Gay Lussac, *J. Physique*, 1805, 60, 129.

[6] See p. 295.

[7] *Nicholson's Journal*, 1801, iv., 186.

## NATURAL WATERS.

For domestic and ordinary chemical purposes water is invariably obtained by the purification of natural waters from various sources. Enormous quantities are required by civilised communities, as is evident from the accompanying data giving the average number of gallons consumed per head per day in the cities named :

| | Gallons. | | Gallons. |
|---|---|---|---|
| Glasgow | 58 | Buffalo | 250 |
| Edinburgh | 38 | Philadelphia | 211 |
| London | 35 | Chicago | 169 |
| Leeds | 34 | New York | 120 |
| Sheffield | 25 | Berlin | 28 |
| Bristol | 22 | Madras | 25 |

The above figures, of course, refer to the consumption of purified water for all purposes, and not merely for domestic use.

A convenient method for classifying natural waters is that adopted for potable or domestic supplies. Such a classification must be based largely upon local conditions of climate, population, etc. For example, waters that would have been perfectly wholesome a century ago may now be suspicious and even dangerous, in consequence of the enormous increase in population. Bearing these reservations in mind, the following scheme is reasonably applicable to British waters :

### CLASSIFICATION OF POTABLE WATERS.

| | |
|---|---|
| Wholesome | Deep spring.<br>Deep well.<br>Upland surface. |
| Suspicious | Stored rain.<br>Shallow spring.<br>Surface, from cultivated areas. |
| Dangerous | Many lake.<br>Most river.<br>Shallow well. |
| Unsuitable | Sea. |

1. **Spring water,** particularly that derived from deep-seated springs, is usually beautifully clear and sparkling. The clearness is mainly due to thorough filtering during percolation through the soil, whilst the sparkle is caused by the presence of gases, mainly carbon dioxide, in solution. The temperatures of different springs may vary considerably. Water from deep springs is usually cold, whilst that from shallow springs varies with the seasons. Should the temperature of the water be appreciably above that of the atmosphere the spring is termed a *thermal spring.* Typical thermal waters in England are those at Bath [1] (Somerset), the temperature of the different springs ranging

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[1] See *Squire's Companion to the British Pharmacopœia* (Churchill, 1916) ; Masson and Ramsay, *Trans. Chem. Soc*, 1912, 101, 1370.

from 31° C. (88° F.) to 50° C. (122° F.). The springs supplying the Corporation baths are stated[1] to yield upwards of half a million gallons of water per day at 45° C. (113° F.) At Coulsworthy[2] (Shropshire) the temperature is 11° C. (52° F.), that is, the waters are warmer in winter but cooler in summer than the average temperature of the atmosphere. The Bath waters are aerated and sold in bottles as *sulis water.*

Very frequently deep-spring waters contain dissolved salts which impart to them characteristic properties. Such springs as yield these are termed *mineral springs*, and are classified according to the nature of the dissolved impurities. Many towns owe their popularity as health resorts entirely to the reputed medicinal properties of their mineral waters. It is not improbable that many of the curative properties are either due to, or enhanced by, the presence of radioactive substances, and this would account for the well-known fact that artificially prepared mineral waters do not always possess the same medicinal values as the natural waters. Radium or radioactive material, for example, has been discovered in the springs at Bath[3] and Buxton, in this country; numerous other springs in France,[4] Spain,[5] the Jura mountains,[6] Tuscany,[7] Alps,[8] Switzerland,[9] Italy,[10] Austria,[11] Tyrol,[12] Silesia,[13] Bohemia,[14] Indiana,[15] at Carlsbad,[16] the Taunus,[17] Wiesbaden,[18] Kissingen,[19] Durkheim,[20] and other parts of Germany [21], Hungary,[22] Norway,[23] Sweden,[24] Russia,[25] Roumania,[26] Greece,[27] Canada,[28] Yellow-stone Park,[1] Colorado,[2] New York,[3] Canary Islands,[4] The Philippines,[5] Iceland,[6] and Sardinia.[7]

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[1] Baddeley's *Guide to Bath and Bristol* (Nelson, 1908).

[2] *Squire's Companion*, etc.

[3] Strutt, *Proc. Roy. Soc.*, 1904, 73, 191; Masson and Ramsay, *loc. cit.*; Ramsay, *Chem. News*, 1912, 105, 133.

[4] Brochet, *Compt. rend.*, 1908, 146, 175; Répin, *ibid*, 1908, 147, 387; Massol, *ibid.*, p. 844; Besson, *ibid.*, p. 848; Moureu and Lepape, *ibid.*, 1908, 148, 834; Brochet, *ibid.*, 1910, 150, 145, 291, 423; Danne and Crémieu, *ibid*, 1911, 153, 870; Massol, *ibid.*, 1910, 151, 1124; Loisel, *ibid.*, 1919, 169, 791; Lepape, *ibid*, 1920, 171, 731, 858.

[5] de Castillo, *Anal. Fis. Quim.*, 1906, 4, 119, 147, 189, 263; 1908, 6, 237, 290, 291, 350, 398, 400, 489; de Castillo and de Rada, *ibid.*, 1908, 6, 485; Chofré, *ibid.*, 1909, 7, 482; de Rada, *ibid*, 1912, 10, 113.

[6] Perrot and Jaquerod, *Arch. Sci. phys. nat.*, 1918, [4], 45, 277, 336, 418.

[7] Magri, *Atti R. Accad. Lincei*, 1906, [5], 15, ii., 699.

[8] Blanc, *Phil. Mag.*, 1905, [6], 9, 148; Henrich, *Zeitsch. angew. Chem.*, 1920, 33, 5, 13, 20.

[9] Sarasin, Guye, and Micheli, *Arch. Sci. phys. nat.*, 1908, [4], 25, 36; Schweitzer, *ibid.*, 1909, [4], 27, 256; 1910, [4], 30, 46.

[10] Nasini and Levi, *Atti R. Accad. Lincei*, 1908, [5], 17, ii., 551; Bamberger, *Monatsh.*, 1908, 29, 1141.

[11] Bamberger, *Monatsh.*, 1908, 29, 1131.

[12] Bamberger and Kruse, *ibid.*, 1910, 31, 221; 1911, 32, 797.

[13] Woy, *Zeitsch., öffentl. Chem.*, 1911, 17, 181.

[14] Stĕrba, *Jahrbuch Radioaktiv. Elektronik.*, 1911, 8, 23.

[15] Ramsey, *Phil. Mag.*, 1915, [6], 30, 815; Steichen, *ibid.*, 1916, [6], 31, 401.

[16] Knett, *Chem. Zentr.*, 1906, i., 400; Kolhörster, *Ber. deut. physikal. Ges.*, 1912, 14, 356.

[17] Schmidt, *Physikal. Zeitsch.*, 1905, 6, 34; *Chem. Zentr.*, 1905, i., 492.

[18] See Henrich, *Zeitsch angew. Chem.*, 1904, 17, 1757; *Monatsh.*, 1905, 26, 149.

[19] Jentzsch, *Physikal. Zeitsch.*, 1907, 8, 887: 1908, 9. 120.

[20] Levin, *ibid.*, 1910, 11, 322; Ebler and Fellner, *Zeitsch anorg. Chem.*, 1911, 72, 233.

[21] Müller, *Physikal. Zeitsch.*, 1910, 11, 545, etc.

[22] Szilárd, *Compt. rend.*, 1912, 154, 982.

[23] Poulsson, *Chem. Zentr.*, 1914, ii., 1469.

[24] Sjogren and Sahlbom, *Arkiv. Kem. Min. Geol.*, 1908, 3, i., No. 2; Sahlbom, *ibid.*, 1916, 6, No. 3.

[25] Mezernitzky, *J. Russ. Phys. Chem. Soc.*, 1911, 43, *Phys. Part*, 244. Swinne, *ibid.*, 1913, 45, *Phys. Part*, 454. von Weimarn, *ibid.*, 1914, 46, 742; Burkser, *ibid.*, 1915, 47, 21.

[26] Hurmuzescu and Patriciu, *Ann. Sci. Univ. Jassy*, 1908, 5, 159.

[27] Komnenos, *Chem. Zentr.*, 1910, i., 1634.

[28] Eve, *Trans. Roy. Soc. Canada*, 1910, [3], 4, iii., 53; Boyle and M'Intosh, *ibid.*, 1913, [3], 7, 163; Satterly and Elworthy, *ibid.*, 1917–1918, [3], 11, 17.

The actual amount of radioactive material in the waters is of course infinitesimal, being of the order, in some typical cases, of $10^{-11}$ grams per litre,[8] whilst in others it is very much less.[9] The springs at Bagnères de Luchon (France) are amongst the most radioactive in the world, and contain from 0·4 to 41·5 millimicrocuries of radium emanation per litre,[10] equivalent to from $4\times10^{-10}$ to $4\cdot15\times10^{-8}$ gram of radium per litre.

The term mineral spring has also been extended to include certain springs containing very little, if any, more than the normal amount of dissolved material, but which are regarded as possessing medicinal properties. Such, for example, are the Buxton and Malvern waters.

A convenient method of classifying mineral waters is as follows:

1. *Muriated.*—These contain chiefly sodium chloride with varying amounts of the chlorides of potassium, calcium, and magnesium. The Droitwich (Worcestershire) and two of the Cheltenham (Pittville and Lansdown) springs are characterised by their high content of sodium chloride, the waters being in considerable demand for rheumatic and sciatic affections. The Airthrey Waters (Bridge of Allan, Scotland) closely resemble many continental spa waters, and contain chlorides of calcium and magnesium as well as common salt.

2. *Sulphatic* waters contain sulphates mainly as sodium, calcium, and magnesium salts, and are consequently *aperient*. *E.g.*, Bath, Cheltenham (Chadnor Villa Well), and Scarborough. If ferrous sulphate is present, as at Trefriw (Carnarvon, N. Wales), the waters are termed—

3. *Chalybeate* or *Ferruginous.*—Usually these waters contain iron in solution, as the soluble ferrous hydrogen carbonate $FeH_2(CO_3)_2$. Tunbridge Wells, Flitwick (Beds), Cheltenham (Cambray Well), and Leamington, are well-known examples. The corresponding manganous salt may also be present.

4. *Carbonated* waters may hold sodium hydrogen carbonate, $NaHCO_3$, in solution, as their chief salt, as for example in Apollinaris water. *Magnesian* waters contain magnesium hydrogen carbonate, $MgH_2(CO_3)_2$, and *calcareous* waters the corresponding calcium salt, $CaH_2(CO_3)_2$. Such springs may be looked for in dolomitic, limestone, and chalky districts.

5. *Sulphuretted* waters are characterised by the presence of hydrogen sulphide which imparts to them its taste and odour A considerable

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[1] Moore and Schlundt, *7th Inter. Cong. Applied Chem*, 1909, section x., p. 189.

[2] Schlundt, *J. Physical Chem.*, 1914, 18, 662; Lester, *Amer. J. Sci.*, 1918, [4], 46, 621

[3] Namely the Saratoga Springs. Moore and Whittemore, *J. Ind. Eng. Chem.*, 1914, 6, 552.

[4] de Rada, *Anal. Fis. Quim.*, 1908, 6, 242.

[5] Wright and Heise, *J. Physical Chem.*, 1917, 21, 525; Heise, *Philippine J. Sci.*, 1917, [A]. 12, 293, 309.

[6] Thorkelsson, *Mémoires de l'Acad Royale des Sciences et des Lettres de Danemark, Copenhague*, 1910, [7], 8, 182.

[7] Bernini, *Nuovo Cim.*, 1911, [6], 1, i., 455.

[8] Wright and Heise, *loc. cit.*, etc.

[9] See, for example, Loisel (*Compt. rend.*, 1919, 169, 791), who gives $6\cdot8\times10^{-13}$ gram of dissolved radium per litre as the mean value for Bagnoles spring.

[10] Lepape, *loc. cit.* By the decision of the Radiology Congress in Brussels in 1910, a "curie" is defined as the quantity of emanation in equilibrium with one gram of radium. A millimicrocurie is one thousand-millionth of a curie, and thus corresponds to $10^{-9}$ gram of radium.

number of these springs occur in the British Isles, perhaps the best known being those at Harrogate (Yorks), The Leper's Well (Dinsdale, Durham), Lisdoonvarna (Clare, Ireland), Llandrindod Wells (Wales), Llanwrtyd (Wales), Moffat (Dumfries), Peebles, and Strathpeffer (Ross). Such waters have frequently been used in bygone years for secret correspondence. Letters written with a solution of lead acetate become legible when dipped, for example, in Harrogate water.[1]

6. *Lithiated* waters are in high pharmaceutical repute, the lithium being usually present as chloride. Baden-Baden (Germany) and Kissingen (Bavaria) are two well-known resorts of this type.

7. *Arsenical*, and 8. *Bromiuretted* (Woodhall, Lincolnshire) waters contain small quantities of arsenic and bromine (as an alkali bromide) respectively.

9. *Goitrigenic.*—Certain waters are particularly liable to cause abnormal activity of the thyroid gland, resulting in the enlargement known as goitre or Derbyshire neck. This is usually attributed to the presence in the water of organic matter, possibly a protozoon, but the suggestion has also been made that a connection may exist between radioactivity and goitrigenic properties of certain springs.[2]

The following analyses of various well-known spring and spa waters are characteristic :

## BUXTON THERMAL WATER.[3]

Temperature . . 25·8° C.
Density at 25·8° C. . 0·99686

| | Parts per 100,000. | Grains per Gallon.[4] |
|---|---|---|
| Calcium bicarbonate . | 20·014 | 14·010 |
| Magnesium ,, . . | 8·587 | 6·011 |
| Ferrous ,, . . | 0·044 | 0·031 |
| Manganous ,, . . | 0·040 | 0·028 |
| Barium sulphate . . | 0·069 | 0·048 |
| Calcium ,, . . | 0·273 | 0·191 |
| Potassium ,, . . | 0·888 | 0·622 |
| Sodium ,, . . | 1·205 | 0·844 |
| Lead ,, . . | 0·006 | 0·004 |
| Sodium nitrate . . | 0·037 | 0·026 |
| Calcium fluoride . . | 0·028 | 0·020 |
| Sodium chloride . . | 4·412 | 3·088 |
| Ammonium ,, . . | 0·003 | 0·002 |
| Magnesium ,, . . | 1·361 | 0·953 |
| Silicic acid . . . | 1·356 | 0·949 |
| Lithium . . . | trace | trace |
| Strontium . . . | trace | trace |
| Phosphoric acid . . | trace | trace |
| Organic matter . . | 0·033 | 0·023 |
| Free carbon dioxide . | 0·287 | 0·201 |
| Nitrogen . . . | 0·272 | 0·190 |

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[1] See *Chemical Catechism*, Parkes (London, 1810), p. 255.

[2] Répin, *Compt. rend.*, 1908, **147**, 387.

[3] Thresh, *The Examination of Waters and Water Supplies* (Churchill, 1913), p. 341.

[4] These figures are obtained by multiplying those in the previous column by 0·70.

Analyses of Cheltenham Spa Waters by Thorpe gave the following results:

| No. 1.[1] Cheltenham Magnesia Water. | | No. 2. Cheltenham Alkaline Water. | | No. 3. The Cheltenham Sodium Sulphate Saline. | |
|---|---|---|---|---|---|
| | Grains per Gal. | | Grains per Gal. | | Grains per Gal. |
| Sodium chloride | 27·980 | Sodium chloride | 466·470 | Sodium chloride | 391·710 |
| Sodium bromide | 0·015 | Sodium bromide | 0·388 | Sodium bromide | 0·001 |
| Sodium iodide | 0·037 | Sodium iodide | 0·099 | Sodium iodide | 0·021 |
| Sodium sulphate | 60·893 | Sodium sulphate | 115·095 | Sodium sulphate | 155·720 |
| Sodium silicate | 1·469 | Sodium silicate | 2·961 | Sodium silicate | 1·763 |
| Potassium sulphate | 4·779 | Sodium bicarbonate | 38·961 | Potassium sulphate | 9·990 |
| Lithium chloride | traces | Potassium sulphate | 4·520 | Lithium chloride | traces |
| Calcium carbonate | 36·372 | Lithium chloride | traces | Calcium carbonate | 27·200 |
| Calcium sulphate | 63·460 | Calcium carbonate | 4·583 | Calcium sulphate | 2·447 |
| Magnesium sulphate | 117·659 | Calcium phosphate | traces | Magnesium carbonate | 14·115 |
| Manganous carbonate | 0·023 | Magnesium carbonate | 10·866 | Magnesium sulphate | 22·667 |
| Ferrous carbonate | 0·038 | Manganous carbonate | traces | Manganous carbonate | traces |
| Aluminium phosphate | 0·011 | Ferrous carbonate | 0·056 | Ferrous carbonate | 0·021 |
| Ammonium nitrate | 0·018 | Aluminium phosphate | traces | Aluminium phosphate | traces |
| Organic matter | traces | Ammonium bicarbonate | 0·078 | Organic matter | traces |
| | | Organic matter | traces | | |

**Droitwich brine** contains:

| | |
|---|---|
| Sodium chloride | 22·452 per cent. |
| Sodium sulphate | 0·390 ,, |
| Calcium sulphate | 0·387 ,, |
| Calcium carbonate | 0·052 ,, |
| Magnesium carbonate | 0·115 ,, |

With traces of alkali bromides and iodides, phosphates of calcium and iron, and silica.[2]

### *The Harrogate Mineral Waters.*[3]

Since the discovery of the Tewit Well by Captain Slingsby in 1571, the mineral waters of Harrogate have attracted considerable attention; about eighty springs are known, differing in type and quality. These may be divided into two main groups—namely, sulphatic and chalybeate waters.

The principal sulphur wells occur about a mile on either side of Harlow Hill, the highest point of the district.

Opinions differ as to whether the waters have a common origin, or each spring has its own independent source. The difference of level of adjacent wells favours the latter view, whilst the temperatures indicate that they are neither superficial nor come from enormous depths. Most probably each spring has its own independent source, with which it is connected by a separate and distinct channel formed by the alternating series of impervious and porous strata which connect Harrogate with the hilly regions to the west, for it is only from such a source as this that a large body of water could flow year after year, with

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[1] To convert these into parts per 100,000 divide by 0·70.

[2] See Worth, *The Tourist's Guide to Worcestershire* (Stanford, 1889).

[3] Lowson, *Analyst*, 1921, 46, 125.

## HARROGATE SULPHATIC WATERS.

(Parts per 100,000.)

| | Old Sulphur Well, Nov. 1912. | Mild Sulphur Well, Nov. 1912. | Strong Montpellier, Dec. 1913. | Mild Montpellier, Apr. 1913. | Magnesia Well, Oct. 1913. | No. 36, Jan 1913. | Harlow, July 1915. | Beckwith, Aug. 1915. | Starbeck, Feb 1914. |
|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. $\left(\frac{15° C.}{15° C.}\right)$ | 1·0113 | 1·0056 | 1·0076 | 1·0068 | 1·0021 | 1·0033 | 1·0006 | 1·0004 | 1·0019 |
| Total solids | 1508·5 | 680·1 | 1003·3 | 874·0 | 258·15 | 415·7 | 52·2 | 45·03 | 222·3 |
| Sodium | 506·3 | 220·25 | 327·5 | 300·4 | 85·7 | 143·9 | 10·1 | 11·04 | 76·9 |
| Potassium | 6·5 | 3·35 | 4·56 | 4·51 | 1·68 | 2·43 | 0·66 | 0·56 | 0·94 |
| Lithium | 0·13 | trace | trace | trace | trace | trace | trace | trace | trace |
| Ammonium | 1·58 | 1·16 | 1·27 | 0·51 | 0·29 | 0·78 | .. | .. | 0·27 |
| Magnesium | 18·24 | 11·26 | 15·44 | 15·49 | 3·10 | 4·5 | 3·62 | 1·60 | 2·70 |
| Calcium | 44·0 | 23·3 | 36·86 | 34·7 | 78·2 | 11·09 | 6·09 | 3·99 | 7·35 |
| Strontium | trace | trace | trace | trace | trace | trace | .. | .. | .. |
| Barium | 6·04 | . | 0·47 | 4·9 | 3·36 | 1·88 | .. | .. | 0·89 |
| Iron | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Aluminium | .. | .. | .. | .. | .. | .. | .. | trace | .. |
| Manganese | trace | .. | trace | .. | trace | .. | .. | trace | .. |
| Chloride | 879·1 | 382·5 | 578·0 | 499·9 | 134·5 | 221·2 | 4·30 | 3·00 | 103·5 |
| Bromide | 2·67 | 0·9 | 2·0 | 1·6 | 0·4 | 0·8 | .. | .. | trace |
| Iodide | trace | .. | .. | trace | .. | .. | .. | .. | .. |
| Silicate ($SiO_3$) | 1·20 | 0·76 | 1·04 | 1·11 | 1·62 | 1·08 | 1·21 | 1·20 | 1·77 |
| Sulphate ($SO_4$) | .. | 11·14 | 5·73 | 0·48 | 0·53 | 1·65 | 4·0 | .. | 7·2 |
| Phosphate ($PO_4$) | .. | .. | .. | .. | .. | .. | .. | trace | .. |
| Carbonate ($CO_3$) | 59·7 | 53·0 | 54·9 | 80·8 | 67·1 | 61·4 | 61·6 | 46·6 | 66·15 |
| Sulphur (as Sulphide) | 8·94 | 4·85 | 4·97 | 6·64 | 0·68 | 4·06 | 0·93 | 1·18 | 0·86 |

## HARROGATE CHALYBEATE WATERS.

(Parts per 100,000.)

| | Kissingen. June 1914. | Chloride of Iron, Oct. 1914. | Alexandra Chalybeate, Dec. 1914. | Pure Chalybeate, Nov. 1914. | Tewit Well, Mar. 1915. | John's Well, Feb. 1915. | Alum Well, Apr 1915. |
|---|---|---|---|---|---|---|---|
| Sp. gr. $\left(\frac{15° C.}{15° C.}\right)$ | 1·0071 | 1·0051 | 1·0027 | 1·0001 | 1·0004 | 1·0002 | 1·0028 |
| Total solids | 988·1 | 686·3 | 319·7 | 12·96 | 42·15 | 18·19 | 358·5 |
| Sodium | 293·1 | 207·8 | 110·4 | 0·86 | 1·91 | 1·46 | 118·1 |
| Potassium | 4·33 | 2·44 | 2·20 | 0·27 | 0·25 | 0·22 | 2·05 |
| Lithium | trace | trace | trace | trace | trace | trace | trace |
| Ammonium | . . | . . | . . | . . | . . | . . | . . |
| Magnesium | 16·80 | 12·11 | 3·78 | 0·66 | 2·87 | 1·06 | 3·97 |
| Calcium | 41·2 | 29·44 | 10·41 | 1·54 | 5·60 | 2·49 | 10·83 |
| Strontium | trace | trace | trace | . . | . . | . . | . . |
| Barium | 4·80 | 3·13 | 2·80 | 0·06 | . . | 0·06 | 0·75 |
| Iron | 1·55 | 5·05 | 3·58 | 0·83 | 1·71 | 0·91 | 3·45 |
| Aluminium | . . | . . | . . | . . | trace | . | trace |
| Manganese | trace | 0·07 | trace | trace | trace | 0·02 | trace |
| Chloride | 578·3 | 397·3 | 178·2 | 1·39 | 2·29 | 1·50 | 186·8 |
| Bromide | 1·0 | 1·0 | 1·0 | . . | trace | . | . |
| Iodide | . . | trace | . . | . . | . . | . . | |
| Silicate ($SiO_3$) | 1·76 | 1·69 | 0·97 | 1·43 | 2·36 | 3·13 | 1·24 |
| Sulphate ($SO_4$) | 1·47 | 0·13 | 0·96 | 0·85 | 13·96 | 0·62 | 6·14 |
| Phosphate ($PO_4$) | trace | trace | trace | trace | 0·11 | trace | trace |
| Carbonate ($CO_3$) | 76·5 | 41·1 | 82·0 | 42·1 | 35·8 | 42·03 | 58·04 |

such slight alteration both in quality and quantity. The chemical impregnation of the water appears to be effected during its passage through these strata, and it is from this source that the bases of all the salts are derived.

The analyses are given by Lowson (pp. 211–212).

As mentioned before, a century ago secret correspondence was often carried on by means of Harrogate water.

### *Trefriw Springs.*

These are situate in the valley of the Conway (Carnarvon), and may be classed either as ferruginous or sulphatic springs. Hassell's analyses [1] are as follow, expressed in grains per gallon :

| | Spring No. I. | Spring No. II. |
|---|---|---|
| Temperature . . . | 48° F. (9° C.) | 50° F. (10° C.) |
| Ferrous oxide . . | 180·85 | 81·11 |
| Alumina . . . | 14·73 | 10·20 |
| Magnesia . . . | 5·30 | 6·94 |
| Soda . . . . | 1·44 | 2·38 |
| Lime . . . . | 11·42 | 13·70 |
| Manganese . . . | trace | trace |
| Sulphuric acid . . | 263·20 | 149·83 |
| Chlorine . . . | 0·76 | 0·53 |
| Silica . . . . | 10·43 | 11·74 |
| Total . . | 488·13 | 276·43 |

The chalybeate spring of Tunbridge Wells contains the following constituents : [2]

| | Parts per 100,000. |
|---|---|
| Sulphate of lime . . . . | 3·000 |
| Carbonate of lime . . . . | 0·642 |
| ,, ,, magnesia . . . | 1·596 |
| Potassium chloride . . . | 0·335 |
| ,, carbonate . . . | 0·854 |
| Sodium chloride . . . . | 4·540 |
| Carbonate of iron . . . . | 5·589 |
| ,, ,, manganese . . . | trace |
| Silica . . . . . . | 0·750 |
| Organic matter . . . . | trace |
| Free carbon dioxide . . . | 69·35 c.c. per litre. |

The relative richness of these waters in dissolved solids is easily recognised when it is realised that a lake water of high purity such as that of Loch Katrine may total only 3 parts of solid matter per 100,000.

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[1] See *Climate and Baths of Great Britain and Ireland* (Macmillan, 1902), vol. ii., p. 327.

[2] J. Thomson, *J. Chem. Soc.*, 1858, 10, 223.

**2. Well Water.**—As a general rule, a well drains a volume of earth much the shape of an inverted cone, the apex of which is the bottom of the well, whilst the base lies at the well's mouth and covers a circular area of radius equal to four times the depth of the well. These statements are only approximately correct, for the porosity of the soil, and the extent to which the well is used, exert an appreciable influence. A well is considered shallow if 50 feet or less in depth. A deep well should be 100 feet or more. Shallow wells are open to suspicion owing to the relative ease with which surface water can find entry. The top of the well is usually protected by a ring of masonry to prevent surface water from draining into the well without being filtered by soaking through the soil.

For temporary supplies, Abyssinian Tube wells are useful, consisting of iron tubes, perforated below, which are driven into the ground, a pump being attached to the top. For domestic purposes, however, shallow well water is open to grave suspicion in this country.

Deep wells still yield very valuable supplies of drinking water, which has had a proportionately better chance of undergoing thorough filtration than that collecting in shallow wells. The new wells at Watford (Herts) are driven deep down into the chalk and yield an abundant supply of good water.

Chalk does not necessarily yield good water, however, for, being soluble, fissures are frequently formed through which the water pours without being properly filtered. The hardness varies; the total dissolved solids average 30 per 100,000 of water.

### ANALYSES OF WATERS FROM WELLS IN CHALK NEAR LONDON.

(Parts per 100,000).[1]

| | Eton. | Datchet | Shepherd's Bush. | Lambeth. |
|---|---|---|---|---|
| $CaCO_3$ . . . . | 21·8 | 16·3 | 5·0 | 12·75 |
| $CaSO_4$ . . . . | 6·4 | . . | . . | . . |
| $MgCO_3$ . . . . | . . | 3·6 | 3·5 | 7·85 |
| $MgCl_2$ . . . . | 2·3 | . . | . . | . . |
| $Na_2CO_3$ . . . . | . . | 3·4 | 21·6 | 6·9 |
| $Na_2SO_4$ . . . . | . . | 7·6 | 24·1 | 11·1 |
| NaCl . . . . | 1·1 | 5·8 | 22·6 | 14·4 |
| $NaNO_3$ . . . . | 3·5 | 1·3 | . . | . . |
| $SiO_2$, etc. . . . | 1·4 | 1·4 | 0·6 | 1·0 |
| Total . . | 36·5 | 39·4 | 77·4 | 54·0 |

*Artesian* wells have been known from very early times, having been used by the Arabs, Chinese, and other ancient peoples, thousands of years ago. They are made by drilling through a hard, impervious stratum into a porous rock below, which may require up to 25 per cent.

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[1] Thresh, *The Examination of Waters and Water Supplies* (Churchill, 1913), p. 352.

of its water to saturate it. Large stores of water may thus be held in the rock. The waters may rise up through the bore-hole on account of hydrostatic pressure, or through the pressure exerted by imprisoned gases or the rock above. In any case the waters have travelled some distance underground, and are thus more likely to be pure and wholesome. Where the natural flow is maintained without resort to pumping, the wells are known as " boiling wells."

The state of purity of well water must depend very largely upon the nature of the rocks and soil through which it has flowed. Waters from granite and gneissic districts are usually very pure, soft, and palatable. Their organic content is low. Silurian rocks—slate, shale, and sandstone—are also good, containing but little organic matter, although their saline content may be slightly higher. The salts, however, are generally innocuous, having been washed out of the rocks. Limestone rocks yield clear, hard water, whilst Devonian and Permian sandstones, and millstone grit yield clear waters, but of variable hardness.

3. **Upland surface water** may be very good, provided the sources are free from habitation. Vegetable organic matter is present, sometimes in large quantity, so much so that the water may possess a decided yellowish-brown tint. Animal matter will be absent, so that the nitrogen content should be low, any ammonia, nitrates, or nitrites present being in such amounts as are contained in rain water. Chlorides are low and, unless the soil is calcareous, the water is soft.

4. **Rain Water.**—Most countries are dependent, either directly or indirectly, upon rain for their water supplies.

The average annual rainfall of the earth is estimated at approximately 33 inches, and is equivalent to a volume of 200,000 cubic miles.

The total annual rainfall *on the land* of our planet is estimated [1] at 29,347·4 cubic miles, and of this quantity 6524 cubic miles, or approximately one-fifth, drains off into the sea through rivers and streams. A cubic mile of river water weighs approximately 4200 million tons, and contains on the average some 420,000 tons of dissolved material. Each year, therefore, some 2735 million tons of dissolved matter find their way into the seas, irrespective of the enormous quantities carried down in suspension, or washed into the sea by purely mechanical force.[2] It is interesting to note that

1 inch of rain = 4·67 gallons per square yard.
= 22,617 gallons per acre.
= 101 tons per acre.

It has been calculated that the rain falling on the land is apportioned as follows:

25 per cent. of land surface receives $<12$ inches.
,, ,, ,, 12–24 ,,
,, ,, ,, 24–48 ,,
,, ,, ,, $>48$ ,,

Considering only the land which is drained by rivers into the sea, it is calculated that only 30 per cent. of the water returns to the sea in this way, the remaining 70 per cent. being removed by evaporation.

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[1] Murray, *Scottish Geol. Mag.*, 1887, 3, 65.

[2] Clarke, *Smithsonian Miscell. Coll.*, 1910, 56, No. 5.

The distribution of rain, however, varies enormously even within comparatively small areas. Thus, for example, whilst at Shoeburyness in 1905 the fall was only 14 inches, at the Stye in Cumberland in 1903 it was 223 inches.

In some parts of Scotland and in the north of England some 6 or 7 inches of rain have been known to fall in twenty-four hours. During the so-called "cloud-burst" at Louth in Lincolnshire, in May 1920, 4·7 inches fell in two and a half hours; but such deluges in the British Isles are exceptional.

## AVERAGE RAINFALL IN THE BRITISH ISLES.[1]

(All data are expressed in inches per annum.)

### England.

| | | | | | |
|---|---|---|---|---|---|
| Barnstaple | 37·11 | Greenwich | 23·96 | Rothamsted | 29·50[2] |
| Bath | 30·17 | Harrogate | 29·58 | St. Leonards | 28·99 |
| Birmingham | 26·95 | Hull | 25·72 | Salisbury | 32·44 |
| Blackpool | 33·83 | Kew | 24·15 | Scarborough | 26·61 |
| Brighton | 27·46 | Lincoln | 23·60 | Sheffield | 32·12 |
| Buxton | 49·66 | Liverpool | 28·60 | Shields | 24·56 |
| Carlisle | 32·22 | Lowestoft | 23·67 | Shoeburyness | 19·27 |
| Cheltenham | 27·02 | Margate | 23·42 | Southport | 32·54 |
| Clacton | 19·31 | Norwich | 27·06 | Tunbridge Wells | 29·99 |
| Durham | 25·96 | Plymouth | 35·63 | Worksop | 24·32 |
| Eastbourne | 30·92 | Portsmouth | 27·39 | York | 24·85 |
| Falmouth | 44·23 | Rothamsted | 27·51 | | |

### Wales.

| | | | | | |
|---|---|---|---|---|---|
| Cardiff | 41·74 | Llandudno | 30·52 | Pembroke | 34·89 |

### Scotland.

| | | | | | |
|---|---|---|---|---|---|
| Aberdeen | 30·34 | Glasgow | 37·72 | Leith | 23·86 |
| Dumfries | 37·16 | Glencarron (26 years) | 88·16 | Stornoway | 48·62 |
| Dundee | 28·57 | | | | |
| Fort William | 78·11 | | | | |

### Ireland.

| | | | | | |
|---|---|---|---|---|---|
| Armagh | 31·82 | Dublin (Phœnix Park) | 28·03 | Kilkenny | 33·02 |
| Belfast | 33·99 | Killarney | 54·25 | Waterford | 38·87 |
| Dublin (City) | 27·84 | | | | |

### Miscellaneous.

| | | | | | |
|---|---|---|---|---|---|
| Douglas (I.O.M.) | 42·32 | Jersey | 33·62 | Ventnor (I.O.W.) | 29·42 |
| Guernsey | 36·71 | Scilly Is. | 32·40 | | |

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[1] Average for the thirty-five years, 1876 to 1910. From *The Meteorological Office Reports*, 1913, vol. xxx., pp. 250 *et seq.*

[2] Average for the last fifty years. Christmas, *Nature*, 1921, 108, 307.

These amounts appear small when compared with some foreign falls.

| | |
|---|---|
| Cherra Punji, Assam, India | 610 inches.[1] |
| Coimbra, Portugal | 224 „ |
| Belize, Honduras | 153 „ |
| Guadaloupe Matonba, W. Indies | 285 „ |
| S. Luis de Maranhão, Brazil | 276 „ |

The world's record rainfall is 41 inches, which fell at Suva, Fiji, on 8th August 1906, in about thirteen hours—that is, at the rate of some 3 inches per hour.

The rain water that falls in country districts is highly aerated, soft, and wholesome. It usually contains 25 c.c. dissolved gases per litre, namely:

| | c.c. |
|---|---|
| Oxygen | 8·5 |
| Nitrogen | 16·0 |
| Carbon dioxide | 0·5 |

Both the quantity and relative proportions of these gases vary, not merely with the district, but also with the temperature. This is evident from the following table, in which are given the figures obtained by Bunsen[2] about 1855, expressed as percentages of the total gas dissolved:

| Temperature ° C. | 0 | 5 | 10 | 15 | 20 |
|---|---|---|---|---|---|
| Oxygen | 63·20 | 63·35 | 63·49 | 63·62 | 63·69 |
| Nitrogen | 33·88 | 33·97 | 34·05 | 34·12 | 34·17 |
| Carbon dioxide | 2·92 | 2·68 | 2·46 | 2·26 | 2·14 |

Nitrogen compounds are also usually present in rain water in the form of ammonia, nitrites, and nitrates, the two latter particularly during and after a thunderstorm owing to the combination of oxygen and nitrogen induced by the lightning and electric disturbances generally.

Rain falling in inhabited areas is contaminated with products of combustion, in consequence of domestic fires, either alone as, for example, at Malvern in Worcestershire, or in addition to industrial furnaces, as at Sheffield and Manchester. In normal times industrial smoke is fairly constant in quantity all the year round, whilst domestic smoke varies largely with the weather, being greater in winter than in summer. The following results (p. 218) are interesting as showing the enormous effect of industrial smoke upon the composition of rain.[3] The data are expressed in metric tons per square kilometre—the unit chosen by the London Committee on Atmospheric Pollution—but can be converted into tons per square mile by multiplying by 2·55.

As is emphasised in the Report, however, the foregoing data do not indicate *the actual extent of atmospheric pollution.* When curves are drawn showing the monthly variations in rainfall and pollution, the periods of maximum pollution are seen to coincide with those of maximum rainfall. For strictly comparative results, therefore, rain should fall at a uniform rate, and should continue either all day or at the same period of each date. These conditions, however, are not attainable in nature. The tables do, however, give a clear idea of the nature and quantity of the substances actually brought down by the rain over a given period.

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[1] In 1861 the rainfall was 805 inches, no fewer than 366 inches falling in July. See Coles-Finch, *Water, its Origin and Use* (London, 1908).

[2] Bunsen, *Annalen*, 1855, 93, 48. See also Baumert, *ibid.*, 1853, 88, 17; Pettersson and Sondén, *Ber.*, 1889, 22, 1439.

[3] Taken from the *Report of the Investigation of Atmospheric Pollution*, 1914–1915, drawn up by Wynne and presented to the Health Committee of Sheffield City Council.

### IMPURITIES BROUGHT DOWN BY RAIN, 1st JANUARY TO 30th APRIL 1915.

| Town. | Tar. | Insoluble Matter. | Dissolved Solids. | Total. | $SO_4$ | Cl. | $NH_3$ |
|---|---|---|---|---|---|---|---|
| Malvern . . | 0·01 | 0·85 | 5·01 | **5·86** | 1·68 | 0·86 | 0·15 |
| Sheffield— | | | | | | | |
| Attercliffe . | 0·60 | 45·10 | 28·01 | **73·11** | 8·51 | 6·75 | 0·32 |
| Weston Park | 0·27 | 19·02 | 22·48 | **41·50** | 9·34 | 2·77 | 0·14 |
| Manchester— | | | | | | | |
| Ancoats Hospital. . | 0·41 | 64·03 | 42·29 | **106·32** | 19·63 | 4·36 | 0·30 |
| Fallowfield . | 0·20 | 26·22 | 21·99 | **48·21** | 10·66 | 2·39 | 0·19 |

An interesting contribution to this subject is afforded by Longmuir,[1] who collected rain water in Sheffield in 1911 during a shower of three hours' duration. The different samples were taken at different points within an area of half a square mile, and are seen to exhibit a most remarkable variation in composition.

| Sample. | Total Chlorides expressed as Cl. | | Total Sulphates expressed as $SO_3$. | |
|---|---|---|---|---|
| | Grams per Gallon. | Grams per Litre. | Grams per Gallon. | Grams per Litre. |
| 2 | 0·9800 | 0·0140 | 0·4167 | 0·0059 |
| 4 | 1·2548 | 0·0179 | 3·3180 | 0·0474 |
| 5 | 8·0836 | 0·1154 | 7·3096 | 0·1044 |
| 11 | 0·2549 | 0·0036 | 1·6831 | 0·0240 |
| 8 | 1·5286 | 0·0218 | 2·6930 | 0·0384 |

No. 8 represents rain-drippings from the foliage of a tree.

Another industrial area is that of Leeds, where,[2] on the average working day, 20 tons of soot are sent into the air, of which half a ton falls on an area of 4 square miles, and of the latter from 20 lb. to 25 lb. stick, that is, are not removable by rain.

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[1] Longmuir, *J. Iron Steel Inst*, 1911, i., 147.

[2] See Cohen and Ruston, *Nature*, 1909, 81, 468.

The results of analyses of rain water from ten representative stations in the city, and, for the sake of comparison, one from Garforth, nearly 8 miles due east of the city, and situated in the country, are given herewith:

## ANALYSIS OF RAIN WATER, LEEDS AND GARFORTH.

(Total for Year, expressed in Pounds per Acre.)

| Collecting Station. | Suspended Matter | Tarry Matter. | Mineral Matter. | Free Acidity as $H_2SO_4$. | $SO_3$. | $SO_2$. | Chlorine. | Nitrogen as $NH_3$. | Nitrogen as $N_2O_5$. | Nitrogen as Albuminoid. Ammonia. | Total Nitrogen. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Industrial— | | | | | | | | | | | |
| 1. Leeds Forge | 1886 | 110 | 1113 | 35 | 123 | 34 | 164 | 13·0 | 0·0 | 4·7 | 17·7 |
| 2. Hunslet | 1565 | 69 | 655 | 90 | 185 | 24 | 198 | 15·5 | 0·0 | 2·9 | 18·4 |
| 3. Beeston Hill | 1163 | 149 | 709 | 30 | 269 | 54 | 101 | 14·4 | 0·5 | 3·5 | 18·4 |
| Residential— | | | | | | | | | | | |
| 4. Philosophical Hall (Town) | 849 | 78 | 423 | 45 | 149 | 38 | 75 | 14·4 | 0·3 | 2·2 | 16·9 |
| 5. Headingley | 659 | 43 | 199 | 11 | 118 | 32 | 41 | 11·1 | 1·1 | 0·8 | 13·0 |
| 6. Armley | 593 | 34 | 216 | 29 | 110 | 37 | 108 | 9·9 | 1·0 | 3·2 | 14·1 |
| 7. Observatory | 399 | 32 | 146 | 26 | 85 | 39 | 51 | 8·4 | 0·8 | 1·6 | 10·8 |
| 8. Kirkstall | 352 | 28 | 141 | 8 | 77 | 56 | 57 | 7·7 | 0·2 | 2·3 | 10·2 |
| 9. Weetwood Lane | 147 | 26 | 54 | 11 | 82 | 13 | 34 | 8·3 | 1·1 | 2·1 | 11·5 |
| 10. Roundhay | 90 | 14 | 49 | 0 | 53 | 16 | 38 | 5·8 | 0·7 | 1·3 | 7·8 |
| 11. Garforth (Country) | .. | .. | .. | 28 | 65 | 21 | 22 | 5·0 | 3·2 | 1·1 | 9·3 |

During gales, rain from the sea is frequently highly charged with sodium chloride. It is recorded[1] from East Kent that, during the winter of 1910, a very heavy gale from the south-east with a deluge of rain occurred in the night; on the following day all the windows which faced south-east had quite a frosted appearance when dry. Some of the substance scraped off and dissolved in distilled water was proved to consist of common salt.

Soot, which finds its way into the atmosphere, is usually rich in sulphur compounds, as the following analyses indicate:[2]

| | Sulphur as $SO_3$. Per cent. |
|---|---|
| Dining-room chimney | 5·68 |
| Kitchen chimney | 8·24 |
| ,, ,, | 6·14 |
| Locomotive | 3·60 |
| ,, | 8·51 |

A shower, therefore, which brings to earth the soot floating in the air must be proportionately contaminated.

The amounts of dissolved compounds of nitrogen, chlorine, and sulphur in rain water collected from various parts of the world during the present century are given in the following table, expressed as parts per million :

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[1] *Nature*, 1911, 87, 257; from *Reports and Transactions of the East Kent Scientific and Natural History Society*, ending 30th Sept. 1910.

[2] Longmuir, *loc. cit.*

| Locality. | Date. | Annual Rainfall, inches. | Nitrogen. | | Cl. | $SO_3$. |
|---|---|---|---|---|---|---|
| | | | As $NH_3$. | As Nitrates. | | |
| Pretoria [1] . . | 1904–5 | 24·31 | 1·194 | 0·196 | . . | . . |
| Barbados [2] . . | 1908 | 40·28 | 0·032 | 0·384 | 8·38 | . . |
| Dehra Dun [3] . | 1904–5 | 87·45 | 0·110 | 0·070 | . . | . . |
| Cawnpore [3] . | 1904–5 | 49·36 | 0·220 | 0·069 | . . | . . |
| Lincoln (N.Z.) [4] . | 1907–8 | 21·48 | 0·170 | 0·238 | 6·1 | 3·28 |
| ” . | 1908–9 | 32·11 | 0·094 | 0·117 | 5·5 | 2·86 |
| Hebrides [5] . . | 1908–12 | 39·70 | 0·034 | 0·032 | . . | . . |
| Iceland [5] . . | 1911–12 | 38·34 | 0·091 | 0·030 | . . | . . |
| Grahamstown [6] . | 1911–12 | 24·37 | 0·171 | 0·132 | 4·26 | . . |
| Bloemfontein [6] . | 1910–11 | 27·82 | 0·582 | 0·258 | 1·06 | . . |
| ” . | 1911–12 | 15·49 | 1·389 | 0·388 | 0·66 | . . |
| Durban [6] . . | 1911 | 42·34 | 0·381 | 0·129 | 6·39 | . . |
| ” . . . | 1912 | 31·07 | 0·556 | 0·178 | 10·01 | . . |
| Cedara (Natal) [6] . | 1910–12 | 26·68 | 0·780 | 0·143 | 2·68 | . . |

Seasonal fluctuations are also observed in the constituents of rain water. Thus summer rain is not saturated with oxygen, although that which falls during the rest of the year is practically so.[7] As a general rule, rain water is nearly saturated with oxygen when its temperature, as collected, is below 15° C., but when above this point, the dissolved oxygen is always below saturation, sometimes as much as 25 per cent. (see table below). The reason for this is not apparent. The relative temperatures of the rainclouds and of the air at the ground level in summer and winter, if they have any influence at all, should produce a result exactly opposite to that found. In other words, one would expect summer rain to be supersaturated.

Results of numerous experiments at the Rothamsted Experimental Station (Hertfordshire) indicate that rain water is richer in chlorine but poorer in ammoniacal and nitrate nitrogen in winter than in summer. This is shown by the following table [8] (p. 221).

As a rule the amount of nitrate nitrogen is approximately half that of the ammoniacal. The ammonia appears to arise from several sources. The sea, the soil, and the atmospheric pollution consequent upon inhabited areas may all contribute. That the soil is an important factor is suggested by the fact that the ammonia content of rain water is high during periods of great biochemical activity in the soil, and low during periods of less vigorous biochemical activity. The close relationship between the amounts of ammoniacal and nitrate nitrogen indicates either the oxidation of ammonia, or a common origin for the two; conceivably both.

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[1] Ingle, *Transvaal Agric. J.*, 1905, 4, 104.

[2] Bovell, *Report Agric. Work Barbados : Imp. Dept. Agric. West Indies for 1907–1909 ; Chem. Soc. Abstr.*, 1910, ii., 994.

[3] Leather, *Ann. Report Imp. Dept. Agric.*, 1904–1905, p. 55.

[4] Gray, *Canterbury Agric. Coll. Mag New Zealand*, 1910, 24.

[5] Miller, *J. Scot. Meteor. Soc.*, 1913, 16, 141.

[6] Juritz, *S. African J. Sci.*, 1914, 10, 170.

[7] Richards, *J. Agric. Sci.*, 1917, 8, part 3, p. 331.

[8] Russell and Richards, *ibid.*, 1919, 9, part 4, 309.

| | Parts per Million. | | Lb. per Acre. | |
|---|---|---|---|---|
| | Nov.–Feb. | May–Aug. | Nov.–Feb. | May–Aug. |
| Ammoniacal nitrogen | 0·35 | 0·45 | 0·78 | 1·00 |
| Nitrate nitrogen | 0·18 | 0·21 | 0·40 | 0·47 |
| Chlorine | 3·38 | 1·38 | 7·50 | 3 08 |
| Dissolved oxygen | 11·2 | 9·0 | 26·0 | 20·8 |

It is on account of its softness and aeration that rain water is particularly corrosive in its action on metals, and, if it is to be used for domestic purposes, great care must be exercised in its collection and storage. Iron tanks are readily corroded, and lead is dissolved. Stone or concrete tanks may be used.

5. **River Water.**—The composition of river water is largely dependent upon the nature of the soil through which both it and its tributaries flow. Originating, perhaps, in a little spring of relatively pure water issuing from granitic or schistose rock, it may pass through a mountainous district, gradually swelling in size as it absorbs the waters of other pure springs and streamlets, until it reaches the fertile plains below. Here it takes up large quantities of soluble matter both directly and through its tributaries, and finally discharges its burden into another river, into a lake, or direct into the sea itself.

An excellent illustration of this is the Cache la Poudre River in Colorado, which passes through country analogous to that described above and ultimately discharges into the River Platte. Three analyses of the waters are given[1] on p. 222 in which the dissolved substances are expressed as grains per imperial gallon, one taken near its mouth some three miles below Greeley, the second two miles above Greeley, and the third nearer its source (above the north fork). The enormous increase in the amount of dissolved solids as the river leaves the granite for the plains is noteworthy, rising from 2·6 to 111 grains per gallon above Greeley.

Whilst the absolute amount of dissolved material carried to the sea will gradually increase from the source to the mouth, the actual concentration, as expressed in grains per gallon, may fall as the river increases in bulk through dilution by purer tributaries. During times of flood, too, the proportion of salts may differ very considerably from the normal, and the composition of the water near the mouth of a river may give a clear indication of the particular area in which the excessive rainfall or flooding has occurred.

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[1] Clarke, "The Data of Geochemistry," *U.S. Geol. Survey, Bulletin* 616, 3rd ed., 1916.

## ANALYSES OF THE CACHE LA POUDRE RIVER WATER.

(Expressed as grains per gallon.)

| | Near the Source | Two Miles above Greeley | Three Miles below Greeley. |
|---|---|---|---|
| CaO . . . | 0·5238 | 18·938 | 14·087 |
| MgO . . . | 0·1257 | 12·190 | 5·592 |
| $Na_2O$ . . . | 0·3750 | 14·590 | 9·117 |
| $K_2O$ . . . | 0·0855 | 0·451 | 0·372 |
| $(Al, Fe)_2O_3$ . . | 0·0113 | 0·079 | 0·039 |
| $Mn_2O_3$ . . . | 0·0018 | trace | 0·078 |
| $CO_2$ . . . | 0·6029 | 5·920 | 5·087 |
| $SiO_2$ . . . | 0·6053 | 1·035 | 0·951 |
| $SO_3$ . . . | 0·1946 | 54·970 | 30·374 |
| $Cl_2$ . . . | 0·1037 | 2·770 | 2·145 |
| Total . . | 2·6296 | 110·943 | 67·842 |

The following analyses are representative of the data obtainable from the examination of large rivers :

## ANALYSIS OF THAMES RIVER WATER, TAKEN AT HAMPTON.[1]

(Parts per 100,000.)

| | | | |
|---|---|---|---|
| Chlorine . . . . . . | 1·9 | Organic nitrogen . . | 0·052 |
| Free ammonia . . . . . | 0·012 | Organic carbon . . . . . | 0·258 |
| Albuminoid ammonia . . . . | 0·0280 | Total hardness . . | 21·5 |
| Nitrogen as nitrates and nitrites . | 0·273 | Permanent hardness . . . | 5·0 |
| Total combined nitrogen . . | 0·335 | Total solids . . . . . | 31·24 |

## ANALYSIS OF WATER FROM MISSISSIPPI RIVER.[2]

(Parts per 100,000.)

| | | | |
|---|---|---|---|
| $CaCO_3$ . . . . | 6·640 | N (as nitrate) . | 0·110 |
| $MgCO_3$ . . . . | 4·890 | N (as nitrite) . | 0·0008 |
| $CaSO_4$ . . . . | 1·750 | $CO_2$ . . . . | 9·300 |
| $NaCl+KCl$ . . | 6·980 | $NH_3$ (free) . . | 0·004 |
| $SiO_2$ . . . . | 1·38 | $NH_3$ (albuminoid) | 0·048 |
| $Fe_2O_3+Al_2O_3$ . | 0·20 | Total solids . . | 21·92 |

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[1] Rideal, *Water and its Purification* (Crosby Lockwood, 1897).

[2] R. Morgan, *Chem. News*, 1921, 123, 19.

## ANALYSES OF RIVER WATERS.

(Expressed as parts per 100,000.)[1]

| | Thames[2] (Twickenham). | Seine (above Paris) | Rhine (Strassburg) | Rhone (Geneva). | Spree (Berlin). | Danube[3] (Vienna) |
|---|---|---|---|---|---|---|
| Calcium carbonate . | 18·23 | 9·20 | 13·56 | 7·89 | 6·50 | 8·37 |
| Magnesium ,, . | 1·47 | 3·90 | 0·51 | 0·49 | 0·90 | 1·50 |
| Calcium sulphate . | 0·64 | 2·00 | 1·47 | 4·66 | .. | 0·29 |
| Magnesium ,, . | .. | 1·00 | .. | 0·63 | .. | 1·57 |
| Sodium ,, . | 2·86 | | 1·35 | 0·74 | 0·60 | 0·20 |
| Potassium ,, . | 0·95 | .. | .. | .. | 0·60 | |
| Calcium chloride . | 2·50 | 1·00 | .. | .. | .. | .. |
| Sodium ,, . | .. | .. | 0·20 | 0·17 | 1·20 | .. |
| Sodium nitrate . . | .. | .. | .. | 0·85 | 0·30 | .. |
| Potassium ,, . . | .. | .. | 0·38 | .. | .. | .. |
| Iron oxide . . | .. | 0·80 | 0·58 | .. | 1·30 | 0·20 |
| Alumina . . . | .. | | 0·25 | 0·39 | | |
| Silica . . . | 0·39 | | 4·88 | 2·38 | .. | 0·49 |
| Organic matter . . | 4·97 | .. | .. | .. | .. | .. |
| Total solids . | 32·01 | 17·90 | 23·18 | 18·20 | 11·40 | 12·62 |

6. **Lake waters** derive much of their solid material from the rivers feeding them. If the lake has an exit, in the form of a river or series

## ANALYSES OF THE WATER OF THE DEAD SEA.

(Per cent. by weight.)

| | Genth,[4] 1857. | Stutzer and Reich,[5] 1907. | Friedmann,[6] 1912. | |
|---|---|---|---|---|
| | | | At 50 cm. Depth. | At 300 cm. Depth. |
| KCl . . | 1·008 | 1·357 | 1·5208 | 1·4318 |
| NaCl . . | 7·583 | 8·788 | 7·8550 | 7·9325 |
| NaBr . . | .. | .. | 0·5200 | 0·5212 |
| $CaCl_2$ . . | 2·898 | 2·384 | 3·6800 | 3·6903 |
| $MgCl_2$ . . | 10·163 | 8·991 | 10·0299 | 10·3125 |
| $MgBr_2$ . . | 0·534 | 0·368 | .. | .. |
| $CaSO_4$ . . | 0·090 | 0·141 | 0·1460 | 0·1412 |
| $CaCO_3$ . . | 0·004 | .. | trace | trace |
| $Fe_2O_3$ . . | 0·008 | trace | trace | trace |
| Organic matter | 0·020 | .. | trace | trace |
| Total solids . | 22·30 | 22·02 | 23·8500 | 24·1309 |
| Density . | 1·1823 at 17·5° C. | 1·1546 at 17·5° C. | 1·1241 at 15° C. | 1·1336 at 15° C. |

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[1] See *Engineering Chemistry*, by Phillips (Crosby Lockwood, 1894), where numerous analyses are given.

[2] Rideal, *Water and its Purification* (Crosby Lockwood, 1897).

[3] Several other analyses are given by Wolfbauer, *Monatsh.*, 1883, 4, 417.

[4] Quoted by Stutzer and Reich, *Chem. Zeit.*, 1907, 31, 845.

[5] See Stutzer and Reich, *loc. cit.*

[6] Friedmann, *ibid.*, 1912, 36, 147. See also Fresenius, *Verh. Ges. Deut. Naturforsch. Aerzte*, 1913, p. 118.

of rivers and streams, a natural balance, subject to minor fluctuations, will be maintained between the entering waters and those leaving for the sea, and the mean composition of the later waters will not be very different from that of the entering waters. But if the lake is completely surrounded by high ground, entirely without channels through which the water can escape in a normal manner, the excess of water must be expelled through percolation and evaporation, particularly the latter in hot climates. The result is that the lake becomes increasingly saline, and saturation may, in course of ages, be reached, and the excess salts deposited. Such, for example, is the case with the Dead Sea in Palestine, which receives the waters of the Jordan and other minor streams and rivulets, but maintains a fairly constant level mainly through evaporation.

It will be observed that in the results given by Friedmann the water is slightly more dense at the lower depths (300 cm.) than at 50 cm. The waters feeding the Dead Sea are mainly fresh and, being much less dense, tend to remain in the surface layers, diffusion taking place relatively slowly. No doubt this accounts for many of the variations observed in the densities of the waters of inland lakes and seas as determined by different investigators who have not usually stated the precise depth at which their samples were taken. This phenomenon is very marked in the case of certain tidal rivers, and has long been known. Mallet, for example, in 1840 drew attention to it in connection with the River Bann in N. Ireland.[1]

7. **Sea Water.**—The sea may be regarded as an enormous lake, fed by most of the rivers of the world, and itself without any means of discharging its excess water except through evaporation. Mention has already been made of the fact that the world's rivers are continually pouring enormous quantities of dissolved salts into the sea, estimated at about 2735 million tons per annum, with the result that the sea is becoming increasingly saline. This is probably not the only factor affecting the composition of sea water. Another lies in the fact that the sea is continually encroaching on the land in some districts and receding in others. Thus, on the East Yorkshire coast, south of Bridlington, near Kilnsea, it is eroding the boulder clay at an average rate of 7 feet per year. But for every square mile washed away on the Yorkshire coast, 3 square miles have been gained in the Humber and the Wash; [2] but of course the composition of the new soil is different, and the difference represents the solvent action of the sea. This type of change, taking place continuously all over the globe, is, therefore, a second factor.

No doubt there are others, some being of a compensatory nature. Such, for example, is the elimination of calcium carbonate as coral, chalk, etc., through biological agencies.

The changes in composition of the water, however, on account of its vast bulk, are so minute that analysis is quite unable to detect them. It has been estimated [3] that 680,000 years would be required for the rivers of the world to discharge at their present rate sufficient calcium salts into the sea to double the existing amount.

The most abundant dissolved substances in sea-water are sodium chloride and magnesium chloride, potassium salts and bromides also being present but in smaller quantity; the presence of the last-named class of salts is of interest because practically the only sources of bromine at present are sea water and the saline deposits from dried-up seas.

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[1] Mallet, *Reports B.A.*, 1840, p. 227.

[2] Avebury, *The Scenery of England* (Macmillan, 1902), p. 168.

[3] Murray and Irvine, *Proc. Roy. Soc. Edin.*, 1889, 17, 100.

By the *salinity* of sea water is understood the number of grams of total salts in 1000 grams of the water. This may be determined gravimetrically or volumetrically, the latter method being the most usual, the chlorine being determined, and from it the total salts calculated. This method of course implies suitable laboratory facilities, and if these are not available the water must be stored until such time as it can be tested. To obviate this difficulty attempts have been made to determine salinity by electric conductivity measurements. By employing a standard sea water and comparing its conductivity with that of the unknown samples, it is claimed that very accurate results are easily obtained at sea or under conditions entirely unsuitable for ordinary laboratory work.[1]

The analysis of Atlantic waters may be regarded as typical of large oceans. The Mediterranean waters are more concentrated,[2] partly because of the high rate of evaporation, and partly because few rivers flow into it. Even more concentrated are the waters of the Red Sea,[3] for similar reasons.

The water of the Baltic Sea,[2] on account of the continual influx of river water and its relatively limited contact with the open ocean, is comparatively free from dissolved solid matter; it contains up to 18 parts per 1000. An open ocean like the Atlantic contains from 32 to 38 parts [4] per 1000.

An interesting comparison of the waters of the Atlantic Ocean and Mediterranean Sea is given by Schloesing as follows: [4]

### DISSOLVED SALTS IN THE ATLANTIC AND MEDITERRANEAN.

(Parts per 1000 at 20° C.)

| | Atlantic. | Mediterranean. |
|---|---|---|
| Calcium carbonate . . | 0·099 | 0·127 |
| Lime (not included above) . | 0·519 | 0·599 |
| Sulphuric acid . . . . | 2·120 | 2·551 |
| Chlorine . . . . . | 17·830 | 21·376 |
| Bromine . . . . . | 0·060 | 0·072 |
| Magnesia . . . . . | 1·993 | 2·361 |
| Sodium oxide . . . . | 13·410 | 16·017 |
| Potassium oxide . . . | 0·413 | 0·510 |
| Total salts per litre at 20° C. . | 36·444 | 43·613 |

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[1] See Thuras, *J. Washington Acad. Sci.*, 1921, **11**, 160.

[2] Clearly shown by the data in the tables, p. 226.

[3] Analyses are given by Natterer, *Monatsh.*, 1900, **21**, 1037, 1899, **20**, 1.

[4] Schloesing, *Compt. rend.*, 1906, **142**, 320.

From the foregoing data the ratio of the amount of salts in the Atlantic to that in the Mediterranean is 0·836.

The mean results of analyses of 22 samples of water taken from the Atlantic are given by Makin[1] as follow (expressed as parts per 1000):

| | | | |
|---|---|---|---|
| Sodium chloride | 28·023 | Calcium sulphate | 1·365 |
| Potassium chloride | 0·770 | Magnesium bromide | 0·075 |
| Magnesium chloride | 3·672 | Calcium carbonate | 0·129 |
| Magnesium sulphate | 2·399 | Total solids | 36·433 |

Density 1·0275 at 15·5° C

The waters of the Irish Sea contain the following salts dissolved in them[2] expressed as parts per 1000:

| | | | | | |
|---|---|---|---|---|---|
| $NaCl$ | 26·439 | $MgSO_4$ | 2·066 | $CaCO_3$ | 0·048 |
| $KCl$ | 0·746 | $MgCO_3$ | trace | $NH_4Cl$ | 0·0004 |
| $MgCl_2$ | 3·151 | $Mg(NO_3)_2$ | 0·002 | $FeCO_3$ | 0·005 |
| $MgBr_2$ | 0·071 | $CaSO_4$ | 1·332 | $SiO_2$ | trace |

Total solids 33·860.
Density at 0°, 1·02721; at 15°, 1·02484

## COMPOSITION OF SEA WATER.

(Parts per 1000.)

| | Atlantic Ocean[3] | North Sea.[4] | Mediterranean Sea.[5] | Baltic. Sea.[6] | Black Sea.[7] | Pacific Ocean.[8] |
|---|---|---|---|---|---|---|
| Cl | 18·84 | 18·95 | 21·10 | 10·37 | 9·57 | 18·95 |
| Br | 0·33 | 0·29 | ? | .. | 0·005 | 0·31 |
| $CO_3$ | .. | .. | 0·14 | .. | 0·248 | .. |
| $SO_4$ | 2·88 | 2·56 | 5·72 | 0·72 | 1·25 | 2·79 |
| Na | 10·46 | 10·12 | 10·69 | 5·89 | 5·51 | 10·26 |
| Mg | 1·18 | 1·31 | 3·00 | 1·61 | 0·66 | 1·32 |
| Ca | 0·53 | 0·48 | 0·05 | 0·04 | 0·13 | 0·47 |
| K | 0·59 | 0·68 | 0·004 | .. | 0·10 | 0·60 |
| Fe | .. | .. | .. | .. | 0·127 | .. |
| Total | 34·81 | 34·39 | 40·704 | 18·63 | 17·600 | 34·70 |

The density of sea water may be calculated with a fair degree of accuracy by a determination of the refractive index,[9] which, for a constant temperature is directly proportional to the density calculated at 0° C. In other words,

$$n'_t - n_t = K(d'_o - d_o),$$

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[1] Makin, *Chem. News*, 1898, 77, 155, 171.

[2] Thorpe and Morton, *Trans. Chem. Soc.*, 1871, 24, 506.

[3] At Cape Horn, Bibra, *Annalen*, 1851, 77, 90. Several analyses of Atlantic waters off the Argentine coast are given by Corti and Alvaréz, *Anal. Soc. Quim. Argentina*, 1918, **6**, 108.

[4] Bibra, *loc. cit.*

[5] At Marseilles, Laurens, *J. Pharm.*, 1835, 21, 93.

[6] Pfaff, *Schweigger's J.*, 1817, 22, 271.

[7] Gobel, quoted in Thorpe's *Dictionary of Applied Chemistry* (Longmans, 1913), vol. v., p. 695.

[8] Bibra, *loc. cit.*, 3·5 metres from surface.

[9] Vaurabourg, *Compt. rend.*, 1921, 172, 863.

where $n'_t$ and $n_t$ are the refractive indices of sea water and distilled water respectively at $t^\circ$ C. $d'_0$ and $d_0$ their densities at 0°, and K is a constant depending on the temperature.

## FORMATION OF WATER.

Water is produced in the oxidation of hydrogen by free or combined oxygen. The relative volumes of free oxygen and hydrogen at 0° and 760 mm. which undergo combination are 1 : 2 00288, or approximately 1 : 2. Although a mixture of the two gases in these proportions, known as "detonating gas," is stable under ordinary conditions, no change being observable even after prolonged periods of storage in the absence of light at room temperature, the interaction of the gases can be accelerated in various ways.

1. Sunlight can produce a slow but appreciable combination between the gases,[1] the action being due to the ultra-violet rays. Ultra-violet radiation affects both detonating gas and water-vapour tending in each case to produce an equilibrium between the vapour and the constituent elements; [2] with increase in intensity of the illumination the equilibrium shifts in favour of further dissociation, but the proportion of dissociated vapour at the position of equilibrium is very small. The process of combination probably proceeds by the stages [3]

$$H_2+O_2=H_2O_2;$$
$$H_2O_2+H_2=2H_2O.$$

2. Radioactive substances can induce the combination of hydrogen and oxygen; the effect being possibly due in part to a primary conversion of the oxygen into ozone, but this cannot represent the sole mechanism as once more the change leads only to an equilibrium, and water-vapour under similar conditions becomes partially resolved into its elements.[4] The $\alpha$-rays are most active in this respect, although it is possible that $\beta$ and $\gamma$ radiations also exert a subordinate influence.[5] A mixture of hydrogen and oxygen may even explode under the influence of radium emanation.[6]

The silent electric discharge appears to be relatively inactive towards detonating gas.[7]

3. Rise in temperature is, in practice, the simplest process for inducing chemical action between hydrogen and oxygen. It is supposed by some chemists that the absence of chemical action in detonating gas at the ordinary temperature in the absence of light or of radioactive substances is only apparent, the actual rate of combination merely being too small for detection by the usual methods; with increase in temperature the combination is accelerated so that it becomes perceptible or even explosive. The necessary heat can be applied in

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[1] Baker, *Proc. Chem. Soc.*, 1902, 18, 40.

[2] Andréeff, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1342; Coehn, *Ber.*, 1910, 43, 880; Kernbaum, *Bull. Acad. Sci. Cracow*, 1911, [A], 583; Thiele, *Ber.*, 1907, 40, 4914; Tian, *Compt. rend.*, 1911, 152, 1012, 1483

[3] Coehn and Grote, *Festschrift W. Nernst*, 1912, p. 136.

[4] Davis and Edwards, *J. Soc. Chem. Ind.*, 1905, 24, 266; Lind, *J. Amer. Chem. Soc*, 1919, 41, 531.

[5] Debierne, *Ann. Physik*, 1914, ix., 2, 97.

[6] Scheuer, *Compt. rend.*, 1914, 159, 423

[7] Kirkby, *Phil. Mag*, 1904, [6], 7, 223; 1905, 9, 171.

various manners, for example by sudden compression,[1] by an electric spark, by a flame, or by an incandescent solid. The ignition temperature in detonating gas at which self-maintaining combustion is initiated is variable on account of the influence of several factors, but is generally between 500° and 600° C.[2] Although ordinarily "dry" detonating gas will explode readily, a very carefully dried mixture, such as that obtained by prolonged exposure to phosphorus pentoxide, is much less prone to chemical change. A silver wire may be heated to fusion in this gas without causing more than local combination of hydrogen and oxygen;[3] however, an electric spark will induce explosion equally well in the dried and undried gas,[4] probably on account of the higher degree of heat applied. Combination can occur below the ignition temperature, but will then be continuous (in the absence of catalysts) only as long as the temperature is maintained by external sources of heat.

It is of interest to note that the presence of foreign gases has a considerable inhibiting effect on the explosiveness of a mixture of hydrogen and oxygen. The following numbers[5] giving the volume of various gases required to prevent the explosion of one volume of detonating gas by an electric spark are only of relative and not of absolute value, because rather wide divergencies may be observed with different conditions:

| | | | | | |
|---|---|---|---|---|---|
| Hydrogen sulphide | 0·5 | Carbon dioxide | 3 | Hydrogen | 9 |
| Ethylene | 1 | Carbon monoxide | 4 | Air | 12 |
| Ammonia | 1 | Hydrogen chloride | 4 | Oxygen | 14 |
| Sulphur dioxide | 2 | Nitrous oxide | 9 | | |

This is due probably in part to the unequal effect of the surface of the reaction vessel.

The effect of the walls of the containing vessel on the combination of hydrogen and oxygen is merely a special case of a general phenomenon which has already received mention (p. 70). Hydrogen streaming on to a warm platinum spiral in air will raise the temperature of the spiral to redness by the heat of its combustion on the surface of the metal, and indeed may even inflame.[6] Platinum wire or foil will not cause the ignition of detonating gas unless previously warmed to above 50° C., but in a finer state of division such as the "sponge" or "black" obtainable by decomposing ammonium chlorplatinate or chlorplatinic acid, platinum, even without previous warming, will induce such vigorous combination of the two gases as to cause an explosion.[7] Such finely divided platinum in a short time loses its activity, especially if brought into contact with certain substances such as ammonia, hydrogen sulphide, or carbon disulphide vapour. It can, however, be revivified by moistening with nitric acid and drying at 200° C.[1] It appears probable that the presence of moisture is necessary to the catalytic activity of finely divided platinum towards detonating gas at the ordinary temperature.[2]

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[1] See Dixon, *Trans. Chem. Soc.*, 1910, 97, 674; 1914, 105, 2034, 2036.

[2] See Dixon, *loc. cit.*; Falk, *J. Amer. Chem. Soc*, 1906, 28, 1517; 1907, 29, 1536; Mallard and Le Chatelier, *Compt. rend.*, 1880, 91, 825. See also Freyer and Meyer, *Ber.*, 1892, 25, 622; Mitscherlich, *ibid.*, 1893, 26, 160, 399.

[3] Baker, *Trans. Chem. Soc.*, 1902, 81, 400.

[4] Dixon and Bradshaw, *Proc Roy. Soc.*, 1907, [A], 79, 234.

[5] Henry, *Ann. Phil.*, 1838, 25, 462. See also Turner, *Edin. Phil. J.*, 1824, 11, 99; 1825, 12, 311; Turner and Faraday, *Ann. Phys. Chem.*, 1834, [2], 33, 140; Bunsen, *Gasometrische Methoden* (Vieweg, 1877); Regnault and Reiset, *Ann. Chim. Phys.*, 1849, [3], 26, 329; Budde, *Zeitsch. anorg. Chem.*, 1912, 78, 169; Coward and Brinsley, *Trans. Chem. Soc.*, 1914, 105, 1859.

[6] Dulong and Thénard, *Ann. Chim.*, 1823, 23, 440; 24, 380; Berliner, *Ann. Physik*, 1888, [2], 35, 791.

[7] Delarive and Marcet, *Ann. Chim Phys.*, 1828, 39, 328; Henry, *Phil. Mag.*, 1829, 6, 364; 1831, 9, 324; Doebereiner, *Schweigger's J.*, 1822, 34, 91: 1823, 38, 321, 39, 159; 1829, 42, 60; 1831, 63, 465.

Other metals than platinum also can affect the rate of formation of water from gaseous hydrogen and oxygen.[3] Palladium resembles platinum in activity, but many other metals are less effective, examples being osmium, iridium, gold, and silver; mercury appears to be without influence even at its boiling-point. Reduced copper, when heated in detonating gas, commences to oxidise near 250° C., the oxide becoming vigorously reduced with incandescence at a somewhat higher temperature;[4] copper oxide exerts a marked catalytic effect at 300° C. without undergoing visible reduction.[5] Such behaviour suggests that the catalytic action of the nobler metals cited above may depend on a primary combination with one of the constituents of the gaseous mixture followed by regeneration of the metal with formation of water.[6] The activity of the noble metals may, however, be, at least in part, analogous to that possessed by all heated solid surfaces, especially porous ones, for example, pumice, glass, porcelain, carbon, although these have the power only in a much less degree. In the colloidal condition platinum[7] and palladium[8] accelerate the union of hydrogen and oxygen.

The combination of hydrogen and oxygen is accompanied by the liberation of a large quantity of energy generally in the form of heat; this accounts for the vigour of the explosion of a mixture of the gases[9]

$$2(H_2)+(O_2)=2H_2O+2\times 68{,}360 \text{ calories.}$$

A calculation of the temperature produced by the combustion of hydrogen in oxygen or air, based on the above number and the specific heat of the steam produced and of the nitrogen present in the case of air, gives a figure greatly in excess of that actually observed. The discrepancy is due to a combination of several causes. Thus the process is not instantaneous but gradual, so that there is time for loss of heat, radiation especially being an important factor. The increased specific heat of steam at such high temperatures and a somewhat incomplete change on account of a slight dissociation of steam at the temperature attained, are other factors (see p. 130).

The water produced by the direct combination of hydrogen and oxygen frequently contains traces of hydrogen peroxide and of nitric acid. The occurrence of the former indicates the possibility that the primary change may be a simple coupling of molecules with formation of hydrogen peroxide, this compound subsequently decomposing into the more stable substances, water and oxygen (compare p. 77); by continuous repetition of the process the oxygen is at last completely converted into water. This possibility receives some confirmation from the fact that an equimolecular mixture of oxygen and hydrogen has a lower ignition temperature than electrolytic detonating gas, although the evidence is not final.[1] Traces of nitrogen as impurity in the gases used explain the frequent occurrence of small quantities of nitric acid in the water produced.

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[1] Schweigger, *Schweigger's J.*, 1831, 63, 375.

[2] French, *Chem. News*, 1900, 81, 292.

[3] Dulong and Thénard, *loc cit.*; Delarive and Marcet, *loc. cit.*; Quennessen, *Compt. rend.*, 1904, 139, 795. See also this series, Vol. IX, Part I.

[4] Campbell, *Amer. Chem. J.*, 1895, 17, 681.

[5] Joannis, *Compt. rend.*, 1914, 159, 64.

[6] See Berliner, *Ann. Physik*, 1888, [2], 35, 791.

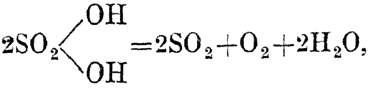
[7] See Ernst, *Zeitsch. physikal. Chem*, 1901, 37, 448.

[8] Paal and Hartmann, *J. prakt. Chem.*, 1909, 80, 337.

[9] Employing the earlier data of Thomsen, *Ber.*, 1872, 5, 769; 1873, 6, 1553; 1882, 15, 2998. Roth (*Zeitsch. Elektrochem.*, 1920, 26, 288) gives 68,380 calories$_{15°}$ at 18° C. under constant pressure

4. Water may be produced by the union of hydrogen with combined oxygen, as, for example, during the reduction of oxides. Advantage has been taken of this fact to determine gravimetrically the composition of water, as witness Dumas' classical researches on the formation of water by the reduction of copper oxide.

5. Water may also be formed by the decomposition of a complex molecule containing hydrogen and oxygen atoms or by the interaction of two complex molecules. As an example of the former may be mentioned the action of heat on a hydroxylated substance. Thus, sulphuric acid when dropped on to a red-hot plate decomposes to water, sulphur dioxide, and oxygen.



$$2SO_2\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} = 2SO_2 + O_2 + 2H_2O,$$

and copper hydroxide yields the anhydrous oxide

$$Cu(OH)_2 = CuO + H_2O.$$

An illustration of the latter type is afforded by the interaction of sulphur dioxide and hydrogen sulphide:

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

## PURIFICATION OF WATER.

### *Purification of Water for Chemical Purposes.*

For accurate scientific work water must be freed from most of the impurities detailed above, and the usual procedure is to distil from the ordinary tap supply. The liquid is heated preferably in a copper vessel and the steam condensed by passage through a cooled tube of some material, *e.g.* tin, silver, or even platinum, which will resist the action of steam. Such "distilled water" is sufficiently pure for most ordinary purposes, but for special purposes a higher degree of purity is necessary; in such cases the water is redistilled after the addition of potassium permanganate and potassium hydroxide[2]; if traces of ammonia are to be avoided yet another distillation with the addition of a little potassium hydrogen sulphate is necessary. In all these distillations the first portion of the distillate should be rejected and also a considerable residue allowed to remain undistilled.

The need for water of a high degree of purity is especially felt in experimental work on the electrical conductivity of aqueous solutions, and many modifications of the distillation apparatus and process have been proposed for preparing such water.[1] A relatively simple distillation apparatus (Bourdillon) is outlined in Fig. 36.

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[1] See Dixon, *Trans. Chem. Soc.*, 1910, 97, 661.

[2] Stas, *Jahresbericht*, 1867, 134.

The boiler A, of approximately 13 litres capacity, is connected by a rubber bung with a copper tube B and cylinder C, which serve to remove particles of spray. In order to prevent excessive condensation B and C are jacketed with non-conducting material. The vertical tin tube D acts as condenser and is water-cooled at the two glass jacket cooling tubes; during the distillation a current of purified air slowly ascends from the inlet E. Tap water is placed in the boiler and a little potassium hydrogen sulphate is added. After a short time the steam is free from carbon dioxide. Passing up the tin tube the steam is condensed at the upper glass jacket, so that the condensed water during its descent

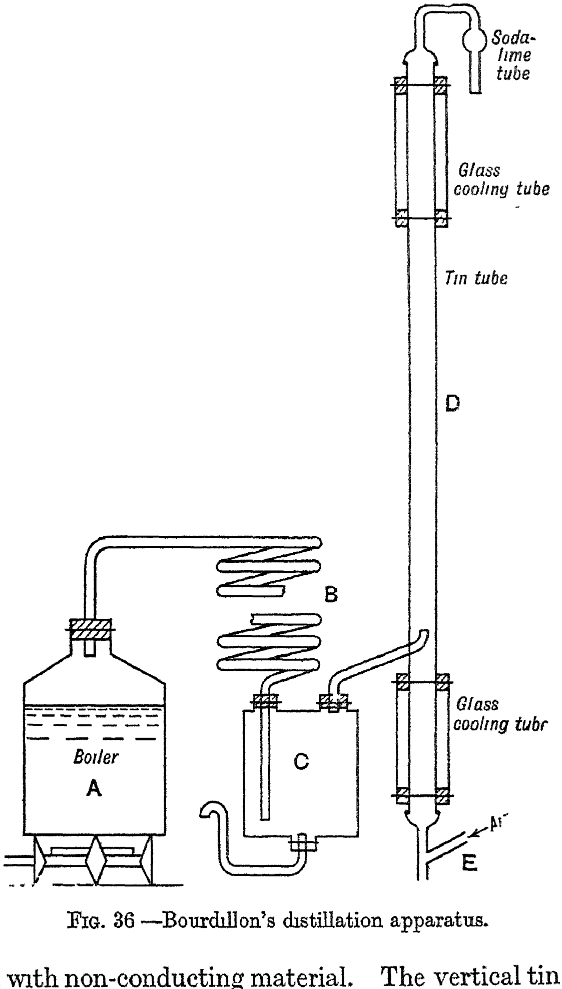

Fig. 36 —Bourdillon's distillation apparatus.

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[1] Jones and Mackay, *Zeitsch. physikal Chem.*, 1897, 22, 237; Bousfield, *Trans. Chem. Soc.*, 1905, 87, 740; 1912, 101, 1443; Hartley, Campbell, and Poole, *ibid.*, 1908, 93, 428; Thole, *ibid.*, 1912, 101, 207; Bourdillon, *ibid.*, 1913, 103, 791; Paul, *Zeitsch. Elektrochem.*, 1914, 20, 179; Hulett, *Zeitsch. physikal. Chem.*, 1896, 21, 297. See also Kohlrausch, *ibid.*, 1902, 42, 193.

is submitted to a "scrubbing" action by the ascending steam and pure air. The water collected is of a high degree of purity, but of course contains dissolved nitrogen and oxygen. Its electrical conductivity is roughly $1/10^7$ reciprocal ohm at 18° C. (see p. 275).

### *Purification of Water for Domestic Purposes.*

This is a problem of enormous economic importance. Owing to the large number of factors involved, numerous systems of water purification are in use in various parts of the world.

**Storage.**—Experiment shows that such natural waters as are not very pure to begin with, are greatly improved for potable purposes by storage. Suspended impurities gradually subside, carrying with them a portion of the bacterial content of the water, thus rendering the supernatant liquid considerably purer.

In addition to this, other actions take place involving a diminution in the number of bacteria,[1] although sometimes there is an initial rise, followed by decline. The bactericidal effects are induced by a variety of causes, the more important of which are:

1. Sunlight.—Although diffused daylight has but little action, direct sunlight is a powerful bactericide.[2]
2. Many common forms of life, such as protozoa, rapidly consume or exterminate pathogenic germs.[3]
3. Starvation.—The bacteria may consume the whole of their food supply.
4. Toxins.—The excretory products of the bacteria may accumulate to such an extent as to poison them. Such toxins may even prove dangerous to higher forms of life, so that complete absence of bacteria does not necessarily prove that water is wholesome.

If, however, the water is very good to begin with, as, for example, deep well water, storage cannot improve it; indeed it may be detrimental to store the water, inasmuch as the entry of any pollution would give the accompanying bacteria a free field for rapid multiplication.

In addition to a reduction of the bacterial content, most natural waters undergo during storage several other changes which improve them for potable purposes. Thus the organic matter tends to disappear, either through settling or through oxidation to water, carbon dioxide, etc. The hardness is reduced either by abstraction of soluble calcium salts by plants and animals, or through evolution of some of the dissolved carbon dioxide into the atmosphere whereby the calcium bicarbonate becomes transformed into the normal carbonate and separates out as an insoluble deposit. The nitrogen compounds, such as ammonia, nitrates, and nitrites, tend similarly to disappear.

Purification of water through sedimentation may be greatly assisted by the introduction of powdered substances and particularly of colloids, although these latter take longer to settle. Frankland,[4] in a series of experiments in which some 20 grams of powdered chalk, coke, charcoal, or spongy iron were added per litre of water, was able to effect the removal of from 90 to 100 per cent. of the organisms present in polluted waters. Savage races have long used mucilaginous substances, such as quince seeds, the acid juices of plants, and astringent and tanninoid precipitants, such as Peruvian bark, for purifying water for drinking purposes in the above manner; the sweetening of the waters of Marah by Moses (Exodus xv. 23) by casting a tree into them is probably an example of this primitive method of treating waters.

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[1] See Houston, *Research Reports of the Metropolitan Water Board*, 1908–1910; Jordan, Russell, and Zeit, *J. Infectious Diseases*, 1904, 1, 641–689.

[2] See Currie, *J.R.I. Public Health*, 1911, 29, 214.

[3] Hautemüller, *Archiv. Hygiene*, 1905, 54, 89; Horhammer, *ibid.*, 1911, 73, 183; Stokvis and Swellengrebel, *J. Hygiene*, 1911, 11, 481.

[4] Frankland, *Micro-organisms in Water* (Longmans, 1894, p. 193); *Proc. Roy. Soc.*, 1885, 38, 390.

It appears that the ancient Egyptians purified their water by allowing it to percolate through earthenware vessels containing alum. Colloidal aluminium hydroxide would thus collect in the pores of the earthenware and assist the process of filtration.

In modern times alum or aluminium sulphate has been added to waters to assist in their purification. It reacts with any dissolved calcium (or magnesium) carbonate converting it into calcium (or magnesium) sulphate, aluminium hydroxide being simultaneously precipitated. Thus:

$$CaCO_3+Al_2(SO_4)_3+3H_2O=2Al(OH)_3+3CaSO_4+3CO_2.$$

The precipitate gradually settles, taking down with it organisms and other suspended impurities. Thus, for example, Leeds[1] found that an addition of 0·5 grain of alum per gallon[2] of a certain sample of water reduced its bacterial content from 8000 to 80 per c.c., that is, by 99 per cent. The precipitate also acts as a decoloriser[3] and has been applied in this capacity for clearing the water at Antwerp.

The foregoing, however, are not purely mechanical effects. Organic matters, particularly coloured constituents of upland and peaty waters, are usually colloid in character[4] and exhibit electrophoresis, migrating to the anode or cathode according as they are negatively or positively charged. In most cases their charge is negative, so that these are precipitable by positive ions and positive colloids. Inasmuch as the precipitating power of an ion is a function of its charge or valency, aluminium with a valency of three has a very much greater precipitating effect than sodium, of valency equal to unity. This serves to explain the particular effectiveness of salts of aluminium and ferric iron which has long been observed. It must be remembered, however, that whilst a positive ion tends to precipitate a negative colloid, a negative ion tends to stabilise the same. Hence the total effect of, for example, an aluminium sulphate solution is the difference between the opposing actions of the aluminium and sulphate ions. By reducing the number of the latter, therefore, the precipitating effect is enhanced. This explains the greater efficiency of basic alums, which are now used in the Brooklyn (U.S.A.) filters, and in which the average deficiency of $SO_3$ is some 8 per cent. of that required to form a neutral salt.[5] Electrical methods for the removal of colour, based on electrophoresis, have been recommended[6] and are of considerable scientific interest to the colloid chemist.

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[1] Leeds, see Rideal, *Water Supplies* (Crosby Lockwood, 1914), p. 80.

[2] That is one part of alum in 140,000 parts of water.

[3] See Kemna, *Trans. Inst. Water Eng*, 1912, pp. 218, 253, 260.

[4] See Biltz and Krohnke, *Ber.*, 1904, 35, 1745.

[5] See analyses by Hale, *J. Ind. Eng. Chem.*, 1914, 6, 632.

[6] Race, *J. Soc. Chem. Ind.*, 1921, 40, 159 T.

One disadvantage of the use of alum is the conversion of the carbonates of calcium and magnesium into sulphates. whereby temporary hardness is converted into permanent. This is objectionable for steam-raising purposes. This disadvantage is not shared by the metallic iron treatment which has been applied successfully to certain American waters. According to this, iron turnings are introduced into the water whereby a portion of the metal dissolves yielding soluble ferrous hydrogen carbonate, $FeH_2(CO_3)_2$. Thus

$$Fe+2H_2O+2CO_2=FeH_2(CO_3)_2+2H.$$

The nascent hydrogen reduces any nitrates or nitrites to ammonia. Atmospheric oxygen converts the ferrous salt into colloidal ferric hydroxide, a reaction that is facilitated by cascade aeration. As it coagulates and settles, the ferric hydroxide purifies the water in an analogous manner to that described for aluminium hydroxide above. The process is rather expensive, however, and for this reason some American towns have added ferrous sulphate direct to their waters. This is less satisfactory as the salt is not oxidised so readily as ferrous bicarbonate; in addition to this, sulphuric acid is introduced into the water.

**Removal of Iron.**—Ferruginous waters are bitter to the taste, even 1 part of iron per million of water being perceptible to the average individual. Such waters, which are widely distributed in Germany and the Netherlands,[1] in America,[2] and elsewhere, are particularly favourable to the growth of minute organisms, such, for example, as the *Crenothrix*,[3] the vitality of which appears to be connected with the secretion of iron within the tissue of its cell walls. This organism flourishes in waters containing 0·3 parts of iron per million of water, and may lead to serious choking of water-mains. Aeration and treatment with lime or with colloidal substances have been adopted with more or less success. Thus, for example, at Amsterdam, intense aeration followed by filtration has reduced the iron content of its water supply from 0·8 parts per million to *nil*.[4] Iron may also be completely removed from water by passage through a manganese permutit filter, as explained on p. 244.

**Algæ** may be removed by treating the water with copper sulphate, 1 part in 10 million of water proving algicidal.

**Filtration.**—Although storage may improve water, further purification by filtration is necessary if the water is to be regarded as safe for domestic purposes. On the large scale water is usually filtered through beds of sand laid in layers of increasing coarseness from the top downwards. The process was originally introduced about the year 1810 in Scotland and Lancashire, and a few years later adopted at Chelsea, with the object of clarifying the water, bacteriology being then an unknown science. It was not until 1885 that Frankland [5] systematically applied bacteriological water tests to the London water supply, and found that more than 99 per cent. of the micro-organisms present in Thames water at Hampton were removed by passage through the sand filters. This has since been confirmed times without number, and the *Report of the London Metropolitan Water Board* for 1913 is of interest in this connection :

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[1] Schwers (*Ann. travaux publ. belg.*, 1912, 3; *Wasser und Abwasser*, 1912, 5, 214) gives detailed accounts of these and the methods employed to remove the iron.

[2] Weston, *Proc. Amer. Soc. Civil Eng.*, 1908, 34, 1324

[3] See Ellis, *Iron Bacteria* (Methuen, 1920).

[4] Don and Chisholm, *Modern Methods of Water Purification* (Arnold, 1913), p. 334.

[5] See G. C. Frankland, *Bacteria in Daily Life* (Longmans, 1903), p. 95; P. F. Frankland, *Proc Roy. Soc*, 1885, 38, 390

| | No. of Micro-organisms per c c. of Water taken from | | |
|---|---|---|---|
| | Thames. | Lee. | New River. |
| Raw water . . | 5250 | 9263 | 2172 |
| Filtered water . . | 16 | 31 | 14 |

A very striking instance of the value of sand filtration was afforded by the outbreak of cholera in Hamburg in 1892. The city drew its water from the Elbe and used it in its raw condition for domestic purposes. No fewer than 1250 per 100,000 of the population perished through cholera. The contiguous town of Altona lost but 221 per 100,000, despite the fact that it drew its domestic water from the Elbe *below* Hamburg, after it had received the sewage pollution from the latter city. This relative immunity was due to the fact that the Altona authorities purified their water by passage through sand filters.

Sand filtration is largely employed in this country, sand being laid to varying depths upon gravel which increases in coarseness with the depth, which ranges from 6 to 8 feet *in toto*. The water is drained away through pipes at the base.

Although it was formerly believed that a filter bed was most efficient when freshly laid, it is now known that such is not the case. The best results are obtained when the filter has been in operation sufficient time to allow a film or " dirt cover " to form on the surface of the bed, which is the chief level at which purification proceeds. The water passing through the filter should not be used for domestic purposes until after the lapse of the necessary " filming time." The film obtained from natural waters is essentially organic and of a semi-colloidal nature. By adding an inorganic colloid, such as alumina, a film may be artificially formed on the sand surface in a short space of time, thus saving delay in the use of the filter. When once such a film, whether natural or artificial, has been satisfactorily formed, micro-organisms will only pass through in small numbers. As time progresses the film becomes increasingly thicker, until ultimately the rate of filtration becomes too slow to be economically efficient, and the bed must be cleaned.

In Great Britain the sand filters generally deal with from 2 to 3 million gallons of water per acre per day, that is, with a downward travel of about 10 to 12 cm. (4 to 5 inches) per hour. The head of water ranges from 60 to 100 cm. (2 to 3¼ feet).[1]

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[1] Many towns, particularly in America, now use " mechanical filters " by means of which water can be filtered much more rapidly than in ordinary open sand filters. For an account of these, see Don and Chisholm, *opus cit.*

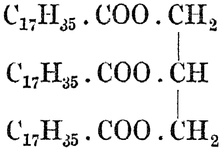
## THE HARDNESS OF WATER.

Waters that do not readily form a lather with soap are termed *hard.* Such hardness may be caused by the presence in considerable quantity of salts of the alkali metals, as, for example, in the case of sea water and brine. More usually, however, the term is reserved for such hardness as is due to the presence of very much smaller quantities of salts of magnesium or calcium.

The majority of vegetable and animal oils and fats[1] consist essentially of an organic salt, comprising glycerine, $C_3H_5(OH)_3$ or $CH_2OH.CHOH.CH_2OH$, as base, combined with an organic acid such as stearic acid, $C_{17}H_{35}.COOH$, oleic acid, $C_{17}H_{33}.COOH$, or palmitic acid, $C_{15}H_{31}.COOH$. Thus, glyceryl stearate or stearin, the essential constituent of mutton fat, is represented by the formula

$$(C_{17}H_{35}.COO)_3C_3H_5,$$

or



$$\begin{array}{l} C_{17}H_{35}.COO.CH_2 \\ \qquad\qquad\qquad\;\; | \\ C_{17}H_{35}.COO.CH \\ \qquad\qquad\qquad\;\; | \\ C_{17}H_{35}.COO.CH_2 \end{array}$$

Olive oil is largely glyceryl oleate, and palm oil, glyceryl palmitate. When warmed with solutions of caustic alkalies, these fats are decomposed, yielding *soaps*, hence the term *saponification.* Thus, for example, with sodium hydroxide, glyceryl stearate yields free glycerine and sodium stearate, which latter is a sodium soap. Thus

$$\underset{\text{Glyceryl stearate.}}{(C_{17}H_{35}.COO)_3C_3H_5}+3NaOH=\underset{\text{Glycerine.}}{C_3H_5(OH)_3}+\underset{\text{Sodium stearate or soap.}}{3C_{17}H_{35}.COONa}$$

The sodium soap is soluble in water and a very small quantity suffices to produce a lather if the water is pure. If, however, it contains dissolved salts of calcium or magnesium the lather is destroyed by these, yielding the familiar insoluble curd, so characteristic of the action of hard water on soap. This curd is really the insoluble soap of the alkaline earth metal formed by double decomposition as shown in the two following equations, in which it is assumed the hardness is due to the presence of calcium carbonate and magnesium sulphate respectively :

$$Ca(HCO_3)_2+2C_{17}H_{35}.COONa=2NaHCO_3+(C_{17}H_{35}.COO)_2Ca\ ;$$

and

$$MgSO_4+2C_{17}H_{35}.COONa=Na_2SO_4+(C_{17}H_{35}.COO)_2Mg.$$

Not until the whole of the alkaline earth metal has been "fixed" as insoluble curd is the sodium soap free to yield a lather. Consequently the higher the percentage of calcium or magnesium, the larger the amount of soap required and the greater the hardness of the water. The amount of soap required to produce a lather is thus a measure of the hardness of the water and, as indicated below, is used in quantitatively determining the same.

Two kinds of hardness are ordinarily recognised, namely *temporary* and *permanent.*

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[1] A *fat* is a solid oil.

**Temporary hardness** is that caused by the presence of the bicarbonates of calcium or magnesium. Whilst the normal carbonates of these metals, namely, $CaCO_3$ and $MgCO_3$ respectively, are practically insoluble in pure water, they readily dissolve in the presence of carbon dioxide—a normal constituent of natural waters, owing to the presence of this gas in the atmosphere—the soluble acid- or bi-carbonates, $CaH_2(CO_3)_2$ and $MgH_2(CO_3)_2$, being produced. The mere process of boiling temporarily hard water suffices to soften it,[1] for the expulsion of the dissolved gases effects the decomposition of the bicarbonates with consequent precipitation of the insoluble normal carbonates.

**Permanent hardness** is caused by soluble salts of calcium and magnesium other than the bicarbonates. The more common of these are the sulphates, chlorides, and nitrates, particularly the first named. Such waters cannot be softened by merely boiling.

The **total hardness** of a given sample of water may be due in part to the presence of bicarbonate and in part to the presence of other soluble salts. When boiled, the normal carbonate is precipitated and, on account of the decrease in solubility of calcium sulphate with rise in temperature above 38° C., there is always a tendency for this substance to separate to some extent with the carbonate. This causes the deposit to form a coherent film on the containing vessel, whereas the pure carbonate gives a more or less powdery suspension. The boiled water is now softer than before, such hardness as it now possesses is termed permanent, whilst its temporary hardness is the difference between the total and permanent hardness, namely, that lost by boiling.

**Degree of Hardness.**—To render comparison easy it is usual to record the hardness in terms of the calcium oxide, CaO, or calcium carbonate, $CaCO_3$, that would produce the same amount of hardness if added to pure water.

In British water reports, according to a decision of the Local Government Board, the number of grains of $CaCO_3$ required per gallon (70,000 grains) of pure water to render it as hard as a given sample, constitutes the degree of hardness or the degree Clark of the sample. Thus a water of 5 degrees of hardness would be obtained by dissolving 5 grains of $CaCO_3$ per gallon of distilled water. According to the metric system, it is usual to express the hardness in terms of $CaCO_3$ per 100,000 of water. This figure is readily obtained from the degree Clark by dividing the latter by 0·7. Thus

1 degree Clark = 1·43 parts of $CaCO_3$ per 100,000.

In Germany it is customary to express the hardness in terms of 10 mg. of CaO per litre. Hence

1 degree German = 1·79 parts $CaCO_3$ per 100,000.

**Determination of Hardness.**—Hardness, whether temporary or permanent, is conveniently estimated by means of Clark's soap test, which consists in adding from a burette small quantities of standard soap solution (*vide infra*) to 50 c.c. of water which have been carefully measured out with a pipette into a 250-c.c. bottle. After each addition of soap solution the bottle is vigorously shaken, and the titration is complete when the lather remains unbroken for five minutes after laying the bottle on its side at rest.

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[1] For a study of some of the reactions involved, see Petit, *Mon. Sci*, 1914, 4, 537.

Should the water be so hard that 8 c.c. upwards of soap solution are required, a smaller volume than 50 c.c. should be taken and diluted to this amount with freshly boiled distilled water. Reference to the table indicates the amount of hardness corresponding to each titration. The total hardness is given by this method. If a second sample of water be boiled and after settling or filtering titrated in a similar manner, the permanent hardness is obtained. Subtraction gives the temporary hardness.

## DEGREES OF HARDNESS (CLARK) CORRESPONDING TO AMOUNTS OF SOAP SOLUTION USED.

| Soap Solution. c.c. | $CaCO_3$ per 100,000. | Soap Solution. c c. | $CaCO_3$ per 100,000. | Soap Solution. c c. | $CaCO_3$ per 100,000 |
|---|---|---|---|---|---|
| 0·7 | 0·00 | 3·0 | 3·25 | 5·6 | 6·86 |
| 0·8 | 0·16 | 3·2 | 3·51 | 5·8 | 7·14 |
| 0·9 | 0·32 | 3·4 | 3·77 | 6·0 | 7·43 |
| 1·0 | 0·48 | 3·6 | 4·03 | 6·2 | 7·71 |
| 1·2 | 0·79 | 3·8 | 4·29 | 6·4 | 8·00 |
| 1·4 | 1·11 | 4·0 | 4·57 | 6·6 | 8·29 |
| 1·6 | 1·43 | 4·2 | 4·86 | 6·8 | 8·57 |
| 1·8 | 1·69 | 4·4 | 5·14 | 7·0 | 8·86 |
| 2·0 | 1·95 | 4·6 | 5·43 | 7·2 | 9·14 |
| 2·2 | 2·21 | 4·8 | 5·71 | 7·4 | 9·43 |
| 2·4 | 2·47 | 5·0 | 6·00 | 7·6 | 9·71 |
| 2·6 | 2·73 | 5·2 | 6·29 | 7·8 | 10·00 |
| 2·8 | 2·99 | 5·4 | 6·57 | 8·0 | 10·30 |

### *Clark's Standard Soap Solution.*

This can be prepared in several different ways. Commonly dry Castile soap is dissolved in 80 per cent. alcohol in such proportions as will yield a solution well above the desired final concentration; 100 grams per litre is a convenient ratio. After allowing this solution to stand at rest for several days for the deposition of undissolved matter, a quantity of the clear liquid is withdrawn (usually 75–100 c.c. per litre of final solution), and so diluted with 80 per cent. alcohol as to produce a solution which on titration with a known weight of calcium chloride solution under the standard conditions will give results in accordance with Clark's table. The calcium chloride solution is best prepared by dissolving 0·2 grams of Iceland spar in dilute hydrochloric acid; excess of acid is removed by evaporation on a water bath and the solution then diluted to 1 litre with distilled water. A mixture of 25 c.c. of this solution, mixed with 25 c.c. of water, should require 7·8 c.c. of Clark's standard solution for the production of a permanent lather.

The standard solution of soap can also conveniently be prepared by neutralising an alcohol solution of oleic acid with a solution of potassium hydroxide in the same solvent; the neutral solution of potassium oleate is then suitably diluted. A solution of potassium soap for dilution can also be obtained by the interaction of lead plaster ("lead soap") and potassium carbonate.

Although the soap method is still widely applied to the determination of hardness, it is inferior in accuracy and general trustworthiness [1] to more recent methods, which also possess the additional advantage of allowing a direct determination of the temporary hardness. In this case, however, the conception of temporary hardness is narrowed so as to include merely the bicarbonates, the whole of the calcium sulphate being included in the permanent hardness. In the simplest of these methods a measured volume of the water is carefully titrated with decinormal hydrochloric-acid solution, using methyl orange [2] as indicator; alizarin is a still better indicator for the purpose, but titration must then be in boiling solution. The titration depends on the decomposition of the bicarbonate of calcium and magnesium with formation of carbon dioxide and the corresponding chlorides.

Permanent hardness can also be estimated by the alkalimetric method of Wartha and Pfeifer. A measured volume (200 c.c.) of the water is boiled with 50 c.c. of a mixture of decinormal solutions of sodium carbonate and hydroxide in equal amounts; after restoring to the original volume and allowing the solution to settle, the residual alkali is determined by titration with standard acid. As the bicarbonates do not cause any consumption of alkali, there is a direct proportionality between the quantity of alkali which disappears and the total amount of sulphates and chlorides of calcium and magnesium. Sodium carbonate alone does not efficiently precipitate magnesium salts from solution, but precipitation as the hydroxide is complete if excess of sodium hydroxide is present; it is for this reason that a mixture of sodium carbonate and hydroxide is applied [3] (see also p. 241).

The last method can also be extended to the measurement of total hardness by first neutralising the bicarbonates as described above for the determination of temporary hardness, and subsequently treating with the mixed alkali solution.

Another satisfactory process for the determination of total hardness, based on a somewhat similar principle, is due to Blacher.[4] The water is first titrated with decinormal hydrochloric acid until it is neutral to methyl orange, as in the method described above for temporary hardness. After the removal of the carbon dioxide by a current of air, the methyl orange is bleached by the addition of a drop of bromine water; a little phenolphthalein and a few drops of alcoholic potassium hydroxide are added, the liquid is just decolorised with decinormal hydrochloric acid and is then titrated with an alcoholic decinormal solution of potassium palmitate until a decided red colour is produced. The quantity of the potassium palmitate solution required is proportional to the total hardness.

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[1] For further details, see Masters and Smith, *Trans. Chem. Soc.*, 1913, 103, 992; Winkler, *Zeitsch anal. Chem*, 1901, 40, 82; Buchner, *Chem. Zeitung*, 1892, 16, 1854; Teed, *J. Soc. Chem Ind.*, 1889, 8, 256; Jackson, *Chem. News*, 1884, 49, 149; Magnanini, *Gazzetta*, 1906, 36, 1, 369

[2] Hehner, *Analyst*, 1883, 8, 77.

[3] Pfeifer, *Zeitsch. angew. Chem.*, 1902, 15, 193; Procter, *J. Soc. Chem. Ind.*, 1904, 23, 8.

[4] Blacher and Jacoby, *Chem Zeit*, 1908, 32, 967; Blacher, Körber, and Jacoby, *Zeit. angew Chem.*, 1909, 22, 967; Blacher, Grunberg, and Kissa, *Chem. Zeit.*, 1913, 37, 56; Winkler, *Zeitsch. anal. Chem.*, 1914, 53, 409.

A water, the total magnesium and calcium salts of which could be represented by an equivalent of approximately 7 parts (or less) of calcium carbonate per 100,000, would generally be considered soft, whilst it would be described as very hard if the quantity exceeded 45 parts per 100,000.

## THE SOFTENING OF HARD WATERS.

As has already been mentioned, waters that are possessed of **temporary hardness** may be softened by boiling. This process is, however, very expensive and impracticable upon a large scale. A more convenient method is that of **Clark,** patented in 1841, according to which the excess of carbon dioxide is precipitated by addition of the requisite quantity of slaked lime. The soluble alkaline earth bicarbonates are thereby converted into their insoluble normal carbonates and separate out. The reactions involved may be represented as follows:

$$CaH_2(CO_3)_2+Ca(OH)_2=2CaCO_3+2H_2O$$
$$MgH_2(CO_3)_2+Ca(OH)_2=MgCO_3+CaCO_3+2H_2O.$$

In neither case is precipitation perfectly complete, for solubility is a relative term, and although the normal carbonates are relatively insoluble when compared with their bicarbonates, they are not *absolutely* insoluble.[1] About 1 grain of calcium carbonate per gallon of water remains in solution in the former reaction, whilst in the latter case some 28 grains of magnesium carbonate may remain behind, although this may be considerably reduced by addition of excess of lime which precipitates magnesium hydroxide, which is less soluble than either carbonate. Water treated in this manner retains, therefore, about 2 degrees of hardness due to dissolved calcium carbonate, and may contain several degrees of hardness due to dissolved magnesium carbonate, in addition to any permanent hardness that was originally present. Although the treatment, even in the case of waters possessing no permanent hardness, does not entirely remove their hardness, it greatly improves them. Furthermore, during sedimentation the calcium carbonate carries down with it any oxides of heavy metals, such as iron and manganese, and also considerable quantities of organic material and living organisms. This partial sterilisation of the water is a very valuable side feature of the process (see p. 232).

**Permanent hardness** is frequently much more difficult to combat. Distillation will effect its removal completely, but only in exceptional cases can such drastic treatment be applied, as, for example, in preparing drinking water from sea water on steamers during long voyages, and in the preparation of pure water from tap water for special scientific purposes for which water of a high grade of purity is required. In softening water for domestic purposes it is usual to remove the temporary hardness only, since small amounts of sulphates of calcium and magnesium have not usually an adverse influence on the general health of the public. But for many manufactures, particularly for steam raising purposes, it is desirable to remove the permanent hardness also.

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[1] The solubilities are as follow (expressed in parts per 100,000 of water), absence of free carbon dioxide being presumed: $CaCO_3$, 1·3 at 16° C; $Mg(OH)_2$, 0·9 at 18° C. Basic magnesium carbonate, 97 at 12° C.

This may be done by the addition of caustic soda or sodium carbonate. The latter reagent converts the dissolved calcium and magnesium salts into relatively insoluble carbonates and thus effects their removal by precipitation. Thus:

$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4$$
$$MgSO_4+Na_2CO_3=MgCO_3+Na_2SO_4.$$

Caustic soda will convert the magnesium salts into the still less soluble hydroxide and thus soften the water more effectively.[1] If sufficient free carbon dioxide is present, dissolved in the water, caustic soda, or a mixture of sodium carbonate and milk of lime, may with advantage be added instead of sodium carbonate, as it is transformed into this latter salt by the carbon dioxide, and then reacts according to the above equations. This "fixes" the dissolved carbon dioxide and prevents it from converting into bicarbonates the normal carbonates precipitated when sodium carbonate is first used, and thereby converting a permanently hard water into one possessing temporary hardness.

In the Stanhope or Gaillet and Huet process, lime water and sodium carbonate are employed as softening agents. The former is prepared as a saturated solution by passage of a certain proportion of the incoming hard water through milk of lime in a saturator. The water enters at the bottom and as the saturated solution rises, the suspended solid particles gradually sink and the clear liquid is discharged at the top. It now mixes with hard water to which soda has been added, and the resultant mixture passes slowly up a clarifying tower, down which the precipitated solids gradually settle, and is freed from the last traces of suspended matter by filtration through wood-wool filters.[2] This mechanical removal of the gradually separated calcium and magnesium compounds is common to most precipitation methods of softening.

The various commercial *lime-soda processes* for softening water are based on the foregoing principles, and differ essentially only in their mechanical details. Their underlying principle is more commonly applied than any other for the purification of water for boiler-feed purposes.

As already explained, it is desirable to precipitate the calcium compounds in the form of carbonate and the magnesium compounds as hydroxide. Commonly a mixture of dissolved sodium carbonate and suspended slaked lime is introduced in the correct proportion by an automatic measuring device. If the hardness is represented as the equivalent number of parts of calcium carbonate per 100,000 parts of water, a simple calculation leads to the following formula for the necessary amounts of sodium carbonate and lime in pounds per 100,000 gallons of water.

$$\text{Weight of sodium carbonate } (Na_2CO_3) = 10{\cdot}6\ P,$$
$$\text{Weight of lime } (CaO) = 5{\cdot}6\ (T+M),$$

where P represents the permanent hardness,
T represents the temporary hardness,
and M represents hardness due to magnesium compounds.

For this purpose the determination of the magnesium hardness is easily effected by treating a measured volume of the carefully neutralised water with a definite quantity of sodium hydroxide or calcium hydroxide solution of known concentration. After allowing a sufficient period for the precipitation of the magnesium hydroxide, the residual excess of the precipitant is estimated, and hence the amount of magnesium which has been removed. As an alternative, the magnesium hardness can be directly estimated by titration after the removal of the calcium compounds by addition of sodium oxalate to the neutralised water.[1]

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[1] The reactions are complicated. See Barton and Lindgren, *J. Amer. Chem. Soc.*, 1907, 29, 1293.

[2] See King, *Chem News*, 1919, 118, 14.

During continuous running of a boiler water-softening plant it is not necessary to make frequently repeated measurements of the magnesium present, the only information required for the constant adjustment of the amount and relative proportions of the softening agents being the total hardness, the temporary hardness, and the alkalinity of the water towards phenolphthalein.[2] The softening process reaches its maximum efficiency when the whole of the calcium has been converted into calcium carbonate and the magnesium into hydroxide without any unnecessary excess of the agents. The solubility of calcium carbonate, which is the more soluble of these two products, therefore represents the approximate limit of efficient softening. At this point the total hardness is entirely "temporary" in character. Also, dissolved calcium carbonate, like sodium carbonate, on titration with mineral acid with phenolphthalein as indicator gives a neutral reaction as soon as conversion into bicarbonate is complete, whilst methyl orange indicates neutralisation only after decomposition of the bicarbonate. If, therefore, the acid used is of equivalent concentration to the soap solution, the following simple relationship will approximately hold at ideal softening:

$$M_0 = T,$$

$$M_0 = 2P$$

where $M_0$ represents the volume of acid required to neutralise the carbonate in the presence of methyl orange, and therefore represents also the temporary hardness,

T represents the total hardness,

and P represents the amount of acid required for neutralisation using phenolphthalein.

All these quantities refer, of course, to equal volumes of the water under examination.

If T is greater than $M_0$, the water still contains some permanent hardness and a greater proportion of sodium carbonate is needed for the softening operation. If P is less than $M_0/2$, the water still contains bicarbonate and a greater proportion of calcium hydroxide is required. If $M_0$ is greater than T, too much "softener" has been applied; and if $M_0$ is less than 2P, an excessive quantity of lime has been used.

If the hardness is represented as parts of calcium per 100,000 parts of water, the limit without excess of softening agent is represented approximately by the values

$$M_0 = T = 2, \quad \text{and } P = 1.$$

In all such precipitation methods of softening water the actual separation of the "insoluble" products takes an appreciable time, and if the water is used or tested before precipitation is complete, misleading results may easily be obtained.[1] For satisfactory separation a period of three hours is advisable during which the treated water circulates slowly through a large filtering chamber or chambers charged with pine wood shavings or similar material. This works more efficiently after it has become coated with the precipitated compounds.[2]

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[1] Froboese, *J. Soc. Chem. Ind.*, 1915, 34, 99, Noll, *Zeitsch angew Chem.*, 1918, 31, 5, 9.

[2] Ristenpart, *Zeitsch. angew. Chem.*, 1910, 23, 392.

**The Permutit Process.**—An interesting process, fraught with great possibilities, lies in the utilisation of certain hydrated silicates of aluminium and the alkali metals. Such substances are found in nature and are known to the mineralogist as *zeolites*—a generic term which covers a series of well defined and inter-related salts. They are secondary minerals, occurring in cavities and veins of basic igneous rocks, and when heated they swell up and appear to boil, whence the name *zeolite*, from Greek ζεῖν, to boil, and λίθος, stone. A curious property of the zeolites is the readiness with which they exchange their bases without altering their aluminium and silicon contents. Thus, for example, a sodium zeolite reacts with a calcium salt yielding, according to the law of mass action, a certain amount of calcium zeolite. For example, in the case of calcium sulphate,

$$\text{Sodium zeolite} + CaSO_4 \rightleftharpoons \text{Calcium zeolite} + Na_2SO_4.$$

If, therefore, a hard water containing a dissolved calcium or magnesium salt is passed through a layer of sodium zeolite, the calcium is abstracted and the corresponding sodium salt passes into solution. In this way the water is readily softened.

In 1906 Gans succeeded in producing zeolites synthetically and named his product *permutit*, from Latin *permutare*, to exchange. The sodium salt may be made by fusing together sodium carbonate, silica and alumina or kaolin. The product is treated with water and yields a crystalline substance of empirical composition represented by the formula $NaAl(SiO_3)_2 . 2H_2O$, which thus closely approximates to the natural zeolite *analcite*, $NaAl(SiO_3)_2 . H_2O$. The commercial product is usually prepared by fusing together soda, clay, felspar, and kaolin. The permutit is placed in a suitable container and hard water allowed to percolate through. The whole of the hardness is thereby removed. The sodium permutit is thus gradually converted into the calcium or magnesium salt. Thus:

$$Na_2\overline{Pm} + CaH_2(CO_3)_2 = 2NaHCO_3 + Ca\overline{Pm}$$
$$Na_2\overline{Pm} + MgSO_4 = Na_2SO_4 + Mg\overline{Pm},$$

and so on.

The regeneration of the permutit is effected by soaking with a 10 per cent. solution of sodium chloride, whereby sodium permutit is regenerated and soluble calcium and magnesium chlorides pass into solution and are washed away.

$$Ca\overline{Pm} + 2NaCl = CaCl_2 + Na_2\overline{Pm}$$

and

$$Mg\overline{Pm} + 2NaCl = MgCl_2 + Na_2\overline{Pm}.$$

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[1] Wood, *J. Soc. Chem. Ind.*, 1917, 36, 1256

[2] See M'Lellan, *ibid.*, 1917, 36, 911.

When water is very hard it is sometimes partially softened by a preliminary treatment with lime and soda. In some cases the permutit plant fed with such treated waters has ceased to work satisfactorily after a number of years, the permutit becoming contaminated with chalk.[1]

Sodium permutit is gradually attacked by dissolved carbon dioxide and more rapidly by mineral acids. Waters therefore containing acids in solution are filtered through limestone or marble before reaching the permutit.

In this connection it may be mentioned that a manganese permutit filter has been invented for the removal of ferrous salts, which become oxidised in some manner, possibly in part through catalysis, but also through reduction of the manganese permutit, which requires periodic revivifying by treatment with a solution of permanganate of lime.

The following analyses of water before and after softening by permutit are interesting.[2] The data are expressed as parts per million (mg. per litre):

| | Before Softening. | After Softening. |
|---|---|---|
| Silica | 15 | 11 |
| Iron oxide and alumina | trace | trace |
| Lime | 98 | nil |
| Magnesia | 10 | 4 |
| $CO_2$—bound | 81 | 121 |
| $CO_2$—free or half bound | 111 | 78 |
| $SO_3$ | 28 | 28 |
| Cl | 34 | 36 |
| KOH, NaOH | 58 | 234 |
| Total hardness[3] | 11·2 | 0·6 |
| Permanent hardness | 0·9 | nil |

The water is beautifully softened, but is rendered more corrosive towards iron and steel.

## STERILISATION OF WATER.

By sterilisation is understood the destruction of all organisms[4] in the water, whether pathogenic or not. In the absence of suitable mechanical filters or in cases of doubt as to the efficiency of the filters in removing pathogenic germs, sterilisation should be resorted to, for this is the only sure method of preventing the spread of water-borne diseases.

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[1] King, *Chem. News*, 1919, 118, 15.

[2] Bauer and Wetzel, *Mitteilungen königlichen Material-prufungsamt*, Berlin, 1915, 33, 1.

[3] Expressed as parts $CaCO_3$ per 100,000 parts of water.

[4] For the bacterial examination of water, see Frankland, *Micro-organisms in Water* (Longmans, 1894); Savage, *Bacteriological Examination of Food and Water* (Cambridge Press, 1916), 2nd ed

**Physical Methods of Sterilisation.**—One of the oldest and best known methods consists in *boiling* the water whereby very thorough sterilisation results. The boiled water is apt to be insipid and flat to the taste in consequence of the expulsion of its dissolved gases, but this is a matter of minor importance in the preparation of beverages such as tea, coffee, and cocoa. As ordinarily carried out, boiling would be too expensive a process to carry out on a very extensive scale, but the cost may be greatly reduced by utilising the heat of the sterilised water to warm up fresh crude water, so that the purified water shall leave the steriliser at a temperature very little above that at which it entered. This is effected in the Forbes Patent Water Steriliser—to mention one among many. It has been adopted by the American Army authorities and operates in the manner indicated in fig. 37.

The feed water passes upwards through a series of narrow, vertical chambers B, C, D, E, separated by thin, metallic walls from the hot, sterilised water, and enters the boiler F at a high temperature. Here it is raised to boiling and escapes into G, whence it passes down the tower, giving up its excess of heat to the cold, raw water within the metallic partitions, and escapes at H at a temperature only a few degrees above that at which it entered the apparatus. As it passes down the tower it also draws with it from G the dissolved gases which have been expelled during boiling, and reabsorbs them. The sterilised water, as it leaves H, is devoid of the insipidity so characteristic of water that has been boiled in the ordinary way.[1]

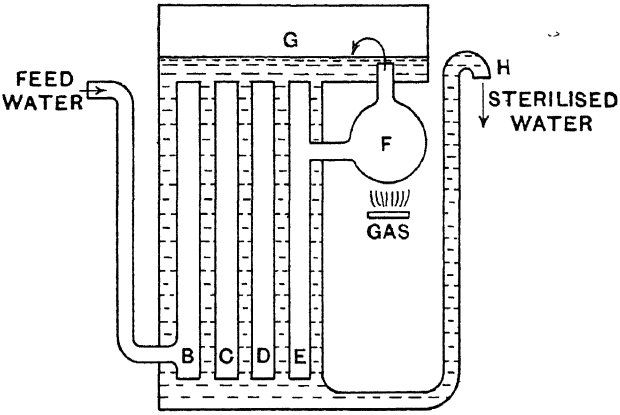

FIG. 37.—The Forbes steriliser.

Ultra-violet light, such as that emitted by a mercury-vapour lamp, exerts a powerful germicidal action on water and ice. In a series of experiments carried out at Marseilles it was observed that a lamp working with 3 amperes at 220 volts destroyed pathogenic organisms in water within a radius of 2½ inches in two seconds.[2] In order to ensure complete sterilisation in a stream of water, the latter is made to flow, by means of a series of baffle plates, close to the lamp on three successive occasions, as shown in fig. 38.

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[1] Many other forms of sterilisers have been devised. See Rideal, *Water and its Purification* (Crosby Lockwood, 1897), etc.

[2] See Don and Chisholm, *Modern Methods of Water Purification* (Arnold, 1913), pp. 353 *et seq.*; S. and K. Rideal, *Water Supplies* (Crosby Lockwood, 1914); also *Engineering News*, 1910, 64, 633; *Trans. Inst. Water Engineers*, 1911, 16, 90.

The efficiency of the process appears to be independent of the amount of dissolved oxygen, the germicidal action being a purely physical action not involving the production either of hydrogen peroxide or of ozone.

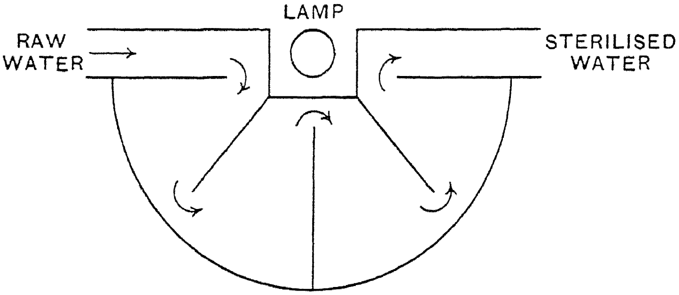

FIG. 38.—The Puech-Chabal ultra-violet light steriliser.

**Chemical Methods of Sterilisation.**—Very efficient sterilisation of suspected waters may be effected by chemical methods, and the cost may be materially reduced by first purifying the water as far as may be by mechanical filtration. The final stage of purification is then effected with a minimum quantity of the chemical reagent.

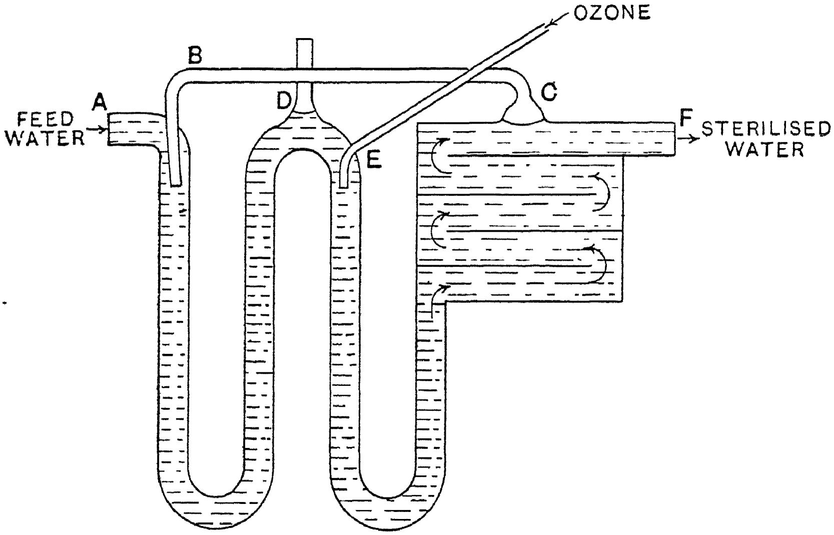

FIG. 39.—The Howard-Bridge steriliser.

One of the most valuable substances for this purpose is *ozone*, for it acts rapidly, imparts no taste to the water, and leaves no solid residue. Numerous ozone installations have been erected for this purpose both in Europe and in America. In 1913 France possessed some thirty different plants, the largest being at the Parisian waterworks of St. Maur. Here the water is first sand filtered and then ozonised, over 24 million gallons being treated daily.[1] The ozone is prepared by commercial methods such as are described in Chapter V., and conducted into sterilisers, of which various forms have been designed.

The *Howard-Bridge* Steriliser is shown in diagrammatic section in fig. 39.

Crude water enters at A, and draws in from pipe B any unused ozonised air which has collected at C. As the water travels round the first bend, all the ozone is usually extracted from the air, which now escapes from the system at D. The thereby partially sterilised water now receives a charge of freshly ozonised air through the pipe E, and passes round the second bend and between the baffle plates until it reaches C. At this point it discharges its excess of air and escapes at F in a highly purified condition. The excess of air at C is continuously drawn away to B to partially sterilise the crude entrant water as explained above.

This system possesses the decided advantage that no external power has to be applied to force the ozone into the water. The gas is drawn in by suction as the water descends the first limb of the apparatus.

Several forms of ozone sterilisers have been described by Vosmaer,[2] a recent (1916) development of which is shown diagrammatically in Fig. 40. The feed water enters through the top left-hand tube, and as it passes down the cylinder meets the ascending stream of ozone which effects its sterilisation, and escapes at A. In the Siemens-Halske steriliser (fig. 41) the feed water passes down a tower containing lumps of some such material as flint, coke, or gravel, to increase its surface, and meets an ascending current of ozone which effects its sterilisation. The escaping air at the top of the vessel is still rich in ozone, and is dried and passed through the ozoniser instead of ordinary air, and thus raised to its previous ozone concentration. About 1·3 grams of ozone will suffice to sterilise 1 cubic meter (1000 litres) of average water.

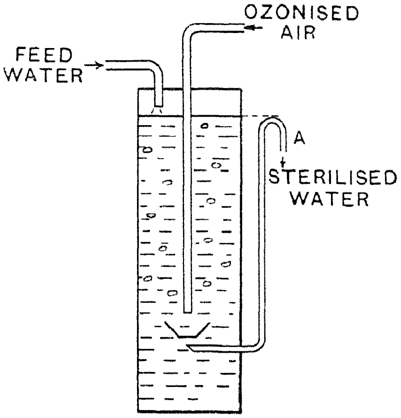

FIG. 40.—A Vosmaer steriliser (diagrammatic).

An ingenious apparatus has been designed,[3] in which the ultra-violet light, produced simultaneously in the silent discharge employed for preparing ozone, is utilised to assist in the sterilisation of water. The last named is first acted on by the light, the partial sterilisation thus induced being completed immediately after by contact with the ozone.

*Hydrogen peroxide* theoretically constitutes an ideal steriliser, for, like ozone, it destroys bacteria without adding any foreign chemical to the water. One part in 10,000 suffices to destroy ciliate infusoria,[4] although a minimum of 1 part per 1000 is necessary for the destruction of bacteria,[1] and even with this concentration the action is rather slow. Owing to its instability and high cost, however, hydrogen peroxide can only be used for sterilising water on a small scale. More convenient are certain metallic peroxides, for these can be obtained in a solid state, of greater stability and sterilising efficiency. *Sodium peroxide*,[2] $Na_2O_2$, for example, possesses a marked germicidal action, and at the same time serves as a softener for hard waters, sodium carbonate being generated by the action of dissolved carbon dioxide, thereby effecting the precipitation of calcium (or magnesium) carbonate, in the case of temporary hardness, by removing the solvent, namely carbonic acid, and in the case of permanent hardness, by double decomposition with the calcium (or magnesium) sulphate. Thus:

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[1] See Rideal, *opus cit.*; Don and Chisholm, *opus cit.*
[2] See Vosmaer, *Ozone* (Constable & Co., 1916).
[3] E Rideal, *English Patent*, 18680 (1910)
[4] Paneth, *Chem. Zentr.*, 1890, i., 174.

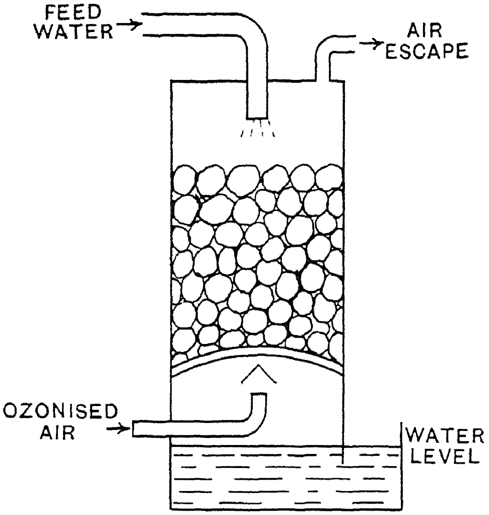

FIG 41.—Diagrammatic representation of Siemens-Halske steriliser.

$$Na_2O_2+CaH_2(CO_3)_2=Na_2CO_3+H_2O_2+CaCO_3;$$

or

$$Na_2O_2+CO_2+H_2O=Na_2CO_3+H_2O_2;$$
$$Na_2CO_3+CaSO_4=Na_2SO_4+CaCO_3.$$

*Calcium peroxide*,[3] $CaO_2$, and *magnesium peroxide*,[4] $MgO_2$, have also been recommended, the former being sold under the name of "bicalzit," whilst an impure form of the latter is used in the sterilisation of bottled mineral waters.

*Chlorine* is a powerful germicide, and is becoming increasingly popular for this purpose.[5] It may be used in the form of liquid chlorine or as chlorine water. It is sometimes more convenient, however, to use *bleaching powder*, 30 lb. of which are, in general, sufficient to sterilise

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[1] See Reichel, *Zeitsch. Hygiene*, 1908, 61, 49.

[2] See Rideal, *Water Supplies* (Crosby Lockwood, 1914), p. 181.

[3] See Jaubert, *English Patent*, 17460 (1900).

[4] Croner. *Zeitsch. Hygiene*, 1908, 58, 487; Young and Sherwood, *J. Ind. Eng. Chem* 1911, 3, 495.

[5] See this series, Vol VIII.

1 million gallons of water.[1] *Sodium hypochlorite* is also employed for the same purpose.[2]

*Sodium hydrogen sulphate*, $NaHSO_4$, in tablet form has been recommended [3] for travellers, and was used in the Boer War, about 15 grains per pint or 1·75 grams per litre being required.

*Citric acid*, 1 part per 1000, is germicidal, but imparts a strong acid flavour to the water. Carbon dioxide under pressure is also effective; and bottled mineral waters, such as soda water, are usually very safe to drink.

*Alkalies* are also powerful germicides. The addition of lime to water in accordance with Clark's process for removing temporary hardness effects the removal of the bulk of the contained bacteria.[4] This is largely due to the mechanical effect of sedimentation which causes the bacteria to be carried down with the lime, only a portion of them being killed. After a time they rise again into the water. By addition of excess of lime, the germicidal action is increased, but even with 0·2 per cent. of lime (calculated as CaO) or 20 parts per 10,000, the sterilisation is not usually complete,[5] whilst at this concentration the water is too strongly alkaline for most purposes.

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[1] Don and Chisholm, *opus cit.*

[2] See Mason, *Chem. News*, 1909, 100, 321.

[3] By Parkes and Rideal in 1901.

[4] In the Colne valley waterworks (Herts) Frankland found the micro-organisms were reduced by 99 per cent. See *Micro-organisms in Water* (Macmillan, 1894), p. 191; also see *Proc Roy. Soc*, 1885, 38, 379.

[5] See Dunbar and Zirn, *Vierteljahr Offentlich Med*, 1898, 16, Supp. p. 138; Kruger, *Zeitsch Hygiene*, 1889, 7, 86; Grether, *Archiv. Hygiene*, 1896, 27, 189. Compare Liborius, *Zeitsch. Hygiene*, 1887, 2, 15; Pfuhl, *ibid.*, 1892, 12, 509; Kaiser, *Centr. Allg. Ges. Pflege*, 1908, p 286.

## CHAPTER VIII.

## PHYSICAL PROPERTIES OF WATER.

WATER is not only able to exist in all three states of matter, namely, as ice, liquid water, and vapour or steam, but several crystalline modifications of the solid form can be produced.

### A. *Physical Properties of Solid Water.*

When the temperature of pure ice is gradually raised under the ordinary atmospheric pressure, melting always commences sharply at a certain invariable temperature, which remains constant until fusion is complete. On account of the ease with which this constant temperature can be attained it has been chosen as the standard zero for the Celsius (Centigrade) and Réaumur thermometric scales. The melting-point is slightly affected by pressure, each increase of one atmosphere lowering the transition temperature of ice to water by approximately 0·0075.

That such ought to be the case was first realised by James Thomson [1] who, in 1849, showed that from theoretical considerations a connection must exist between the melting-point of a solid and the pressure. The following year this was experimentally demonstrated by his brother W. Thomson (Lord Kelvin),[2] who found that under a pressure of 8·1 atmospheres the melting-point of ice was lowered by 0·059° C., equivalent to a fall of 0·0073° per atmosphere. In the table on p. 251 are given the more accurate determinations of Tammann,[3] the third column giving the results calculated in terms of atmospheres.[4]

These data are represented [5] in the pressure-temperature diagram (fig. 42) by the fusion curve AB, which is steep, but curved towards the abscissa,[6] as the results in the last column of the above table clearly demand. This curve represents the equilibrium between ordinary ice or ice I and water, the triple point A representing the condition of equilibrium of water-vapour, liquid water, and ice I. Under a pressure of 2200 kilograms, corresponding to the point B in the figure, there is a break in the fusion curve, a new form of ice appearing, known as ice III, the melting-point of which, in contradistinction to ice I, rises with the pressure, as indicated by BC which slopes away from the ordinate.

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[1] J. Thomson, *Trans. Roy. Soc. Edin.*, 1849, 16, 573.

[2] W. Thomson, *Proc. Roy. Soc. Edin.*, 1850, 2, 267.

[3] Tammann, *Wied. Annalen*, 1899, 68, 553, 629; *Ann. Physik*, 1900, 2, 1, 424 For earlier data, see Dewar, *Proc. Roy. Soc.*, 1880, 30, 533.

[4] A pressure of one atmosphere (76 cm. of mercury) equals 1 033 kilograms per sq cm, or conversely a pressure of 1 kilogram per sq. cm. equals 0 968 atmosphere

[5] The diagram is not drawn to scale, but is exaggerated in order to make the effect readily perceptible.

[6] Curvature of this kind is invariable for fusion curves.

## DEPRESSION OF THE MELTING-POINT OF ICE UNDER PRESSURE.

| Melting-point, ° C. | Pressure in kilograms per sq. cm | Pressure in Atmospheres | Depression in Melting-point per Atmosphere. |
|---|---|---|---|
| 0 | 1 | 0·968 | . . |
| − 2·5 | 336 | 325 | 0·0077 |
| − 5 | 615 | 595 | 0·0084 |
| − 7·5 | 890 | 861·5 | 0·0087 |
| −10·0 | 1155 | 1118 | 0·0089 |
| −12·5 | 1410 | 1365 | 0·0091 |
| −15·0 | 1625 | 1573 | 0·0095 |
| −17·5 | 1835 | 1776 | 0·0099 |
| −20·0 | 2042 | 1977 | 0·0100 |
| −22·1 | 2200 | 2130 | 0·0104 |

At the triple point B, therefore, liquid water, ice I and ice III are in equilibrium, the temperature being −22° C. Tammann[1] found that up to pressures of 2500 kilograms, the solid produced by the spontaneous crystallisation of water is invariably ice I, even in the ice III region. Above this pressure, however, ice III forms, and it is interesting to note that under these conditions the ice has a smaller volume than the liquid water, so that a vessel in which the pressure is greater than 2500 kilo-

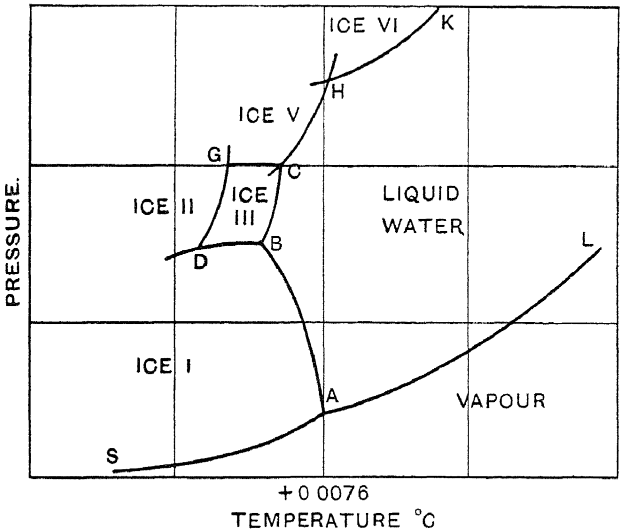

Fig. 42.—The pressure-temperature diagram for water, ice, and water-vapour.

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[1] Tammann, *Zeitsch. physikal. Chem.*, 1910, 72, 609.

grams per sq. cm. cannot be employed to demonstrate the expansive force of ice formation.

Returning to the triple point, B, let us assume a slight increase of pressure, accompanied by a fall in temperature. Liquid water disappears and we move in the direction BD, which represents equilibrium between ice I and ice III. At D another discontinuity occurs, this new triple point representing the equilibrium point of the three solid phases ice I, ice III, and ice II. If now the pressure is slightly reduced and the temperature lowered, the solid phase ice III disappears and we pass along a line not shown in the figure representing the conditions of equilibrium between ice I and ice II. Owing to the slow rate of transformation of ice III, it is possible to travel in the direction BD beyond the point D along a line, which represents the metastable condition of equilibrium between ice I and ice III.

If, on the other hand, on reaching the point D, the temperature and pressure are both raised, instead of lowered, as previously, we pass along DG, which gives the conditions of equilibrium ice II and ice III. At G, ice V appears,[1] this being the triple point at which ice II, ice III, and ice V can co-exist. By again raising the temperature and by a slight increase in pressure, the triple point C is reached, which could also be attained from B by a considerable rise in pressure and a slight rise in temperature.

At C liquid water appears, and is in equilibrium with ice III and ice V.

Increase of pressure, accompanied by rise of temperature, enables us to pass along the curve CH to the triple point H, at which point ice VI appears. This point represents the conditions of equilibrium of ice V, ice VI, and liquid water, and lies above 0° C, namely at +0 16° C. By increasing the pressure and raising the temperature still higher, ice V disappears, HK representing the equilibrium ice VI—liquid water. The remarkable feature of ice VI lies in the fact that it is stable *only at temperatures above* 0° C., increase of pressure serving to raise its melting-point.[1] Indeed, it is possible to have solid water in the form of ice VI even at 80° C. The foregoing conditions of equilibrium are summarised in the following table :

## EQUILIBRIUM PRESSURES AND TEMPERATURES.

| Point in fig. 42 | Phases in Equilibrium. | Pressure. | Temperature, ° C. |
|---|---|---|---|
| A | Water-vapour—liquid water—ice I . . . . . . | 4·579 mm. Hg. | + 0·0076 |
| B | Liquid water—ice I—ice III . | 2115 kilos/cm.[2] | —22 |
| D | Ice I—ice II—ice III . . | 2170 ,, | —34·7 |
| G | Ice II—ice III—ice V . . | 3510 ,, | —24·3 |
| C | Liquid water—ice III—ice V . | 3530 ,, | —17 |
| H | Liquid water—ice V—ice VI . | 6380 ,, | + 0·16 |

The position of ice II is interesting, for it is surrounded by solid phases, and hence can never be in equilibrium with liquid water.

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[1] Bridgman, *Zeitsch anorg. Chem.*, 1912, 77, 377.

It will be observed that no mention has been made of ice IV, the existence of which is uncertain. Tammann obtained certain indications of the possibility of its existence, but Bridgman was unable to confirm, so the term has been left in order that the nomenclature shall not require alteration in the event of the possible existence of this particular form of ice being substantiated.

**Ice I** is the lightest variety of ice known, having a density less than unity, all the other forms being more dense than water. It is the ordinary ice which is always obtained during the normal crystallisation of water under atmospheric pressure.

Numerous attempts have been made to determine accurately the specific gravity[1] of ice at 0° C. with reference to that of water at 0° C. The more important results are given in the following table:[2]

### DENSITY OF ICE AT 0° C.

| Density.[2] | Remarks. | Authority |
|---|---|---|
| 0·9178 | Artificial ice . . | Dufour, *Compt. rend.*, 1862, **54**, 1080. |
| 0·91674 | ,, . . | Bunsen, *Pogg. Annalen*, 1870, **141**, 1. |
| 0·916660 | ,, . . | Zakrzewski, *Wied. Annalen*, 1892, **47**, 155. |
| 0 91807 ±0·00004 | Natural ice such as icicles or blocks. | Nichols, *Phys. Review*, 1899, **8**, 21. |
| 0·91615 ±0·00009 | Artificial ice produced by carbon dioxide and ether. | |
| 0 91661 ±0·00007 | No difference observed between old and new ice. | Barnes, *Phys. Review*, 1901, **13**, 55. |
| 0·9160 | Artificial ice weighed, mean of six determinations. | Vincent, *Proc. Roy. Soc.*, 1902, **69**, 422. |
| 0·92999 | At −188·7° C.. . | Dewar, *ibid.*, 1902, **70**, 237. |
| 0 9176 | Artificial ice . . | Leduc, *Compt. rend.*, 1906, **142**, 149. |

The density of ice at −188·7° C. is given as 0·9300.[3]

The approximate densities of the polymorphic forms of ice are as follows:

| | | | |
|---|---|---|---|
| Ice II . . . | 1·03 | Ice V . . . | 1·09 |
| Ice III . . . | 1·04 | Ice VI . . . | 1·06 |

---

[1] The specific gravity at 0° C. differs from the true density of ice at 0° C. by an exceedingly small amount, since 1 gram of water at 0° C. has a volume of 1·000132 c.c., and thus differs from 1 c.c. by only 0 013 per cent.

[2] Earlier data are now of historical interest only The first experiments were those of Boyle, who described them in his *Experimental History of Cold* (see Boyle's Works, 1772, ii., 551). He found that 82 parts of water yielded 91½ parts of ice by volume when frozen in a glass vessel by the application of snow and salt. This corresponds to an ice density of 0 903.

[3] Dewar, *Proc. Roy. Soc.*, 1902, 70, 239.

It will be observed that these are all greater than unity.

It will be noticed that Bunsen's value for the density of ice I differs only by about 0·1 per cent. from that of Leduc, and the latter author suggests that the difference is mainly due to the fact that Bunsen had not removed every trace of air from his water. Compared with all the results, however, Leduc's value appears somewhat high, and Roth,[1] in a critical survey, recommends the mean value 0·9168 as probably most nearly correct.

This being granted, the volume of 1 gram of ice at 0° C. is 1·09075 c.c., and the contraction on melting is 0·09062 c.c. (1 gram of water at 0° C. has a volume of 1·00013 c.c.)—that is about 8·2 per cent. The magnitude of this change in volume is evident from a consideration of the following data, which give the percentage volume changes—in most of these instances, expansions—when certain solid elements melt.[2]

| Element . . . . | Cd. | Hg. | K. | Na. | P. | Pb. | Sn | Bi. |
|---|---|---|---|---|---|---|---|---|
| Volume change per cent . | 4·72 | 3·67 | 2·6 | 2·5 | 3·5 | 3·39 | 2·80 | −3·31 |

It is interesting to note that the density of natural ice is slightly different from artificial, as made by cooling water in a freezing mixture. This was first observed by Dufour in 1862, and confirmed by Nichols in 1899. Possibly this is a question of age, the ice undergoing slight change on standing; although Barnes found no appreciable difference between old and new ice. In any case the variation is extremely small. The expansion of water upon solidification plays an important part in the natural disintegration of rocks.[3] It may be experimentally demonstrated in the case of water[4] by filling a cast-iron cylinder with air-free water and tightly closing it with a well-fitting screw. On allowing it to lie in a mixture of ice and salt the water freezes and bursts the cylinder. This is simply a modification of the experiment apparently first carried out by Hughens in 1667.[5] The experiment was repeated by Boussingault[6] in 1871, a temperature of −24° C. being attained without congelation, as was proved by the fact that an enclosed steel ball still rattled when the cylinder was shaken.

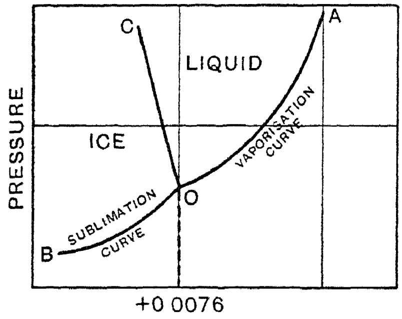

FIG. 43.

The hardness of ice is 1·5 (Mohs' scale).

At low temperatures ice is exceedingly hard and very resistant to shock. Above −12° C. it begins to soften appreciably.[7] Bishop Watson states that, at the marriage of Prince Gallitzin in 1739, the Russians fired ice cannon in honour of the event, the cannon withstanding the shock more than once without bursting.[1]

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[1] Roth, *Zeitsch. physikal Chem.*, 1908, 63, 441.

[2] Vicentini and Omodei, *Wied. Beiblatter*, 1888, 12, 177. *Atti R. Accad. Torino*, 1887, 23, 8.

[3] Water, however, is not the only liquid that expands in this manner. Liquid bismuth, antimony, and iron behave similarly.

[4] Rudorff, *Ber.*, 1870, 3, 60.

[5] Boussingault, *Compt. rend.*, 1871, 73, 77.

[6] Boussingault, *loc. cit*; see also Krebs, *Pogg. Annalen*, 1872, 146, 194, Martins and Chancel, *Ann. Chim. Phys.*, 1872, 26, 548; Schroder, *Annalen*, 1859, 109, 45; Schrotter, *Sitzungsber. K. Akad. Wiss. Wien.*, 1853, 10, 527; *Jahresber.*, 1853, p. 80.

[7] Andrews, *Proc. Roy. Soc.*, 1886, 40, 544.

Ice exerts a definite vapour pressure which, at 0° C., is identical with that of water, so that at this point the three phases—solid, liquid, vapour—can co-exist. This is not the real triple point, because pressure lowers the melting-point of ice, and by definition 0° C. is the melting-point of ice under a pressure of one atmosphere. The true triple point therefore lies at +0·0076° C., and in the absence of air, OB, which represents the vapour pressure of ice at various temperatures, is termed the sublimation curve (fig. 43).

The vapour pressure of ice at various temperatures below 0° C. has been determined by several investigators,[2] the results of Scheel and Heuse being given in the following table :

## VAPOUR PRESSURE OF ICE.

| Temperature, ° C | Vapour Pressure, mm Hg. | Temperature, ° C. | Vapour Pressure, mm. Hg |
|---|---|---|---|
| 0 | 4·579 | −15 | 1·253 |
| − 1 | 4·219 | −20 | 0·784 |
| − 2 | 3·885 | −25 | 0·480 |
| − 3 | 3·575 | −30 | 0·288 |
| − 4 | 3·288 | −35 | 0·168 |
| − 5 | 3·022 | −40 | 0·096 |
| − 6 | 2·776 | −45 | 0·053 |
| − 7 | 2·548 | −50 | 0·0296 |
| − 8 | 2·337 | −55 | 0·0156 |
| − 9 | 2·143 | −60 | 0·0073 |
| −10 | 1·963 | −65 | 0·0023 |

The vapour pressure, $p$, of ice at any temperature $t$° C. may be calculated from either of the following equations :

$$\text{(i)}\quad \log p/4{\cdot}579 = 9{\cdot}632(1 - 0{\cdot}00036t)t/\mathrm{T}.^{*}$$

$$\text{(ii)}\quad \log p = 6{\cdot}5343 - \frac{2611{\cdot}7}{\mathrm{T}} - 1{\cdot}75 \log \mathrm{T} - 0{\cdot}00210\mathrm{T}.^{\dagger}$$

Several determinations have been made of the expansion and contraction of ice with rise and fall of temperature, and the more important results for the *coefficient of expansion* are given in the accompanying table :[3]

---

[1] Samuel Parkes, *Chemical Catechism*, London, 1810, p. 110.

[2] The most recent data are those of Juhlin, *Bihang Svenska Akad. Handl.*, 1891, 17, i., 58 ; Scheel and Heuse, *Ann. Physik*, 1909, [4], 29, 723.

* Thiessen, *Ann. Physik*, 1909, 29, 1057.

† Nernst.

[3] Earlier results are those of Brunner, *Pogg. Annalen*, 1845, 64, 116 ; Marchand, *J. prakt. Chem.*, 1845, 35, 254.

## COEFFICIENT OF EXPANSION OF ICE WITH RISE OF TEMPERATURE.

| Temperature Range, ° C. | Coefficient of Expansion. | Authority. |
|---|---|---|
| - 27 to -2 | 0·0000514 (linear)<br>0·000154 (cubic) | Struve, Landolt-Börnstein, *Tabellen*, 1912, p. 336; from *Mém. Acad. Petrograd*, 1850, [6], 4, 297. |
| . . | 0 0000528 (linear)<br>0 000158 (cubic) | Plucker and Geissler, *Pogg. Annalen*, 1852, **86**, 265. |
| -5 to 0 | 0 000077 (cubic) | Zakrzewski, *Wied. Annalen*, 1892, **47**, 155; *Anzeiger Akad. Wiss. Krakau*, 1892, p. 153. |
| -8 to -12 | 0·000054 ±0·000002 (linear)<br>0·000162 (cubic) | Nichols, *Phys. Review*, 1899, **8**, 184. |
| -189 to 0 | 0·000081 (cubic) | Dewar, *Proc. Roy. Soc.*, 1902, **70**, 237. |
| -10 to 0 37 | 0·000152 (cubic) | Vincent, *ibid.*, 1902, **69**, 422. |

Judging by the results of Dewar and Vincent the temperature coefficient is high, the expansion coefficient covering the lower temperature being only about half of that over the range -10° to 0° C. The results of Struve (1850) closely agree with the more modern work of Vincent (1902).

Ice, when free from air bubbles, is colourless and transparent, except in thick masses, when it appears slightly blue. When formed from water at temperatures of -1·5° to 0° C. the ice is usually clear, and possesses a maximum density and cohesion. If produced at temperatures below -3° C., minute bubbles of air render the ice milky.[1]

Ice crystals usually belong to the hexagonal system,[2] the axial ratio being:

$$A : C = 1 : 1{\cdot}617.$$

According to Hartmann,[3] the crystallites separating from various undercooled aqueous solutions are of three kinds, according to the concentration and extent of undercooling. Hexagonal crystal skeletons, consisting either of hexagonal plates with six rays or rectangular plates with four rays, are produced when the degree of undercooling is small. Spherulites are formed when the undercooling exceeds a certain limit, whilst feathery growths only occur with very dilute solutions. That the different forms are identical is shown by the fact that undercooled, pure water freezes at the same temperature when inoculated with any one of them.

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[1] Pictet, *Jahresber*, 1877, p. 54; *Arch. Sci. phys. nat.*, 1877, 59, 154. See also Turettini, *Jahresber*, 1877, p. 54.

[2] Berten, *Ann. Chim Phys*, 1878, [5], 13, 283; Groth, *Tabellarische Uebersicht Mineralien*, 1898, p 41. See also Rinne, *Jahrb Min.*, 1919, *Ref.*, 25–27; *J. Chem. Soc. Abstr*, 1920, ii., 245; *Ber. K. Sachs. Ges. Wiss. Math. phys. Klasse*, 1917, 69, 57; *J. Chem. Soc Abstr.*, 1918, ii., 75; St. John, *Proc. Nat Acad. Sci*, 1918, 4, 193; Dennison, *Physical Review*, 1921, 17, 20; Bragg, *Proc. Physical Soc.*, 1922, 34, 98.

[3] Hartmann, *Zeitsch. anorg. Chem.*, 1914, 88, 128.

Prendel[1] has concluded that ice is dimorphous, crystallising in both the hexagonal and cubic systems. Ice crystals are brittle, and their viscosity varies with the direction of shear.[2]

The refractive index for sodium light is 1 310.[3] In conductivity of heat ice resembles ordinary water,[4] except that the value varies slightly with the direction in the ice crystal. Its coefficient of compressibility between 100 and 500 megabars[5] at −7° C. is 0 000.0120, as determined experimentally by Richards and Speyers, a value only about one-fourth of that of liquid water at neighbouring temperatures,[6] about five times that of glass, and somewhat less than that of metallic sodium. It appears to have an abnormally high temperature coefficient, as the following computations indicate:[7]

## COMPRESSIBILITY OF ICE.

| Temperature, ° C | Average Compressibility of Ice between Zero Pressure and the Melting Pressure (Megabars.) |
|---|---|
| 0 | 0·000,033 |
| − 5 | 0 000,023 |
| − 7 | 0·000,021 |
| −10 | 0·000,019 |
| −15 | 0 000,018 |

It will be observed, however, that the computed compressibility at −7° C. is appreciably higher than that actually found, and the authors quoted suggest that in part this "may possibly be due to a considerable softening of the ice just before melting."

When rubbed by liquid water, ice becomes positively electrified,[8] a fact of considerable meteorological interest.

The specific heat of ice is approximately half that of water, namely,[9] 0·5057 at 0° C., and expressed in 20° calories (see p. 271). Its heat capacity when pure varies but little with the temperature,[10] and the following equation is given[9] as representing the specific heat, $Q_t$, at various temperatures, $t$:

$$Q_t = 0{\cdot}5057 + 0{\cdot}001{,}863t.$$

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[1] Prendel, *Zeitsch. Kryst. Min.*, 1894, 22, 76.

[2] See Deeley, *Proc. Roy. Soc.*, 1908, [A], 81, 250; *Geol. Mag.*, 1895, [4], 2, 408; M'Connel, *Proc. Roy. Soc.*, 1891, 49, 323.

[3] Pulfrich, *Wied. Annalen*, 1888, 34, 326.

[4] Trouton, *Proc. Roy. Soc. Dublin*, 1898, 8, 691; Straneo, *Atti R. Accad. Lincei*, 1897, [5], 6, ii., 262, 299.

[5] The *megabar* is the C.G.S. atmosphere of 1 million dynes per cm.$^2$ and equivalent to 0·987 ordinary atmosphere (Richards and Stull, *J. Amer. Chem. Soc.*, 1904, 26, 412).

[6] Richards and Speyers, *J. Amer. Chem. Soc.*, 1914, 36, 491.

[7] Calculation by Bridgman, given by Richards and Speyers, *loc. cit.*, p. 494.

[8] Observed by Faraday, confirmed by Sohncke, *Wied. Annalen*, 1886, 28, 550; *Beiblätter*, 1886, 10, 58.

[9] Dickinson and Osborne, *J. Wash. Acad. Sci.*, 1915, 5, 338.

[10] A. W. Smith, *Phys. Review*, 1903, 17, 193.

At low temperatures the specific heat falls considerably, as is evident from Dewar's[1] researches, the results of which are given in the following table:

## SPECIFIC HEAT OF ICE AT LOW TEMPERATURES.

| Temperature Range, ° C. | Specific Heat of Ice. |
|---|---|
| 18 to − 78 | 0·463 |
| − 78 to −188 | 0·285 |
| −188 to −252·5 | 0·146 |

The latent heat of fusion of ice has been the subject of much research. The most noteworthy determinations are given in the table on p. 259.

Under atmospheric pressure. the value 79·7 would appear to be a fair mean, accurate to about 0·1 per cent., employing the 15° calorie. Increase of pressure reduces both the melting-point and latent heat of fusion, as the following data show:

| | | | | | |
|---|---|---|---|---|---|
| Temperature, ° C. . | 0 | −5 | −10 | −15 | −20 |
| Latent heat (calories) . | 79·8 | 73·7 | 68·0 | 62·5 | 57·7[2] |

The latent heats of fusion of the polymorphic varieties approximate to that of ice I, and but little exchange takes place during transformation from one variety to another.

The heat of formation of ice from gaseous hydrogen and oxygen at 0° C. is 69·96 Calories$_{15°}$.[3]

Pure ice, free from air bubbles, cavities, and suspended material, frequently exhibits a beautiful blue colour when seen in bulk. This is regarded as an absorption effect, due to the tendency of large molecular aggregates to absorb the long rays of light.[4] The blocks of ice lose their colour upon prolonged exposure to light, and more rapidly upon exposure to direct sunlight.

**Colloidal Ice.**—Ice can readily be obtained as an organosol by rapidly cooling saturated solutions of water in organic media. When, for example, chloroform, saturated with water, is rapidly cooled to −30° C., the ice separates out in particles of colloid dimensions, and the sol may be passed unchanged through filter paper.[5]

### B. *Physical Properties of Liquid Water.*

Although water may be cooled below the freezing-point without crystallisation, it is not possible to raise the temperature of ice, under ordinary pressures, above 0° C. If, therefore, heat is supplied to the system ice-vapour, the temperature remains perfectly constant at almost exactly 0° C. until the whole of the ice has melted. As already explained (see p. 255), the temperature is not exactly 0° C., for this is by definition the temperature at which ice melts under atmospheric pressure, and since increase of pressure lowers the melting-point by 0·0076° C. per atmosphere, the melting-point of ice under its own vapour (pressure 0·4579 cm.) is +0·0076° C. During melting a contraction occurs, 10·90 volumes of ice yielding 10·00 volumes of water.

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[1] Dewar, *Proc. Roy. Soc.*, 1905, [A], 76, 325. See also Nordmeyer and Bernoulli, *Ber. Deut. physikal. Ges.*, 1907, 5, 175; Jackson, *J. Amer. Chem. Soc*, 1912, 34, 1470; Nernst and Koref, *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, pp. 247, 262; Lewis and Gibson, *J. Amer. Chem. Soc*, 1917, 39, 2554.

[2] Bridgman, *Proc. Amer. Acad.*, 1912, 47, 441; *Zeitsch. anorg. Chem.*, 1912, 77, 377.

[3] See Roth, *Zeitsch. Elektrochem.*, 1920, 26, 288.

[4] H. T. Barnes, *Nature*, 1910, 83, 188. Raman, *ibid.*, 1923, 111, 13.

[5] See von Weimarn and Wo. Ostwald, *Kolloid Zeitsch*, 1910, 6, 181; von Weimarn, *J. Russ Phys Chem. Soc.*, 1910, 42, 226

## LATENT HEAT OF FUSION OF ICE.

| Latent Heat. | Remarks. | Authority. |
|---|---|---|
| 79·24 | .. | Regnault. |
| 79·59 | Regnault's result corrected by Guttmann. | Guttmann, *J. Physical Chem.*, 1907, **11**, 279. |
| 79·25 | Mean of 17 experiments . . | De la Provostaye and Desains, *Ann. Chim. Phys.*, 1843, [33], **8**, **5**. |
| 80·03 | Value depends on that assumed for contraction of ice on melting. Bunsen used 0·91674 as density of ice. | Bunsen, *Pogg. Annalen*, 1870, **141**, 1. |
| 79·15 | Bunsen's result recalculated by Leduc, using the value 0·9176 for the density of ice. | Leduc, *Compt. rend.*, 1906, **142**, 46. |
| 334·21<br>79·896<br>80·00 | Joules or mean calories, or calories$_{37^\circ\mathrm{C}}$ (Electrical method, assuming 1 Clark at 15° C.=1·434 volts, and 1 calorie=4·1832 joules.) | A. W. Smith, *Phys. Review*, 1903, **17**, 193. |
| 79·67 | Smith's result recalculated by Guttmann. | Guttmann, *loc. cit.* |
| 79·72 | Smith's result recalculated by Roth for calorie$_{15^\circ\mathrm{C}}$. | Roth, *Zeitsch. physikal. Chem.*, 1908, **63**, 441. |
| 79·61 | Mean of several not very concordant results. | Bogojawlenski, *Chem. Zentr.*, 1905, ii., 945. |
| 79·63 | Calorie$_{15^\circ\mathrm{C}}$ . . . . . | Dickinson, Harper, and Osborne, *J. Franklin. Inst.*, 1913, **176**, 453. |
| 79·76 | Calorie$_{20^\circ\mathrm{C}}$ . . . . . | Dickinson and Osborne, *J. Washington Acad. Sci.*, 1915, **5**, 338. |
| 79·6 | .. | Leduc, *Ann. Physique*, 1916, [9], **5**, 5. |
| 79·67 | Calorie$_{15^\circ\mathrm{C}}$ . . . . . | Calculated. Roth, *Zeitsch. Elektrochem.*, 1920, **26**, 288. |

If the supply of heat is continued, further slight contraction ensues, but accompanied by rise of temperature until 3·98° C. is reached.[1] This is the point of maximum density of water, further rise in temperature now resulting in expansion until the boiling-point is attained.

In the accompanying table are given (1) the *density* or mass in grams of 1 c.c. of water, and (2) the *specific* volume or the volume in c.c. of 1 gram of water [2] at various temperatures.[3]

## DENSITY AND SPECIFIC VOLUME OF WATER BETWEEN 0° AND 100° C.

| Temperature, ° C. | Density Grams. | Specific Volume, c c | Temperature, ° C | Density Grams. | Specific Volume, c.c |
|---|---|---|---|---|---|
| 0 | 0·999868 | 1·000132 | 21 | 0·998019 | 1·001995 |
| 1 | 0·999927 | 1·000073 | 22 | 0·997797 | 1·002208 |
| 2 | 0·999968 | 1·000032 | 23 | 0·997565 | 1·002441 |
| 3 | 0·999992 | 1·000008 | 24 | 0·997323 | 1·002685 |
| 4 | 1·000000 | 1·000000 | 25 | 0·997071 | 1·002938 |
| 5 | 0·999992 | 1·000008 | 26 | 0·996810 | 1·003201 |
| 6 | 0·999968 | 1·000032 | 27 | 0·996539 | 1·003473 |
| 7 | 0·999929 | 1·000071 | 28 | 0·996259 | 1·003755 |
| 8 | 0·999876 | 1·000124 | 29 | 0·995071 | 1·004046 |
| 9 | 0·999808 | 1·000192 | 30 | 0·995673 | 1·004346 |
| 10 | 0·999727 | 1·000273 | 35 | 0·994058 | 1·005978 |
| 11 | 0·999632 | 1·000368 | 40 | 0·99224 | 1·00782 |
| 12 | 0·999525 | 1·000476 | 45 | 0·99025 | 1·00985 |
| 13 | 0·999404 | 1·000596 | 50 | 0·98807 | 1·01207 |
| 14 | 0·999271 | 1·000729 | 55 | 0·98573 | 1·01448 |
| 15 | 0·999126 | 1·000874 | 60 | 0·98324 | 1·01705 |
| 16 | 0·998970 | 1·001031 | 65 | 0·98059 | 1·01979 |
| 17 | 0·998801 | 1·001200 | 70 | 0·97781 | 1·02270 |
| 18 | 0·998622 | 1·001380 | 80 | 0·97183 | 1·02899 |
| 19 | 0·998432 | 1·001571 | 90 | 0·96534 | 1·03590 |
| 20 | 0·998230 | 1·001773 | 100 | 0·95838 | 1·04343 |

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[1] On the hydrogen scale, according to the most reliable data, namely those of Chappuis, *Travaux Mém. Bureau internat. Poids et Mesures*, 1904, 13, 40; and of Thiesen, Scheel, and Diesselhorst, *Wiss. Abhandl Physikalisch-Tech. Reichanstalt*, 1900, 3, 68. Numerous other determinations have been made of the temperature of maximum density, the results ranging from 2·22° C (Dalton) to 4·08° C. (Kopp) The more important of these data are as follow:

| | Temp. ° C. |
|---|---|
| Gay Lussac (*Ann. Chim. Phys*, 1816, [2], 2, 130) | 3·89 |
| Hallstrom (*Pogg. Annalen*, 1835, 34, 220) | 3·9 |
| Depretz (*Ann. Chim Phys.*, 1839, [2], 70, 45) | 4·0 |
| Pierre (*Ann. Chim. Phys.*, 1845, [3], 13, 325, as calculated by Frankenheim, *Pogg. Annalen*, 1852, 86, 451) | 3·86 |
| Joule and Playfair (*Phil Mag*, 1847, [3], 30, 41) | 3·95 |
| Kopp (*Pogg. Annalen*, 1847, 72, 1) | 4·08 |
| Rossetti (*Ann. Chim. Phys.*, 1867, [4], 10, 461) | 4·07 |
| Exner (*Wien. Akad. Ber Math. nat*, 1873, 68, 463) | 3·95 |
| Bornetti (*Ann. Physik, Beibl*, 1884, 8, 805) | 4·01 |
| De Coppet (*Ann. Chim. Phys.*, 1903, [7], 28, 145), using the mercury scale | 4·005 |

[2] The specific volume is the reciprocal of the density.

[3] See Landolt-Bornstein, *Physikalisch-Chemische Tabellen* (Berlin, 1912, pp. 42–44). The data are based on the results of Thiesen, Scheel, and Diesselhorst, *loc. cit.* There is an obvious misprint, here corrected, in Landolt's tables at 21° C.

The explanation usually accepted for the anomalous behaviour of water between 0° and 4° C. is that the observed change in volume is the algebraic sum of two factors, namely, (*a*) normal expansion due to increased distance between the molecules in consequence of their increased energy, and (*b*) contraction due to depolymerisation of bulky "ice" molecules into denser "water" molecules.[1]

Increase of pressure reduces the temperature of maximum density[2]: the two factors being connected by the expression

$$t_p = 3{\cdot}98 - 0{\cdot}0225(p-1),$$

where $t_p$ is the temperature of maximum density under a pressure of $p$ atmospheres.

If water is cooled below 0° C. without solidifying, the expansion with fall of temperature continues, as shown below:[3]

## DENSITY AND SPECIFIC VOLUME OF WATER BETWEEN 0° AND −10° C.

| Temperature, ° C | Density | Specific Volume. |
|---|---|---|
| 0 | 0·99987 | 1·00013 |
| − 1 | 0·99979 | 1·00021 |
| − 2 | 0·99970 | 1·00031 |
| − 3 | 0·99958 | 1·00042 |
| − 4 | 0·99945 | 1·00055 |
| − 5 | 0·99930 | 1·00070 |
| − 6 | 0·99912 | 1·00088 |
| − 7 | 0·99892 | 1 00108 |
| − 8 | 0·99869 | 1·00131 |
| − 9 | 0·99843 | 1·00157 |
| −10 | 0·99815 | 1·00186 |

According to the foregoing data, unit volume of water at 0° C. becomes 1·043295 volumes at 100° C.[4]

The coefficient of expansion, $a$, of water, with rise of temperature from 100° to 200° C.[5] is given by the expression:

$$a = 1 + 0{\cdot}000{,}108{,}679t + 0{\cdot}000{,}003{,}007{,}365t^2. \\ + 0{\cdot}000{,}000{,}002{,}873{,}042t^3 - 0{\cdot}000{,}000{,}000{,}006{,}645{,}7t^4.$$

Between 0° and 20° C., the specific volume V at temperature $t$, may be calculated from the equation

$$V = 1{\cdot}00012(1 - 0{\cdot}000{,}060t + 0{\cdot}000{,}007{,}5t^2),$$

---

[1] See Chapter X.

[2] Van der Waals, *Archives néerland. Sci.*, 1877, 12, 457; Marshall, Smith, and Osmond, *Wied. Annalen*, 1883, 7, 252; Tait, *ibid.*, p. 752; Amagat, *Compt. rend.*, 1893, 116, 946; 1887, 105, 1121.

[3] See Landolt-Börnstein, *opus cit.*, p. 44; based on the results of Pierre, Weidner, and Rossetti.

[4] Kopp (*Annalen*, 1855, 93, 123) found 1·043, Kremers (*Pogg. Annalen*, 1861, 114, 41), 1·04297; Buff (*Annalen, Suppl.*, 1865, 4, 123), 1·043105

[5] Hirn, *Ann. Chim. Phys.*, 1867, [4], 10, 32, 90.

between 0° and 33° C. by[1]

$$V=1{\cdot}000132(1-0{\cdot}46427t+0{\cdot}0585053t^2-0{\cdot}0_7 67898t^3+0{\cdot}0_9 50024t^4),$$

and between −32° and 100° C. from[2]

$$V=0{\cdot}999{,}695+0{\cdot}000{,}005472t^2-0{\cdot}000{,}000{,}011{,}26t^3,$$

the volume at 4° C. being taken as unity.[3]

Mendeléeff[4] gave the formula:

$$a=1-\frac{(t-4)^2}{1{\cdot}9(94{\cdot}1+t)(703{\cdot}51-t)}$$

which is claimed to be correct to 4 parts in 100,000.

Dissolved salts depress the temperature of the maximum density of water, the depression being directly proportional to the concentration of the salt.[5] The depression caused by a highly ionised binary electrolyte, for example, sodium chloride, is the sum of two independent effects, namely, that due to the acid radicle, and that due to the base. It is thus possible to calculate the depression caused by such a salt if the moduli corresponding to the two ions are known.[6]

The molecular volume of water at the boiling-point is given as 18·73.[7]

Water is slightly *compressible*. This was first established by Canton in 1762, and has been confirmed by several investigators since that date. Owing to the exceptional difficulty of determining experimentally the extent of its compressibility, the results obtained exhibit considerable variation. The coefficient of compressibility, $\beta$, is given numerically by the change in volume induced in unit volume by unit change in pressure. Hence

$$\beta=\frac{V_o-V_p}{V_o p}$$

where $V_o$ and $V_p$ are the initial and final volumes under a change of pressure, $p$.

The compressibility at constant temperature varies somewhat with the degree of pressure, becoming smaller as the pressure increases. The best results to illustrate this are those of Richards and Stull,[8] which are given on p. 263, together with data for mercury for the sake of comparison.

These data mean that unit volume of the liquid at 20° C. upon being subjected to a pressure of one megabar (or 0·987 atmosphere) above its original pressure, decreases in volume by the amount indicated in the same horizontal line as that giving the total pressure. Thus, for example, one litre of water at normal pressure would decrease by 0·0000452 litre or 0·0452 c.c. if the pressure were raised by one megabar.

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[1] Scheel, *Wied. Annalen*, 1892, 47, 440.

[2] Matthiessen, *J Chem. Soc.*, 1866, 19, 30.

[3] Kurz, *Ann. Physik, Beiblatter*, 1886, 10, 14.

[4] Mendeléeff, *Phil. Mag.*, 1892, 33, 99.

[5] Depretz, *Ann. Chim. Phys.*, 1839, 70, 49; 1840, 73, 296.

[6] Wright, *Trans. Chem. Soc.*, 1919, 115, 119 See also Coppet and co-workers, *Ann Chim. Phys.*, 1894, 3, 246, 268; *Compt rend.*, 1897, 125, 533; 1899, 128, 1559, 1900, 131, 178; 1901, 132, 1218; 1902, 134, 1208; Rosette, *Ann. Chim. Phys*, 1867, 10, 461; 1869, 17, 370.

[7] Schiff, *Gazzetta*, 1881, 11, 517

[8] Richards and Stull, *J. Amer. Chem. Soc.*, 1904, 26, 399.

## COMPRESSIBILITIES OF WATER AND MERCURY AT 20° C.

| Pressure in Megabars.[1] | Compressibility of Water. | Compressibility of Mercury. |
|---|---|---|
| 0–100 | $4{\cdot}52\times10^{-5}$ | $3{\cdot}88\times10^{-6}$ |
| 100–200 | $4{\cdot}41\times10^{-5}$ | $3{\cdot}82\times10^{-6}$ |
| 200–300 | $4{\cdot}18\times10^{-5}$ | $3{\cdot}79\times10^{-6}$ |
| 300–400 | $4{\cdot}11\times10^{-5}$ | $3{\cdot}76\times10^{-6}$ |
| 400–500 | $3{\cdot}94\times10^{-5}$ | $3{\cdot}71\times10^{-6}$ |

The compressibilities of the majority of liquids at constant pressure increase with rise of temperature. Water, however, is exceptional in this respect, its compressibility falling with rise of temperature, a minimum being reached, according to Pagliani and Vicentini, in the neighbourhood of 60° C. According to Tyrer,[2] the minimum occurs at 50° C. for the isothermal compressibility and at 70° C for adiabatic compressibility. This is usually attributed to the diminishing number of bulky and compressible " ice " molecules as the temperature rises from 0° to 60° C. At this latter temperature their number is negligibly small, and from this point onwards water behaves as a normal liquid.

## ISOTHERMAL COMPRESSIBILITIES OF WATER AT VARIOUS TEMPERATURES.

| Temperature, ° C. | Compressibility per Atmosphere. | Authority. |
|---|---|---|
| 0·0 | $5{\cdot}03\times10^{-5}$ | Pagliani and Vicentini, *Nuovo Cimento*, 1884, **16**, [3], 27; *Ann. Physik, Beiblätter*, 1884, **8**, 794. |
| 2·4 | $4{\cdot}96\times10^{-5}$ | |
| 15·9 | $4{\cdot}50\times10^{-5}$ | |
| 49·3 | $4{\cdot}03\times10^{-5}$ | |
| 61·1 | $3{\cdot}89\times10^{-5}$ | |
| 66·2 | $3{\cdot}89\times10^{-5}$ | |
| 77·4 | $3{\cdot}98\times10^{-5}$ | |
| 99·2 | $4{\cdot}09\times10^{-5}$ | |
| 0·0 | $5{\cdot}12\times10^{-5}$ | Röntgen and Schneider, *Wied. Annalen*, 1888, **33**, 644. |
| 9·0 | $4{\cdot}81\times10^{-5}$ | |
| 18·0 | $4{\cdot}62\times10^{-5}$ | |
| 9·0 | $4{\cdot}53\times10^{-5}$ | Hulett, *Zeitsch. physikal. Chem.*, 1900, **33**, 237. (0–100 atmospheres.) |
| 17·0 | $4{\cdot}46\times10^{-5}$ | |
| 50·0 | $4{\cdot}19\times10^{-5}$ | |

---

[1] 0 987 atmosphere. One megabar is 1000/$g$ where $g$=acceleration due to gravity =1000/980·6, or 101·98 per cent. of a kilogram per sq cm., or 98·70 per cent. of an atmosphere at sea-level and 45° latitude.

[2] Tyrer, *Trans. Chem. Soc.*, 1914, 105, 2534.

## ISOTHERMAL AND ADIABATIC COMPRESSIBILITIES OF WATER BETWEEN 1 AND 2 ATMOSPHERES.

(Tyrer, 1914.)[1]

| Temperature, ° C. | Isothermal Compressibility per Atmosphere. | Adiabatic Compressibility per Atmosphere |
|---|---|---|
| 0 | $5{\cdot}078\times10^{-5}$ | $5{\cdot}075\times10^{-5}$ |
| 10 | $4{\cdot}843\times10^{-5}$ | $4{\cdot}838\times10^{-5}$ |
| 20 | $4{\cdot}645\times10^{-5}$ | $4{\cdot}615\times10^{-5}$ |
| 30 | $4{\cdot}520\times10^{-5}$ | $4{\cdot}452\times10^{-5}$ |
| 40 | $4{\cdot}469\times10^{-5}$ | $4{\cdot}360\times10^{-5}$ |
| 50 | **$4{\cdot}462\times10^{-5}$** | $4{\cdot}302\times10^{-5}$ |
| 60 | $4{\cdot}489\times10^{-5}$ | $4{\cdot}270\times10^{-5}$ |
| 70 | $4{\cdot}544\times10^{-5}$ | **$4{\cdot}260\times10^{-5}$** |
| 80 | $4{\cdot}631\times10^{-5}$ | $4{\cdot}276\times10^{-5}$ |
| 90 | $4{\cdot}743\times10^{-5}$ | $4{\cdot}305\times10^{-5}$ |
| 100 | $4{\cdot}863\times10^{-5}$ | $4{\cdot}335\times10^{-5}$ |

Tait[2] gives the following expression whereby the compressibilities of water between 6° and 15° C. can be calculated for pressures ranging from 150 to 500 atmospheres :

$$\frac{V_0-V}{pV_0}=0{\cdot}0000489-0{\cdot}00000025t-0{\cdot}0000000067p,$$

where $V_0$ is the volume at $t$° C. under 1 atmosphere, and V the volume at $t$° C. under a pressure of $p$ atmospheres.

As a general rule, aqueous solutions are less compressible than pure water,[3] due, probably, to a reduction in the number of "ice" molecules in the presence of the dissolved salt. The value for sea-water at 17·5° C. is $4{\cdot}36\times10^{-5}$.[4]

Although the compressibilities of natural waters are thus exceedingly small, their effect upon the distribution of land and water on the crust of the earth is important. It has been calculated that, in consequence of the compressibility of sea-water, the mean sea level is 116 feet lower than it would be if water were absolutely incompressible, with the result that two million square miles of land are now uncovered which would otherwise be submerged.[5]

Water is not usually regarded as possessing any appreciable tensile strength. If, however, precautions are taken to prevent its diameter from varying, a cylindrical column of water may be shown to possess a high tensile strength. This was first demonstrated by Berthelot in 1850,[1] who almost completely filled a glass tube with water, leaving a small bubble of water-vapour after sealing hermetically. The whole was then warmed until the water, possessing a higher coefficient of expansion than the glass, completely filled the tube. On cooling, the liquid continued to fill the tube, thus showing that it resisted rupture under very appreciable tension. The result was only qualitative; but repetition in a modified apparatus by Dixon and Joly [2] indicated a tension of 7 atmospheres. Results obtained by an entirely different method led Budgett [3] to conclude that under special conditions the tensile strength of water may amount to as much as 60 atmospheres. At about 320° C. the tensile strength becomes negligible [4]—a result to be anticipated from its proximity to the critical point (374° C.).

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[1] Tyrer, *Trans. Chem. Soc.*, 1914, 105, 2534 ; 1913, 103, 1675. Earlier data are those by Quincke, *Wied. Annalen*, 1883, 19, 401 ; Grassi, *Ann Chim. Phys.*, 1851, 31, 437.

[2] Tait, *Properties of Matter*, 1885, p 190 (1st ed.) ; Regnault (*Mémoires Institut France*, 1847, 21, 429) gave the value 0·000048 for the compressibility presumably at room temperature (the actual temperature was not specified) ; Grassi (*Ann. Chim Phys.*, 1851, [3], 31, 437) gave $5{\cdot}03\times10^{-5}$ at 0° C., rising to $5{\cdot}15\times10^{-5}$ at 1·5° C , but gradually falling from this temperature onwards to $4{\cdot}41\times10^{-5}$ at 53° C. The existence of this maximum compressibility between 0° and 4° C. was not confirmed, however, by Pagliani and Vicentini (*loc cit.*).

[3] See the investigations of Rontgen and Schneider, *Wied Annalen*, 1886, 29, 165 ; 1887, 31, 1000.

[4] Grassi, *loc. cit.*

[5] Tait, *loc. cit.*

The viscosity of water has been measured frequently since the classic research of Poiseuille [5] in 1843. The most reliable data are given in the accompanying table.

## VISCOSITY OF WATER IN C.G.S. UNITS.

(Dynes per cm.$^2$)

| Temperature, ° C. | Poiseuille (1843). | Thorpe and Rodger (1894) [6] | Hosking (1909).[7] | Bingham and White (1912).[8] |
|---|---|---|---|---|
| 0 | 0·01776 | 0·01778 | 0·017928 | 0·01797 |
| 10 | 0·01309 | 0·013025 | 0·013105 | 0·01301 |
| 20 | 0·01008 | 0·010015 | 0·01006 | 0·01006 |
| 30 | 0·00803 | 0·007975 | 0·00800 | 0·007998 |
| 40 | 0·00653 | 0·006535 | 0·00657 | 0·006563 |
| 50 | .. | 0·005475 | 0·005500 | 0·005500 |
| 60 | .. | 0·00468 | 0·00469 | 0·004735 |
| 70 | .. | 0·00406 | 0·00406 | 0·004075 |
| 80 | .. | 0·00356 | 0·00356 | 0·003570 |
| 90 | .. | 0·003155 | 0·00316 | 0·003143 |
| 100 | .. | 0·00283 | 0·00284 | (0·002993 at 95°) |

Poiseuille's results are included as illustrative of the high degree of accuracy attained by that investigator. Between 0° and 25° C. the viscosity of water may be calculated from the equation [7]

$$\eta_t=\frac{0\cdot017928}{1+0\cdot03445t+0\cdot000235t^2}.$$

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[1] Berthelot, *Ann. Chim. Phys.*, 1850, 30, 232

[2] Dixon and Joly, *Phil Trans*, 1895, [B], p. 568.

[3] Budgett, *Proc. Roy. Soc.*, 1912, [A], 86, 25.

[4] Skinner and Entwistle, *ibid*, 1915, [A], 91, 481.

[5] Poiseuille, *Ann. Chim. Phys*, 1843, [3], 7, 50. See also Girard, *Mem. Acad. Sci.*, 1816: Sprung, *Pogg. Annalen*, 1876, 159, 1; Slotte, *Wied Annalen*, 1883, 20, 257.

[6] Thorpe and Rodger, *Phil. Trans.*, 1894, [A], 185, 397.

[7] Hosking, *J. Roy. Soc. New South Wales*, 1908, 42, 34; 1908, 43, 34; *Phil. Mag.*, 1909, [6], 18, 260; 1909, [6], 17, 502.

[8] Bingham and White, *Zeitsch. physikal. Chem.*, 1912, 80, 684. See also for critical discussion of viscosity measurements, Bingham, *Trans. Chem. Soc*, 1913, 103, 959.

The value for $\eta$ remains constant even under exceedingly low rates of shear.[1]

The viscosity of supercooled water is as follows : [2]

| Temperature, ° C. . | 0 | $-4\cdot7$ | $-7\cdot23$ | $-9\cdot30$ |
|---|---|---|---|---|
| $\eta$ . . | 0·01793 | 0 02121 | 0·02341 | 0·02549 |

Increase of pressure tends to reduce the viscosity of water at temperatures below 36° C.[3] In this respect water differs from most liquids that have been examined, as these become more viscous under increased pressure. No doubt the explanation lies in the tendency of the higher pressures to reduce the percentage of bulky and viscous ice molecules.

The *vapour pressure* of water rises with the temperature, as is evident from the following data,[4] which give the tension in millimetres of mercury :

## VAPOUR PRESSURE OF WATER BETWEEN −15° AND 370° C.

| ° C | mm. | ° C | mm | ° C. | mm. | ° C. | mm. |
|---|---|---|---|---|---|---|---|
| −15 | 1·445 | +11 | 9·845 | +25 | 23·763 | +75 | 289·0 |
| −10 | 2·160 | 12 | 10·519 | 26 | 25·217 | 80 | 355·1 |
| − 5 | 3·171 | 13 | 11·233 | 27 | 26·747 | 85 | 433·5 |
| 0 | 4·579 | 14 | 11·989 | 28 | 28·358 | 90 | 525·8 |
| + 1 | 4·926 | 15 | 12·790 | 29 | 30·052 | 95 | 634·0 |
| 2 | 5·294 | 16 | 13 637 | 30 | 31·834 | 100 | 760·0 |
| 3 | 5·685 | 17 | 14·533 | 35 | 42·188 | 120 | 1488·9 |
| 4 | 6·101 | 18 | 15·480 | 40 | 55·341 | 150 | 3568·7 |
| 5 | 6·543 | 19 | 16·481 | 45 | 71·90 | 200 | 1164·7 |
| 6 | 7·014 | 20 | 17·539 | 50 | 92·54 | 250 | **40·476** [5] |
| 7 | 7·514 | 21 | 18·655 | 55 | 117·85 | 300 | **87·41** [5] |
| 8 | 8·046 | 22 | 19·832 | 60 | 149·19 | 350 | **168·12** [5] |
| 9 | 8·610 | 23 | 21·074 | 65 | 187·36 | 360 | **189·63** [5] |
| 10 | 9·210 | 24 | 22·383 | 70 | 233·53 | 370 | **213·73** [5] |

The vapour pressure of water between 0° and 50° C. may be calculated with great exactness by means of Thiessen's formula : [6]

$$(t+273)\log p/760=5\cdot409(t-100)-0\cdot508\times10^{-8}\{(365-t)^4-265^4\}.$$

---

[1] A. and C Griffiths, *Proc. Phys Soc. London*, 1921, 33, 231.

[2] White and Twining, *Amer. Chem. J.*, 1913, 50, 380.

[3] Hauser, Drude's *Annalen*, 1901, 5, 597.

[4] Temperatures −15° to 0° C. (Scheel and Heuse, *Ann. Physik*, 1909, [4], 29, 723), 0° to 50° C. (Scheel and Heuse, *loc. cit.*, 1910, [4], 31, 715), 50° to 200° C. (Holborn and Henning, *ibid.*, 1908, [4], 26, 833), 200° to 370° C. (Holborn and Baumann, *ibid.*, 1910, [4], 31, 945). A complicated formula applying with great accuracy between 0° and 50° C. is given by Schreiber, *Physikal. Zeitsch.*, 1919, 20, 521. See also Brunelli, *Nuovo Cim*, 1917, [6], 14, ii., 55.

[5] These data are as given by the authors in kilograms per sq cm. equivalent 0·968 atmosphere.

[6] Thiessen, *Wied. Annalen*, 1899, 67, 692; applied by Scheel and Heuse, *loc. cit.* Many other formulæ have been suggested.

Mention has already been made (p. 250) of the fact that when the temperature of pure ice is gradually raised under the ordinary atmospheric pressure, melting always takes place exactly at 0° C. The converse, however, is not equally true.

If water is cooled, solidification may not occur immediately a temperature of 0° C. is reached. Under suitable conditions it is possible to reduce the temperature many degrees below 0° without freezing taking place, even at atmospheric pressures.

This was first observed by Fahrenheit, who, in 1724, succeeded in cooling water in cleaned tubes down to 15° F. (−9·4° C.) without solidification.[1] Gay Lussac cooled water down to −12° C., the liquid condition being maintained until a fragment of solid ice was added. The surface of the water was covered with oil to prevent contamination with dust.

Dalton [2] stated that—

"If the water be kept still, and the cold be not severe, it may be cooled in large quantities to 25° or below, without freezing; if the water be confined in the bulb of a thermometer, it is very difficult to freeze it by any cold mixture above 15° of the old scale; but it is equally difficult to cool the water much below that temperature without its freezing. I have obtained it as low as 7° or 8°, and gradually heated it again without any part of it being frozen."

Dalton also knew that—

"When water is cooled below freezing and congelation suddenly takes place, the temperature rises instantly to 32°."

*Capillary Water.*—Sorby [3] pointed out that water kept in glass tubes of diameter ranging from 0·025 to 0·25 inch may easily be cooled to −5° C. without congelation, even when the tube is shaken. By keeping the tube quiet an even lower temperature may be obtained, as has been mentioned above.

When contained in capillary tubes, water offers very great resistance to freezing, unless it is in contact with ice. Thus Sorby found that no congelation took place, even upon shaking, when water was cooled to −15° C. in glass tubes of diameter 0·003 to 0·005 inch. The temperature could even be reduced to −16° C. if the tubes were kept very quiet, although at −17° C. the water froze immediately. In a tube of diameter approximately 0·01 inch the water froze at −13° C. but not at −11° C. In contact with ice, however, water freezes readily in capillary tubes, and ice thaws as usual at 0° C. when in tubes in which water will not congeal in the absence of the solid phase above −16° C.

Müller-Thurgau [4] states that filter paper moistened with distilled water freezes at −0·1° C., whilst a clay sphere, under similar conditions, has been found to freeze at −0·7° C.[5] These observations refer to the actual freezing-points under the conditions named, and are quite apart from supercooling effects, which, as shown above, may be extended to much lower temperatures.[6]

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[1] Fahrenheit, *Phil. Trans.*, 1724, 39, 78. See also Tellier, *Compt. rend.*, 1872, 75, 506.

[2] Dalton, *A New System of Chemical Philosophy* (London, 1808), Part I, p. 135. The temperatures are those on the Fahrenheit scale.

[3] Sorby, *Phil. Mag.*, 1859, [4], 18, 105.

[4] Muller-Thurgau, *Landwirtschaft. Jahrb*, 1880, 9, 176.

[5] Bachmetjew, *Zeitsch. Wiss. Zool*, 1899, 66, 584.

[6] See for further data Foote and Saxton, *J. Amer. Chem. Soc.*, 1917, 39, 627; 1916, 38, 588.

The presence of finely divided particles of solid materials, such as ferric hydroxide, alumina, etc., causes an appreciable depression of the freezing-point.[1]

A convenient method of cooling water below 0° C. consists in preparing a mixture of chloroform and olive-oil in such proportions that the product has the same density as water. Drops of water suspended in this mixture may be cooled down to very low temperatures (*c.* —20° C.) without freezing. Such water is termed *supercooled* or *superfused,* and is stable only so long as the solid phase is absent. It is therefore said to be *meta-stable.* The water will usually solidify immediately upon exposure to air or dust, or on the introduction of some foreign material. Even the act of scratching the inside wall of the containing vessel will suffice to induce crystallisation. If the supercooling is carried beyond a certain amount, solidification takes place spontaneously without the introduction of the solid phase or foreign material. In either case the temperature rises to 0° and remains there until solidification is complete.

The velocities of crystallisation of supercooled water, as determined in a tube 1 metre in length and 0·7 cm. in diameter, and expressed as cms. per minute, are given in the accompanying table.[2]

## VELOCITY OF CRYSTALLISATION OF SUPERCOOLED WATER.

| Temperature, ° C. | Velocity, cms./min. | Temperature, ° C. | Velocity, cms /min. |
|---|---|---|---|
| —2·00 | 31·6 | —7·10 | 266·7 |
| —3·61 | 48·4 | —7·50 | 308·0 |
| —4·67 | 71·4 | —8·19 | 415·2 |
| —5·86 | 107·1 | —8·38 | 513·0 |
| —6·18 | 114·7 | —9·07 | 684·0 |

The maximum velocity of crystallisation evidently lies below —9·07° C., but, owing to spontaneous solidification of the water, it was not found possible to make determinations at lower temperatures.

It is interesting to note that whereas ice produced with a cooling temperature within one or two degrees of the melting-point is usually clear, the product obtained with stronger cooling is milky in appearance on account of the inclusion of minute bubbles of air which was previously in solution.

The vapour pressure of supercooled water is always greater than that of ice at the same temperature.[3] This is evident from the data in the table.[4]

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[1] F. W. Parker, *J. Amer. Chem Soc.*, 1921, 43, 1011

[2] Walton and Judd, *J. Physical Chem.*, 1914, 18, 722.

[3] Ramsay and Young, *Proc Roy. Soc.*, 1884, 36, 499

[4] Scheel and Heuse, *Ann. Physik*, 1909, [4], 29, 723. See also Juhlin, *Bihang Svenska Akad. Handl.*, 1891, 17, I, 58.

## VAPOUR PRESSURE OF SUPERCOOLED WATER.

| Temperature. | Vapour Pressure in mm. Hg. | |
|---|---|---|
| | Ice | Water. |
| 0 | 4·579 | 4·579 |
| — 2 | 3·885 | 3·958 |
| — 4 | 3·288 | 3·418 |
| — 6 | 2·776 | 2·942 |
| — 8 | 2·337 | 2·525 |
| —10 | 1·963 | 2·160 |
| —12 | 1·644 | 1·843 |
| —14 | 1·373 | 1·568 |
| —16 | 1·253 | 1·331 |

This is shown graphically in fig. 44, the broken line indicating the vapour pressure of the supercooled water, and the continuous lines the pressures of liquid water above 0° C. and of ice I below 0° C. As already explained, in the absence of air and in presence of water-vapour only, T represents a triple point, and lies at +0·0076° C. A slight break occurs at T between curves LT and TS, but TC is a continuation of LT.

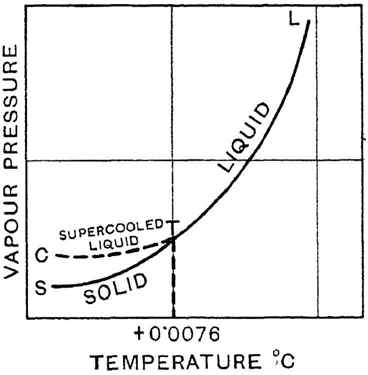

Fig. 44.—Vapour pressure of supercooled water.

It will now be evident why TC represents a meta-stable condition of water. If a piece of ice is introduced into the same closed vessel, the vapour is supersaturated with regard to the ice, and a portion condenses. But this leads to a vapour unsaturated with respect to the supercooled liquid, which, in consequence, vaporises to a corresponding amount. This condensation on the ice and vaporisation of the liquid continues until the whole of the latter has disappeared, leaving only ice and vapour.

Water is generally regarded as a poor conductor of heat, although, compared with other non-metallic liquids, its conductivity is high. The *thermal conductivity*, K, is defined as the number of units of heat (gram calories) which will pass by conduction across unit area (sq. cm.) in unit time (second) with unit temperature gradient (1° C. per cm.). The following values for K have been obtained (p. 270).

The value for K at any temperature between 7·4° and 72·6° C. may be calculated from the equation [1]

$$K = 0{\cdot}001325(1 + 0{\cdot}002984t).$$

---

[1] Jakob, *loc. cit.*

## THERMAL CONDUCTIVITY OF WATER.[1]

| Temperature, ° C. | K | Authority |
|---|---|---|
| 0 | 0·001325 | Jakob, *Ann. Physik*, 1920, **63**, 537. |
| 0 | 0·00150 | Goldschmidt, *Physikal. Zeitsch.*, 1911, **12**, 417. |
| 0 to 34 | 0·00131 | R. Weber, *Ann. Physik*, 1903, **11**, 1047. |
| 11 | 0·00147 | Lees, *Proc. Roy. Soc.*, 1905, **74**, 337. |
| 20 | 0·00143 | Milner and Chattock, *Phil. Mag.*, 1899, **48**, 46. |
| 25 | 0·00136 | Lees, *loc. cit.* |

This poor conductivity manifested by water plays an important part in nature's economics.

Livingstone [2] mentions that the temperature of the surface water of ponds in the central regions of Southern Africa may reach as high as 38° C., but, owing to the poor conductivity of heat, " deliciously cool water may be obtained by anyone walking into the middle and lifting up the water from the bottom."

A study of the *specific heat* of water is particularly important, since the unit of heat or *gram calorie* is the amount of heat required to raise 1 gram of water through 1 degree centigrade. Sometimes the gram calorie at 15° C. (calorie 15° C.) is chosen, sometimes that at 20° C. (calorie 20° C.), whilst at other times the mean value between 0° and 100° C. is adopted. These units are not identical, but the variation is small. As water, owing partly to its abundance, and partly also to the ease with which it can be obtained in a pure condition, is the standard substance for the measurement of heat quantities, it is important to determine with the utmost accuracy the variation of its specific heat with the temperature. Numerous investigations have been carried out with this object in view, very reliable data being those of Callender and Barnes.[3] According to Callender, the specific heat of water, $Q_t$, in terms of the calorie at 20° C., is given by the expression

$$Q_t=0{\cdot}98536+0{\cdot}504/(t+20)+0{\cdot}000084t+0{\cdot}0000009t^2$$

for any temperature between $t=0°$ and $t=100°$ C.

According to Narbutt, the specific heat of water for a temperature range of 0° to 100° C. may be calculated from the following empirical formula : [4]

$$\text{Specific heat}=1{\cdot}00733-0{\cdot}0007416(t-15)+0{\cdot}000016845(t-15)^2 \\ -0{\cdot}00000009552(t-15)^3$$

---

[1] Earlier data are those of Lundquist, *Arskrift Univ. Upsala*, 1869, p. 1 ; H. F. Weber, *Wied. Annalen*, 1880, 10, 103 ; 1880, 11, 345 ; Graetz, *ibid.*, 1883, 18, 79 ; Chree, *Proc. Roy. Soc.*, 1888, 43, 30 ; Wachsmuth, *Wied. Annalen*, 1893, 48, 158.

[2] Livingstone, *Missionary Travels* (Ward Lock), p. 145.

[3] Callender, *Phil. Trans.*, 1912, [A], 212, 1 ; *Proc. Roy. Soc.*, 1912, [A], 86, 254; Barnes, *Phil. Trans.*, 1902, [A], 199, 149

[4] Narbutt, *Physikal. Zeitsch.*, 1918, 19, 513.

which gives values in very close agreement with the best experimental data.

The specific heat of water is abnormally high, and this fact has an enormous influence upon climate and geological phenomena. Liquid ammonia is the only liquid possessing a higher specific heat.

In the following table are the data obtained by Callendar and Barnes:[1]

## SPECIFIC HEAT OF WATER.[2]

| Temperature, ° C | Specific Heat | Temperature, ° C | Specific Heat | Temperature, ° C. | Specific Heat. |
|---|---|---|---|---|---|
| 0 | 1·0094 | 15 | 1·0011 | 30 | 0·9987 |
| 1 | 1·0085 | 16 | 1·0009 | 35 | 0·9983 |
| 2 | 1·0076 | 17 | 1·0007 | 40 | 0·9982 |
| 3 | 1·0068 | 18 | 1·0004 | 45 | 0·9984 |
| 4 | 1·0060 | 19 | 1·0002 | 50 | 0·9987 |
| 5 | 1·0054 | 20 | **1·0000** | 55 | 0·9993 |
| 6 | 1·0048 | 21 | 0·9999 | 60 | 1·0000 |
| 7 | 1·0042 | 22 | 0·9997 | 65 | 1·0008 |
| 8 | 1·0037 | 23 | 0·9995 | 70 | 1·0016 |
| 9 | 1·0032 | 24 | 0·9994 | 75 | 1·0024 |
| 10 | 1·0027 | 25 | 0·9992 | 80 | 1·0033 |
| 11 | 1·0023 | 26 | 0·9991 | 85 | 1·0043 |
| 12 | 1·0020 | 27 | 0·9990 | 90 | 1·0053 |
| 13 | 1·0017 | 28 | 0·9989 | 95 | 1·0063 |
| 14 | 1·0014 | 29 | 0·9988 | 100 | 1·0074 |

It will be observed that the gram calorie at 20° C. equals that at 60° C., whilst the mean value between 0° and 100° C. is 1·0016. A minimum value occurs at 40° C.[3] This fluctuation in specific heat at different temperatures is usually attributed to the influence of depolymerisation as the temperature rises (see p. 296). For supercooled water at $-5°$ C. the value 1·0158 for the specific heat has been obtained in terms of the calorie at 16° C.[4]

As the calorie is inconveniently small for some purposes, a larger unit, the Calorie, is sometimes used equal to 1000 smaller calories, the terms being frequently abbreviated into "cal." and "Cals." respectively; occasionally a unit equal to 100 calories and described as a Kaloric (Kal. or K.) is used.

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[1] For other data see Bartoli and Stracciata, *Beiblätter*, 1891, 15, 761; 1893, 17, 542, 638, 1038; Griffiths, *Phil. Trans.*, 1893, 184, 361, *Proc. Roy. Soc.*, 1897, 61, 479; *Phil. Mag.*, 1895, [5], 40, 431; Rowland, *Proc. Amer. Acad.*, 1879, 15, 75; W. R. Bousfield and W. E. Bousfield, *Phil. Trans.*, 1911, [A], 211, 199; *Proc. Roy. Soc.*, 1911, 85, 302. Earlier data are those of Henrichsen, *Wied. Annalen*, 1879, 8, 83; Pfaundler, *ibid.*, 1880, 11, 237; Münchhausen and Wullner, *ibid.*, 1877, 1, 592. A recalculation of Regnault's data is given by Guillaume, *Compt. rend.*, 1912, 154, 1483.

[2] Taken from Vol. I., p. 87. [3] According to Jäger and von Steinwehr (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1915, p. 424), the minimum occurs at 33·5° C.

[4] Barnes and Cooke, *Phys. Review*, 1902, 15, 65.

The heat of formation of water from gaseous hydrogen and oxygen at 18° C. is 68·38 Calories 15° C.[1]

The *surface tension* of water, like that of all liquids, diminishes with rise of temperature. A ready method of illustrating this consists in pouring water into a shallow, clean metal plate held horizontally until a thin layer is formed. The surface is now dusted over with flowers of sulphur, and heat applied locally to a point near the centre of the under surface of the plate by means of a fine gas jet. As soon as the heat reaches the water, the sulphur is rapidly pulled away towards the circumference of the plate in consequence of the reduction in the surface tension of the warmed central liquid.[2]

The surface tension $\sigma_t$ at $t$ ° C. is practically a linear function of the temperature, and may be calculated according to the equation

$$\sigma_t=\sigma_o(1-at) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\sigma_o$ is the surface tension at 0° C. and $a$ is a constant.

The value for $a$ in the case of water has been repeatedly determined as follows:

| *a*. | Authority |
|---|---|
| 0·0019 | Brunner, *Pogg. Annalen*, 1847, **70**, 481. |
| 0·0018 | Frankenheim, *ibid.*, 1847, **72**, 177. |
| 0·0018 | Wolf, *Ann. Chim. Phys.*, 1857, [3], **49**, 269. |
| 0·0018 | Volkmann, *Wied. Annalen*, 1882, **17**, 353. |
| 0·0022 | Timberg, *ibid.*, 1887, **30**, 545. |
| 0·0023 | Jäger, *Sitzungsber. K. Akad. Wiss. Wien*, 1891, **100**, 245. |
| 0·0021 | Cantor, *Wied. Annalen*, 1892, **47**, 399. |
| 0·0020 | Humphreys and Mohler, *Phys. Review*, 1895, **2**, 387. |
| 0·0020 | Sentis, *J. Physique*, 1897, [3], **6**, 183. |

A mean value of 0·0020 is probably fairly accurate. Forch[3] suggests the equation

$$\sigma_t=\sigma_o\ (1-0{\cdot}00190179t-0{\cdot}0000024991t^2).$$

$\sigma_t$ for water has been determined in a variety of ways by different investigators, the results ranging from 70·6 to 78 dynes per cm. at 20° C.

The results obtained by Ramsay and Shields[4] in their classical research, in which water was in contact with its vapour and the walls of the capillary tube only, are given on p. 273.

Whilst the foregoing results are relatively correct, it appears almost certain that their absolute values are all somewhat too low. The method adopted by Ramsay and Young consisted in measuring the difference in level between water in a capillary tube open at both ends and suspended in a wider glass tube. Richards and Coombs,[1] however, have shown that the diameter of the wider tube must be considerably greater than has hitherto been realised if the disturbing influence of the walls is to be neglected. Thus, in a tube of diameter 2·54 cms. the water was found to lie 0·11 mm. above that in one of 3·8 mm. diameter. Experiments showed that this latter is about the limiting diameter, the effect of the surface tension under these conditions being reduced well below that of the other errors of experiment.

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[1] Roth, *Zeitsch. Elektrochem.*, 1920, 26, 288.

[2] Poynting and Thomson, *Properties of Matter* (Chas. Griffin & Co., 1907), p 163.

[3] Forch, *Ann. Physik*, 1905, 17, 750.

[4] Ramsay and Shields, *Zeitsch. physikal. Chem.*, 1893, 12, 433.

| Temperature, ° C. | $\sigma_t$, dynes/cm. | $\sigma_t\ (Mv)^{\frac{2}{3}}$. | $x \times M$. |
|---|---|---|---|
| 0 | 73·21 | 502·9 | 3·81×18 |
| 10 | 71·94 | 494·2 | 3·68 |
| 20 | 70·60 | 485·3 | 3·55 |
| 30 | 69·10 | 476·1 | 3·44 |
| 40 | 67·50 | 466·3 | 3·18 |
| 60 | 64·27 | 446·2 | 3·00 |
| 80 | 60·84 | 425·3 | 2·83 |
| 100 | 57·15 | 403·5 | 2·66 |
| 120 | 53·30 | 380·7 | 2·47 |
| 140 | 49·42 | 357·0 | 2·32 |

Taking this and several other possible sources of error into consideration, the mean value for the surface tension of water was determined experimentally as equal to 72·62 dynes per cm. at 20·00° C.

As a general rule, the presence of dissolved inorganic salts enhances the value in accordance with the simple mathematical expression

$$\sigma_s = \sigma_w + \mathrm{R}n$$

where $\sigma_s$ is the surface tension of the solution, $\sigma_w$ that of water at the same temperature, $n$ the number of gram equivalents of the salt per litre, and R a constant, depending upon the chemical nature of the dissolved salt. For the undermentioned salts, R has the following values : [2]

| Salt. | R. |
|---|---|
| NaCl | 1·53 |
| KCl | 1·71 |
| $\frac{1}{2}\cdot Na_2CO_3$ | 2·00 |
| $\frac{1}{2}\cdot K_2CO_3$ | 1·77 |
| $\frac{1}{2}\cdot ZnSO_4$ | 1·86 |

Organic salts, on the other hand, frequently reduce the surface tension of the solution. The oleates are cases in point.

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[1] Richards and Coombs, *J. Amer. Chem. Soc.*, 1915, 37, 1656.

[2] Dorsey, *Phil. Mag.*, 1897, 44, 369.

Most other liquids, except mercury, have a lower surface tension than water. This is illustrated by the following data :

| | Mercury | Water. | Carbon disulphide | Ethyl alcohol | Ether. | Olive oil. | Benzene. |
|---|---|---|---|---|---|---|---|
| Surface tension . | 547 | 72·6 | 33·6 | 22·0 | 16·5 | 32 | 29·2 |
| Temperature, °C. . | 17·5 | 20 | 19·4 | 20 | 20 | 20 | 17·5 |

Dissolved gases tend to raise the surface tension. The following values obtained at 15° C. illustrate this :[1]

| | In vacuo. | Hydrogen. | Nitrogen. | Carbon monoxide. | Carbon dioxide | Air. |
|---|---|---|---|---|---|---|
| Surface tension . | 71·3 | 72·83 | 73·00 | 73·00 | 72·85 | 73·1 |

Water is an excellent *solvent*, dissolving not only many acids, bases, and salts, but also many organic compounds, especially such as contain hydroxyl and amino-groups. The solubility of solids and liquids generally increases with rise in temperature, whilst gases, all of which are soluble in water to some extent, are invariably less soluble at higher temperatures. The presence of dissolved solids causes a depression of the freezing- and melting-point of water to an amount proportional to the concentration. This is known as *Blagden's Law*, and is only true provided the solutions are dilute. The extent of the depression for un-ionised substances in dilute solution is such that proportionately one gram molecular weight of the solute in 100 grams of water would cause a depression of 18·5° C.—the *molecular depression*.[2]

The *molecular elevation* of the boiling-point is calculated in a similar manner, and has the value 5·2° C.

The dielectric constant of water is 81·7 at the ordinary temperature.[3] This value is a high one when compared with the same constant for other liquids and it is probably on account of its considerable dielectric power that solutions of bases, acids, and salts in water can conduct the electric current, this conduction being dependent on the electrolytic dissociation of the solute. In aqueous solution, however, some organic substances are partly *associated* to double or even more complex molecules.[4]

Purified water does not appreciably conduct the electric current, so that the conductivity of a sample of water can be used as an indication of freedom from saline impurities.[5]

The purest water hitherto obtained possessed an electrical conductivity of $0·04 \times 10^{-10}$ mhos at 18° C,[6] the increase in the value with rise of temperature being represented by a coefficient of 0·0532 per degree. This coefficient only holds for water of a high degree of purity, such as has not even been exposed to the atmosphere,[7] because slight impurities have a relatively inordinate effect on the conductivity and possess a much lower coefficient of increase with temperature, namely, of the order of 0·021. Pure water, therefore, probably possesses a very slight but definite electrical conductivity which is to be attributed to the existence of a minute proportion of the water in an ionised or electrolytically dissociated condition, that is as $H^{\cdot}$ (positive) and $OH'$ (negative) ions. As the conductivity due to the gram-equivalent weight of these ions in a definite volume can be calculated from the electrical conductivity of acids and alkalies respectively in dilute solution, it is possible to evaluate the proportion of pure water which is ionised at a definite temperature, the result is $6{\cdot}3 \times 10^{-10}$ grams per c.c. at 0°, the corresponding dissociation constant at 18° being $0{\cdot}8 \times 10^{-7}$. The probability of the correctness of this reasoning is borne out by the approximate agreement of the above value for the extent of dissociation with values obtained by quite different physico-chemical methods, such as the hydrolytic action of water on ammonium acetate, etc.[1] In the presence of dissolved electrolytes the dissociation of water is still further depressed.[2] The electrical conductivity of solutions of water in other solvents bears no simple relation to that of the pure liquid, and, indeed, varies widely according to the solvent.[3]

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[1] Bhatnagar, *J. Physical Chem*, 1920, 24, 716. See also Freundlich, *Kapillarchemie* (Leipzig, 1909), p. 85.

[2] See this series, Vol. I., p. 122. Roth (*Zeitsch. Elektrochem.*, 1920, 26, 288) suggests 18·60 as the most probable value.

[3] Drude, *Zeitsch. physikal. Chem.*, 1897, 23, 267.

[4] See Peddle and Turner, *Trans. Chem. Soc.*, 1911, 99, 685.

[5] Doroschevsky and Dvorshantschik, *J. Russ. Phys. Chem. Soc.*, 1913, 45, 1489.

[6] Kohlrausch and Heydweiller, *Zeitsch. physikal. Chem.*, 1894, 14, 317 ; Kohlrausch, *ibid.*, 1902, 42, 193. See also Heydweiller, *Ann. Physik*, 1909, 28, 503.

[7] See Kendall, *J. Amer. Chem. Soc.*, 1916, 38, 1480.

The electrolytic dissociation of water increases with rise of temperature. This is unusual, but is commonly explained on the assumption that most water molecules at ordinary temperatures are polymerised, thus $(H_2O)_x$, the value for $x$ being mainly 2, and that the existing ionisation is that of single molecules $H_2O$. As the temperature rises the proportion of these increases through depolymerisation of the complex molecules, so that whilst the actual percentage of single molecules converted into ions may be reduced, the total number of ions is greater.[4]

In contact with ordinary fresh air, the conductivity of water is 0·7 to $0{\cdot}8 \times 10^{-6}$ mho, the rise being due mainly to the dissolved carbon di-oxide.[5]

The absorption spectrum of water[6] was studied by Soret and Sarasin[7] in 1884, who passed a beam of light through 2·2 metres of water. A faint and narrow band was observed in the orange at a wave length of approximately 6000. This band became slightly more distinct and a general absorption of the extreme red was noticed as the thickness of the water layer was increased from 3·3 to 4·5 metres.

In small quantities water appears colourless, but in deep layers it is possessed of a bluish tinge, which tends to become greenish as the temperature is raised.[8]

The cause of the coloured appearance of natural waters has been the subject of considerable discussion.[9] The light blue hue of water that has been softened by Clark's process has frequently been commented upon,[1] and points to the suggestion that the colour is due to the scattering of light by suspended particles. Threlfall [2] found that the following solution, when viewed through a tube 18 cm. in length, matched with considerable precision the colour of a sample of water from the Mediterranean :

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[1] Noyes, Kato, and Sosman, *J. Amer. Chem. Soc*, 1910, 32, 159; Lorenz and Bohi, *Zeitsch. physikal. Chem.*, 1909, 66, 733; Hudson, *J. Amer. Chem. Soc*, 1909, 31, 1136: Frary and Nietz, *ibid.*, 1915, 37, 2263; Kanolt, *ibid.*, 1907, 29, 1402; Walker, *Trans. Faraday Soc*, 1906, 1, 362; Heydweiller, *Ann. Physik*, 1909, [4], 28, 503.

[2] Poma and Tanzi, *Zeitsch. physikal. Chem.*, 1912, 79, 55.

[3] Walden, *Trans. Faraday Soc.*, 1910, 6, 71.

[4] See p. 296

[5] See Kendall, *J. Amer Chem Soc.*, 1916, 38, 1480, on the specific inductive capacity of water see Beaulard, *Compt. rend.*, 1905, 141, 656.

[6] See also Hartley and Huntington, *Phil Trans.*, 1879, 170, 257; Colley, *J. Russ Phys. Chem. Soc.*, 1906, 38, 431; 1907, 39, 210; Weichmann, *Ann Physik*, 1922, [4], 66, 501; *Physikal. Zeitsch.*, 1921, 22, 535 The infra-red absorption has been studied by Collins, *Physical Review*, 1922, 20, 486.

[7] Soret and Sarasin, *Compt. rend.*, 1884, 98, 624

[8] Duclaux and Wollmann, *J. Physique*, 1912, [5], 2, 263.

[9] See the interesting summaries by Bancroft, *Chem. News*, 1919, 118, 197, 208, 222, 233, 248, 254; Tomkinson, *ibid.*, 1921, 122, 205; and Ramanathan, *Phil. Mag.*, 1923, 46, 543.

500 c.c. distilled water.
0·001 gr. soluble Prussian blue.
5 c.c. saturated limewater just precipitated by the smallest excess of sodium hydrogen carbonate.

Lord Rayleigh [3] attributes the blue colour of the sea to that of the sky, seen by reflection.

According to Aitkin [4] the Mediterranean sea owes its colour to minute suspended particles which reflect rays of all colours, whilst the water, by virtue of selective absorption, allows only the blue rays to escape. The solid particles thus determine the brilliancy of the colour, whilst the selective absorption by the water determines the colour itself. The green colour, so frequently noticed in the sea, is attributed to the presence of yellowish particles in suspension. On the other hand, the green colours of such lakes as Constance and Neuchatel are ascribed by Spring [5] to the mixing of the natural blue of the waters with yellow produced by the presence of finely divided particles of suspended matter, which latter may themselves be quite colourless. Sometimes lakes, normally greenish in colour, become temporarily colourless. This is attributed to the presence of fine reddish mud, containing oxide of iron, which counteracts the green.

Threlfall suggests that the greenish colour of the sea off the coast of Western Australia may be due to the presence of traces of organic colouring matter dissolved out of living or dead seaweed. Buchanan [6] attributes the green colour of Antarctic waters to diatoms and the excretions of minute animals, whilst the sea water at Mogador (Morocco) and off Valparaiso and San Francisco are believed to be coloured green by chlorophyll.

Perfectly pure water is almost a chemical impossibility, inasmuch as contact with any containing vessel must lead to contamination. Even optically pure water is difficult of attainment; it cannot be prepared by mere filtration or distillation. Hartley showed that water, obtained by distillation from acid permanganate solution and subsequent redistillation from a copper vessel in a hydrogen atmosphere, is not optically void.[7] Tyndall obtained optically pure water by melting clear block ice in a vacuum. It showed a blue tinge when examined in a three-foot layer.

Now, if pure water is coloured slightly blue, as is generally conceded, the effect cannot be due to either of the foregoing causes, namely, the presence of suspended or dissolved materials, which are known to accentuate, if not to be the sole cause of, the colours of natural waters. It must be due to a pure absorption effect of the water itself. The relation between colour and constitution is by no means clear, but the suggestion has been made[1] that the greenish tinge acquired on raising the temperature is a consequence of the depolymerisation of the water molecules, the polymerised molecules being bluish in colour, whilst the single monohydrols are green. This receives support from the fact that solutions of colourless salts, which may be expected to contain fewer polymerised molecules, are more green than pure water at the same temperature.

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[1] See Lankester, *Nature*, 1910, 83, 68; Hartley, *ibid.*, p. 487.

[2] Threlfall, *ibid.*, 1899, 59, 461.

[3] Rayleigh, *ibid.*, 1910, 83, 48; *Scientific Papers*, 1912, 5, 540.

[4] Aitkin, *Proc. Roy. Soc. Edin.*, 1882, 11, 472.

[5] Spring, *5th Internat. Cong. Hydrology, etc., Liége*, 1898, *Arch. Sci. phys nat.*, 1908, [4], 25, 217.

[6] Buchanan, *Nature*, 1910, 84, 87.

[7] Hartley, *ibid.*, 1910, 83, 487, Spring, *Bull. Acad. roy. Belg.*, 1899, [3], 37, 174

The brown colours of natural waters are sometimes due to ferrugineous suspensions, but in many cases are attributable to colloidal organic matter.[2] Typical waters of this class occur in the uplands of Lancashire and Yorkshire. The colloid is usually electronegative in character, exhibiting electrophoresis in the direction of the anode,[3] and being precipitable by positively charged ions and colloids, and by electrical treatment.

The refractive index[4] for sodium light at different temperatures is as follows :

| Temperature, ° C. | Refractive Index. | |
|---|---|---|
| | Referred to Air at same Temperature. | Referred to Vacuum. |
| 20 | 1·33299 | 1·33335 |
| 25 | 1·33248 | 1·33284 |
| 30 | 1·33190 | 1·33225 |

Variation of the refractive index, $n$, with temperature, $t$, is given by the expression[5]

$$n=1{\cdot}33401-10^{-7}(66t+26{\cdot}2t^2-0{\cdot}1817t^3+0{\cdot}000755t^4).$$

For the iron E line[6] at 15° C. the refractive index is 1·335636.

The taste of water is largely dependent on its freedom or otherwise from dissolved foreign matter, especially carbon dioxide[7]; with pure distilled water the taste is distinctly flat and unpalatable.

The magnetic susceptibility of water has frequently been determined, the value for $K\times10^6$ at 20° C. being 0·7029 with a temperature coefficient of 0·00013.[1] According to Stearns, it lies between 0·715 and 0·750 at 22° C.[2] The dielectric constant of water at 18° C. is 81·05.[3]

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[1] Duclaux and Wollmann, *loc. cit.*

[2] See Race, *J. Soc. Chem. Ind.*, 1921, 40, 159 T.

[3] See Biltz and Krohnke (*Ber.*, 1904, 35, 1745), who studied sewage colloids.

[4] Baxter, Burgess, and Daudt, *J. Amer. Chem. Soc.*, 1911, 33, 893. See also Bruhl, *Ber.*, 1891, 24, 644 ; Gifford, *Proc. Roy. Soc.*, 1906, [A], 78, 406.

[5] E. E. Hall and Payne, *Physical Review*, 1922, 20, 249

[6] Gifford, *Proc. Roy. Soc.*, 1906, [A], 78, 406.

[7] Friedmann, *Zeitsch. Hyg. Infekt. Krankh.*, 1914, 77, 125 ; *Abstr. Chem. Soc.*, 1914, 106, ii., 645.

### C. *Physical Properties of Gaseous Water.*

The *boiling-point* of a liquid is defined [4] as the highest temperature attainable by a liquid under a given pressure of its own vapour when heat is applied externally and evaporation occurs freely from the surface. Under a normal pressure of 760 mm. of mercury, water boils at 100° C., and the boiling-points at various other pressures are given as follows [5] :

VARIATION OF THE BOILING-POINT OF WATER WITH PRESSURE.

| Pressure, mm Hg. | Temperature, ° C | Pressure, mm. Hg | Temperature, ° C. | Pressure, mm. Hg. | Temperature, ° C. |
|---|---|---|---|---|---|
| 720 | 98·493 | 740 | 99·255 | 760 | 100·000 |
| 722 | 98·570 | 742 | 99·331 | 762 | 100·074 |
| 724 | 98·647 | 744 | 99·406 | 764 | 100·147 |
| 726 | 98·724 | 746 | 99·481 | 766 | 100·220 |
| 728 | 98·800 | 748 | 99·555 | 768 | 100·293 |
| 730 | 98·877 | 750 | 99·630 | 770 | 100·366 |
| 732 | 98·953 | 752 | 99·704 | 772 | 100·439 |
| 734 | 99·029 | 754 | 99·778 | 774 | 100·511 |
| 736 | 99·104 | 756 | 99·852 | 776 | 100·584 |
| 738 | 99·180 | 758 | 99·926 | 778 | 100·656 |

The *hypsometer* is a small, portable piece of apparatus which enables the boiling-point of water to be determined at any place. The water is placed in a small tube or boiler and is heated by means of a spirit flame beneath, whilst the vapour in its passage to the open air heats a delicate thermometer. The instrument is sometimes used for determining the altitude of a place. since the boiling-point of water falls through one degree C. for every 1080 feet rise above sea level. A more general expression is that of Soret, namely:

$$h=295(100-t)$$

where $h$ is the height above sea level expressed in metres, and $t$ the ebullition temperature.[6]

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[1] Weiss and Piccard, *Compt. rend.*, 1912, 155, 1234; Piccard, *Arch. Sci. phys. nat.*, 1913, 35, 458.

[2] Stearns, *Phys. Review*, 1903, 16, 1. Other data are given by Quincke, *Wied. Annalen*, 1888, 35, 137; Townsend, *Proc. Roy. Soc*, 1896, 60, 186; Konigsberger, *Wied. Annalen*, 1898, 66, 698; *Drude's Annalen*, 1901, 6, 506; Jager and Meyer, *Wied. Annalen*, 1899, 67. 712; *Drude's Annalen*, 1901, 6, 870.

[3] Lattey, *Phil. Mag.*, 1921, [6], 41, 829.

[4] This series, Vol. I, p. 35.

[5] Landolt-Bornstein, *Physikalisch-chemische Tabellen* (Berlin, 1912). Based on Regnault's measurements

[6] For factors affecting the boiling-point see Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 477.

A knowledge of the variation of the vapour pressure in the neighbourhood of 100° is frequently of value in checking the accuracy of thermometers by immersion in steam at atmospheric pressure.

In this connection, therefore, the following data are of interest:

| Temperature, ° C. | 95 | 96 | 97 | 98 | 99 | 100 | 101 |
|---|---|---|---|---|---|---|---|
| Vapour pressure, mm. Hg | 634·01 | 657·69 | 682·11 | 707·29 | 733·24 | 760·00 | 787·57 |

Liquid water is incapable of existence above 374° C., this being the critical temperature, the corresponding pressure being 200 atmospheres and the volume 0·00386 approximately.

The more important determinations of the critical constants for water are given in the following table:

## CRITICAL CONSTANTS FOR WATER.

| Critical Temperature, ° C. | Critical Pressure. | Critical Volume, c.c./gram. | Critical Density, gram./c.c. | Authority. |
|---|---|---|---|---|
| 580 | .. | . | .. | Mendeléeff, *Pogg. Annalen*, 1870, **141**, 618. |
| 370 | 195·5 (atm.) | .. | .. | Strauss, *Wied. Annalen, Beiblatter*, 1883, **7**, 676. |
| 358·1 | .. | 2·33 | 0·429 | Nadejdine, *ibid.*, 1885, **9**, 721. |
| 365 | 200·5 (atm.)<br>207 (kilograms per sq. cm.) | .. | .. | Cailletet and Colardeau, *Compt. rend.*, 1888, **106**, 1489 |
| 364·3 | 194·6 (atm.)<br>201 (kilograms per sq. cm.) | 4·812 | .. | Battelli, *Mem. R. Accad. Torino*, 1890, [2], **41**. |
| .. | .. | 4·025 | .. | Dieterici (1904). Quoted by Davis (*vide infra*). |
| 374 | .. | .. | .. | Traube and Teichner, *Ann. Physik*, 1904, **13**, 620. |
| (365° assumed) | .. | 3·04 (calc.) | 0·329 (calc.) | Davis, *Phys. Review*, 1909, **29**, 81. |
| 374·07 to 374·62 | 217·8 (atm.)<br>225 (kilograms per sq. cm.) | .. | .. | Holborn and Baumann, *Ann. Physik*, 1910, **31**, 945. |
| .. | .. | .. | 0·322 | Calculated below. |

The density, *d*, of saturated steam at various temperatures is given by the equation:

$$d=0{\cdot}4552-0{\cdot}0004757(t-160)-0{\cdot}000000685(t-160)^2$$

in grams per c.c. where *t* is the temperature on the centigrade scale.

Assuming the critical temperature to be 365° C., the critical density becomes 0·329 gram per c.c.[1] The more recent work of Holborn and Baumann, however, suggests that 374·3° is a closer approximation than 365° to the critical temperature, and if this value is inserted for *t* in the above equation, the figure for $d_c$ becomes 0·322. This is probably the most accurate value.

The viscosity of water vapour at 20° C. is 0·0000975.[2]

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[1] Davis, *Phys. Review*, 1909, **29**, 81.

[2] Kundt and Warburg, *Pogg. Annalen*, 1875, **155**, 337; Houdaille, *Fortsch. Physik*, 1896, **1**, 442.

The latent heat of vaporisation of water at 100° C. is 539 calories $_{15^\circ}$. Sometimes the value is given for water at 0° C., in which case the amount of heat required to raise the water from 0° to 100° C. must be added to the above quantity. The following are the most noteworthy attempts to determine the latent heat of steam, undoubtedly the most accurate results being those of Richards and of Mathews. It is remarkable that the values obtained by Black and by Watt should approximate so closely to that accepted at the present day.

## LATENT HEAT OF VAPORISATION OF WATER.[1]

| From Water at 0° C | From Water at 100° C | Remarks. | Authority. |
|---|---|---|---|
| .. | 520 | . | Black, *c.* 1750. |
| .. | 525·2 | .. | Watt (1781). |
| 640 | (540) | .. | Brix, *Pogg. Annalen*, 1842, 55, 341. |
| 636·7 | (536·7) | Average of 38 determinations | Regnault, *Mém. de l'Inst. France*, 1847, 21, 635. |
| .. | 535·7 | . | Kahlenberg, *J. Physical Chem*, 1895, 5, 215. |
| .. | 537·2 | Mean of 3 | Louguinine, *Ann. Chim. Phys.*, 1896, [7], 7, 251. |
| .. | 540 | .. | Harker, *Mem. Manchester Lit. Phil. Soc*, 1896, [4], 10, 38. |
| .. | 538·25 at 100·6° C equivalent to 538·7 at 100° C. | Calories $_{15^\circ}$ | Henning, *Ann. Physik*, 1906, [4], 21, 849. |
| .. | 538·1 | Calories $_{15^\circ}$ | Richards and Mathews, *J Amer. Chem Soc*, 1911, 33, 863. |
| .. | 538·9 | Calories $_{21^\circ}$ equivalent to 2251 joules * | |
| .. | 539·0 | Calories $_{15^\circ}$ | Mathews, *J. Physical Chem.*, 1917, 21, 536. |

The amount of heat required to raise 1 gram of water at 0° C. into vapour at $t^\circ$ C. is given in calories $_{15^\circ}$ by the expression[3]:

$$639{\cdot}11+0{\cdot}3745(t-100)-0{\cdot}000{,}990(t-100)^2.$$

The mean specific heat of steam at constant pressure between 100° and 1400° C. is given by the equation:[4]

$$c_p=0{\cdot}4669-0{\cdot}000{,}016{,}8t+0{\cdot}000{,}000{,}044t^2,$$

the experimental data being as follows:

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[1] Other results are those of Ure, *Phil Trans.*, 1818, 108, 385; Depretz, *Ann Chim. Phys.*, 1823, [2], 24, 323; Andrews, *Pogg. Annalen*, 1848, 75, 501; Favre and Silbermann, *Compt. rend.*, 1849, 29, 449; 1846, 23, 441; *Ann. Chim. Phys*, 1853, [3], 37, 461; Berthelot, *Compt. rend.*, 1877, 85, 646; *Ann. Chim. Phys*, 1877, [5], 12, 550; Winkelmann, *Wied. Annalen*, 1880, 9, 208, 358; Schall, *Ber.*, 1884, 17, 2199; Schiff, *Annalen*, 1886, 234. 338; Dieterici, *Wied. Annalen*, 1889, 37, 494; A. W. Smith, *Phys. Review*, 1903, 16, 383; 1903, 17, 231; Joly, *Phil. Trans.*, 1895, 186, 322; Marshall and Ramsay, *Phil. Mag.*, 1896, [5], 41, 38.

* Calorie $_{21^\circ}$ = 4·177 kilojoules or 4177 joules.

[3] H. N. Davis, *Proc. Amer. Acad.*, 1910, 45, 267. See also Henning, *Zeitsch. Physik*, 1920, 2, 197; Steinwehr, *ibid.*, 1920, 1, 333.

[4] Holborn and Henning, *Ann. Physik*, 1905, 18, 739; 1907, 23, 809 See also Holborn and Austin, *Brit. Assoc. Reports*, 1907; Bjerrum, *Zeitsch. Elektrochem.*, 1912, 18, 101; 1911, 17, 731 · Lewis and Randall, *J. Amer. Chem Soc.*, 1912, 34, 1128; Gray, *Phil. Mag.*, 1882, [5], 13, 337.

## MOLECULAR SPECIFIC HEAT OF STEAM AT CONSTANT PRESSURE.

| Temperature, ° C. | $c_p$. | Temperature, ° C. | $c_p$ | Temperature, ° C. | $c_p$. |
|---|---|---|---|---|---|
| 100 | 0·4658 | 500 | 0·4690 | 900 | 0·4877 |
| 200 | 0·4653 | 600 | 0·4726 | 1000 | 0·4941 |
| 300 | 0·4658 | 700 | 0·4767 | 1400 | 0·5296 |
| 400 | 0·4672 | 800 | 0·4817 | | |

The molecular specific heat at constant volume is given by the expression:[1]

$$C_v = 5{\cdot}91 + 0{\cdot}003{,}76t - 0{\cdot}000{,}000{,}155t^2;$$

between 0° and 2900° by:

$$C_v = 5{\cdot}750 + 0{\cdot}783 \times 10^{-3}\,T + 0{\cdot}626 \times 10^{-6}\,T^2 + 4{\cdot}56 \times 10^{-10}\,T^3 - 2{\cdot}18 \times 10^{-17}\,T^5,$$

where T is the absolute temperature,[2] and[3]

$$C_v = 6{\cdot}065 + 0\ 0005t + 0{\cdot}2 \times 10^{-9}t^3$$

between 1300° and 2500° C.

The ratio $C_p/C_v$ has been evaluated at 1·29, agreeing fairly well with the figure expected of a substance consisting of triatomic molecules.[4] The value falls with rise of temperature as is usual. Thus:[5]

| Temperature . . | 110 | 120 | 130 |
|---|---|---|---|
| $\gamma = C_p/C_v$ . . | 1·3301 | 1·3129 | 1·3119 |

Water-vapour exerts a distinct selective action on light,[6] the effect of atmospheric moisture being detectable spectroscopically in sunlight. It manifests absorption in the infra-red region, and the "a" absorption band is interesting as being the one by which the presence of water vapour on Mars was first determined by Slipher in 1908.[7]

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[1] Mallard and Le Chatelier, *Compt rend.*, 1881, 93, 1014.

[2] Siegel, *Zeitsch physikal. Chem.*, 1914, 87, 641.

[3] Pier, *Zeitsch Elektrochem*, 1909, 15, 536. See also Womersley, *Proc. Roy Soc.*, 1922, [A], 100, 483, Kemble and van Fleck, *ibid*, 1923, 21, 653

[4] de Lucchi, *Ann. Physik, Beiblatter*, 1882, 6, 621

[5] Treitz, *Ueber die Fortpflanzungsgeschwindigkeit des Schalles in einigen Dampfen*, Bonn, 1903.

[6] Janssen, *Compt. rend*, 1866, 63, 289, 411, Liveing and Dewar, *Proc. Roy. Soc.*, 1882, 33, 274; von Bahr, *Ber. Deut. physikal. Ges*, 1913, 15, 731; Rubens and Hettner, *ibid.*, 1916, 18, 154; Hettner, *Ann. Physik*, 1918, 55, 476.

[7] See notes in *Nature*, 1908, 77, 497, 606.

# CHAPTER IX.

## CHEMICAL PROPERTIES OF WATER.

WATER is readily decomposed at the ordinary temperature by alkali and alkaline earth metals in compact form. The temperatures at which water, in the form of ice, becomes measurably attacked by the alkali metals have been determined as follow :[1]

| | | | |
|---|---|---|---|
| Sodium . | − 98° C. | Rubidium . | −108° C. |
| Potassium . | −105° C. | Cæsium . | −116° C. |

Many other metals liberate the hydrogen on warming,[2] particularly when in a finely divided condition. Thus pyrophoric iron rapidly decomposes water at 50° to 60° C., and its action is perceptible even below 10° C. Its reactivity appears to be independent of the presence of occluded gases or of carbon, and to be solely dependent upon its fine state of division.[3] Boiling water is slowly decomposed by granulated lead.[4]

Addition of magnesium powder to ten times its own weight of cold water, followed by a little palladous chloride, causes the evolution of hydrogen, which spontaneously ignites.[5]

Although aluminium is not readily attacked by water at the ordinary temperature, in contact with iodine the hydroxide is formed, hydrogen being liberated. This appears to be due to the formation of a little aluminium iodide, $AlI_3$, which is immediately hydrolysed to the hydroxide and hydrogen iodide. This latter then attacks the aluminium, liberating hydrogen,[6] and yielding a further quantity of iodide, which immediately in its turn undergoes hydrolysis. Since the iodine does not enter into the final products, a very small quantity is sufficient to effect the oxidation of an indefinitely large quantity of aluminium ; in other words, it is a catalyst.

Mention has already been made of the fact that the action of water is of considerable value in discriminating between acidic and basic oxides. A somewhat similar series of reactions takes place with chlorides. Thus the acid chlorides $PCl_5$, $PCl_3$, $SiCl_4$, $AsCl_3$, are converted into free hydrochloric acid, and the corresponding acid derived from the non-metal. In the case of chlorides derived from organic acids, analogous results obtain. Thus acetyl chloride, $CH_3.COCl$, yields acetic acid, $CH_3.COOH$, together with hydrochloric acid.

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[1] Hackspill and Bossuet, *Compt. rend.*, 1911, 152, 874.

[2] See van Ryn, *Chem. Weekblad*, 1908, 5, 1.

[3] See this series, Vol. IX., Part II., p. 63.

[4] Regnault, *Ann. Chim. Phys.*, 1836, 62, 337 ; Stolba, *J. prakt. Chem*, 1865, 94, 113.

[5] Knapp, *Chem. News*, 1912, 105, 253

[6] Gladstone and Tribe, *Chem. News*, 1880, 42, 2.

Metallic carbides are frequently decomposed by water, yielding hydrocarbons. One of the best known of these reactions is that with calcium carbide,[1] which yields acetylene. Thus

$$CaC_2+2H_2O=Ca(OH)_2+C_2H_2.$$

Even combined water or "water of crystallisation" may induce this reaction. Sodium carbonate, $Na_2CO_3.10H_2O$, is a useful salt to employ, and the reaction takes place at a more moderate temperature.[2]

By the action of water on aluminium carbide, methane is obtained[3] admixed, however, with a little hydrogen.[4]

$$Al_4C_3+12H_2O=4Al(OH)_3+3CH_4.$$

Other carbides, such as those of thorium, uranium, and glucinum, likewise yield methane, but mixed with various hydrocarbons.[5]

This behaviour of metallic carbides led Mendeléeff[6] tentatively to suggest that the large natural reservoirs of petroleum in America have been formed by the action of water or steam on subterranean metallic carbides.

Phosphides and silicides frequently behave in an analogous manner. Thus, calcium phosphide, $Ca_2P_2$, is decomposed by water yielding phosphorus trihydride, $PH_3$, and liquid phosphoretted hydrogen, $P_2H_4$, which is spontaneously inflammable.

$$3Ca_2P_2+12H_2O=6Ca(OH)_2+4PH_3+2P\,;$$
$$Ca_2P_2+4H_2O=2Ca(OH)_2+P_2H_4.$$

Even yellow phosphorus itself, when warmed with water, yields hydrogen phosphide.[7]

Metallic nitrides and hydrides are decomposed by water either in the cold or on warming, yielding respectively ammonia and hydrogen.

Many organo-metallic derivatives are decomposed by water. Thus zinc methyl yields methane:

$$Zn(CH_3)_2+2H_2O=Zn(OH)_2+2CH_4.$$

Magnesium methyl iodide, $Mg(CH_3)I$, behaves in an analogous manner:[8]

$$Mg(CH_3)I+H_2O=CH_4+Mg(OH)I.$$

Some metallic peroxides, such as sodium peroxide, are decomposed by water. An intimate mixture of powdered aluminium and sodium peroxide inflames when brought into contact with water.[9]

A few metallic sulphides are decomposed by water. The majority, however, are stable in the presence of water, and this fact is made use of in routine methods of qualitative analysis. Water decomposes strontium sulphide, yielding a mixture of hydroxide and hydrosulphide, which can be readily separated on account of their widely differing solubilities,[10] the latter substance being the more soluble:

$$2SrS+2H_2O=Sr(SH)_2+Sr(OH)_2.$$

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[1] First observed by Wohler, *Annalen*, 1862, 124, 267.

[2] See *Engineering*, 1906, 81, 261; Masson, *Trans. Chem. Soc.*, 1910, 97, 851; Turner, *Amer. Chem. J.*, 1907, 37, 106; Dupré, *Analyst*, 1905, 30, 266.

[3] Moissan, *Compt. rend.*, 1894, 116, 16.

[4] Campbell and Parker, *Trans. Chem. Soc.*, 1913, 103, 1292.

[5] See this series, Vol. V., p. 71.

[6] Mendeléeff, *Ber*, 1877, 10, 229.

[7] Weyl, *ibid.*, 1906, 39, 1307.

[8] Grignard, *Ann. Chim. Phys.*, 1901, 24, 438.

[9] Ohmann, *Ber.*, 1920, [B], 53, 1427.

[10] Terres and Brückner, *Zeitsch. Elektrochem.*, 1920, 26, 25.

Hence, by extracting strontium sulphide with hot water and cooling the clear filtrate, pure crystalline strontium hydroxide is obtained.

With barium sulphide the reactions are more complex, and pure barium hydroxide cannot be obtained in the above manner.[1]

When boiled with sulphur in the presence of oxygen in platinum vessels, water yields hydrogen sulphide and sulphuric acid.[2]

Many salts are decomposed by water, particularly when their solutions are boiled, basic salts being produced.[3]

Bismuth chloride almost immediately undergoes such "hydrolysis" to the basic bismuthyl chloride,

$$BiCl_3+H_2O \rightleftharpoons BiOCl+2HCl,$$

this reaction affording a convenient method of separating bismuth salts quantitatively from certain others. Solutions of ferric chloride, and indeed of many salts composed of a strong acid united with a feeble base, are acid in reaction from a similar cause:[4]

$$FeCl_3+3H_2O \rightleftharpoons Fe(OH)_3+3HCl.$$

For analogous reasons, salts containing feebly acidic radicles with strongly basic ones generally give alkaline solutions, *e.g.* potassium cyanide, sodium carbonate, etc.:

$$KCN+H_2O \rightleftharpoons KOH+HCN\,;$$
$$Na_2CO_3+H_2O \rightleftharpoons NaHCO_3+NaOH.$$

The action is referable to the effect of the ionisation of the water; in the presence of one of its salts a weak acid such as hydrocyanic is dissociated to an extent so slight as to be comparable in dissociation with water itself. Under such conditions an appreciable competition will occur between the acid of the salt and the water for possession of the metallic radicle.

Ethereal salts or *esters* derived from the neutralisation of an acid by an alcohol also undergo hydrolysis by water and the fats, which are compounds of this type, are frequently decomposed in this way for the manufacture of glycerine, candles, or soap; the hydrolysis of such esters is catalytically accelerated by the addition of a mineral acid.

When an air-free solution of potassium cobalto cyanide, $K_4CO(CN)_6$, is boiled, hydrogen is evolved, the volume of which equals that of the oxygen absorbed if the solution is rapidly oxidised in air, but to twice the volume absorbed during slow oxidation in air. The excess of oxygen in the former case remains at the close of the reaction as hydrogen peroxide. Thus, in air absence,

$$2K_4Co(CN)_6+2H_2O=2K_3Co(CN)_6+2KOH+H_2\,;$$

with rapid oxidation—

$$2K_4Co(CN)_6+2H_2O+O_2=2K_3Co(CN)_6+2KOH+H_2O_2\,;$$

but with slow oxidation—

$$2K_4Co(CN)_6+H_2O+O=2K_3Co(CN)_6+2KOH.*$$

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[1] Terres and Bruckner, *Zeitsch. Elektrochem.*, 1920, 26, 1

[2] Jones, *Mem. Manchester Phil. Soc*, 1912, 56, No. 14, 1.

[3] See M'Donnell and Graham, *J. Amer. Chem Soc.*, 1917, 39, 1912, Philip and Bramley, *Trans. Chem Soc.*, 1916, 109, 597; 1913, 103, 795

[4] See this series, Vol. IX, Part II.

* See this series, Vol. IX., Part I., p. 69

The influence of water upon the direction of certain reactions, in consequence of the heat liberated by the solution of one product, is beautifully illustrated in the case of sulphur, iodine, and their hydrides. The heats of reaction of hydrogen and solid iodine and sulphur in the dry are as follow:

$$(H_2)+[I_2]=2(HI)-12{,}072 \text{ calories}$$
$$(H_2)+[S]=(H_2S)+\ 2{,}730 \quad ,,$$

hence sulphur will effect the decomposition of hydrogen iodide with marked heat evolution. On the other hand, if the reactions take place in the presence of liquid water, there is a considerable evolution of heat in both cases in consequence of the heats of solution of the hydrides. Thus

$$(H_2)+[I_2]+Aq.=2HI.Aq.+26{,}348 \text{ calories.}$$
$$(H_2)+[S]+Aq.=H_2S.Aq.+\ 7{,}290 \quad ,,$$

Owing to the greater heat of solution of hydrogen iodide, the relative heat evolutions are now actually reversed, and solid iodine, in its turn, can decompose aqueous hydrogen sulphide, the reaction being markedly exothermic.

**Decomposition by Radioactive Substances and Ultra-violet Light.**—Water suffers decomposition when exposed to the action of radium emanation[1] or radioactive substances yielding hydrogen, oxygen, and hydrogen peroxide in varying amounts according to circumstances. All three types of rays, $\alpha$, $\beta$, and $\gamma$, appear to be active in this respect.[2] With the $\beta$ rays hydrogen is the main gaseous product, owing to the reaction proceeding as follows:

$$2H_2O=H_2O_2+H_2.$$

Ultra-violet light behaves like $\beta$ rays in this respect.[3] Water-vapour, free from air, is decomposed by a silent electric discharge in a similar manner, hydrogen and hydrogen peroxide being produced.[4]

**Water as a Catalyst.**—The presence of water has considerable influence on the course of some chemical reactions; thus an alcoholic solution of potassium acetate reacts with carbon dioxide, yielding a precipitate of potassium carbonate, a result which is in striking contrast with the interaction of acetic acid and potassium carbonate in aqueous solution. Also silver nitrate and hydrogen chloride fail to react in anhydrous benzene or ether. Many such precipitation and other reactions[5] fail in the absence of water.

Water-vapour is capable of functioning as a catalyst in many reactions. Attention has already been directed to the combustion of hydrogen (p. 61) and carbon monoxide (p. 85) in oxygen, the presence of small quantities of water being essential. Carbonyl sulphide, COS, will not combine either with oxygen or nitrous oxide when perfectly pure and free from water.[1] Thoroughly dry carbon dioxide is not reduced by dry carbon even at red heat, and no *visible* combustion of pure sugar charcoal is observed even at bright-red heat in oxygen, although carbon monoxide is being slowly produced.[2] Sulphur may be distilled in dry oxygen without visible combustion, and the same appears to be true for sodium and potassium.[3] Calcium is not oxidised by dry oxygen.[4] Boron and red and yellow phosphorus do not burn in the dried gas.[5] Indeed, amorphous phosphorus is not even converted to the red variety when heated to 278° C. in pure, dry nitrogen, although normally the conversion takes place with considerable violence just above 260° C.[6]

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[1] Ramsay, *Trans. Chem. Soc.*, 1907, 91, 931; Cameron and Ramsay, *ibid.*, 1907, 91, 1593; 1908, 93, 966, 992. Compare Rutherford and Royds, *Phil. Mag.*, 1908, 16, 812.

[2] Debierne, *Ann. Physique*, 1914, 2, 97; *Compt rend.*, 1909, 148, 703; Usher, *Jahrbuch Radioaktiv. Electronik*, 1911, 8, 323; Duane and Scheuer, *ibid.*, 1913, 156, 466; Kernbaum, *Compt. rend.*, 1909, 148, 705, Andréeff, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1342; Bergwitz, *Physikal Zeitsch.*, 1910, 11, 273.

[3] Kernbaum, *Compt. rend.*, 1909, 149, 273.

[4] Kernbaum, *ibid.*, 1910, 151, 319.

[5] Hughes, *Phil. Mag.*, 1893, 35, 531.

Water-vapour exerts a considerable influence upon the dissociation of nitrogen trioxide. The effect of prolonged drying of the liquid is apparently to reduce the number of $NO_2$ and NO molecules normally present by causing them to combine to $N_4O_6$ molecules. On vaporisation, these latter molecules dissociate to a mixture of $N_2O_3$, NO, and $NO_2$ molecules, the $N_2O_3$ not undergoing further dissociation.[7] Thus

$$N_4O_6 \rightleftharpoons N_2O_3 + NO + NO_2.$$

The activity of the halogens is greatly influenced by the presence of traces of water. Thus, dry chlorine does not attack copper, and dry hydrogen chloride does not unite with ammonia.[8] Although dry chlorine attacks mercury, mercurous chloride does not dissociate upon heating, when thoroughly dried. The same is true for ammonium chloride [8] at 350° C. and phosphorus pentachloride.

Hydrogen and chlorine do not explode in sunlight when dry [8]; only slow combination takes place. Similarly ammonium chloride and lime do not interact.[8]

Nitric oxide does not unite with perfectly dry oxygen. Experiments indicate that perfectly dry sulphur dioxide and oxygen will not unite in contact with platinised pumice,[9] whilst sulphur trioxide has no action on calcium oxide.[10]

On the other hand, selenium, tellurium, arsenic, antimony, and carbon disulphide appear to burn readily in dry oxygen.[11] Dry ozone is decomposed on warming, but may be prepared in the usual way from dry oxygen.[12] Iron yields its characteristic "tempering" colours when heated in dry air or oxygen.[13] Both lead nitrate and potassium chlorate decompose when dry.

Cyanogen burns and explodes with oxygen in the absence of water.[14]

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[1] Russell, *Trans. Chem. Soc.*, 1900, 77, 361.

[2] H. B. Baker, *Proc. Roy. Soc.*, 1888, 45, 1; *Phil Trans.*, 1888, [A], 179, 571; C. J. Baker, *Trans. Chem. Soc*, 1887, 51, 249

[3] Holt and Sims, *ibid.*, 1894, 65, 432.

[4] Erdmann and van der Smissen, *Annalen*, 1908, 361, 32

[5] The oxidation of the phosphorus is very slow. Russell, *Trans. Chem Soc*, 1903, 83, 1263; 1900, 77, 340.

[6] H. B. Baker, *loc. cit.*

[7] Jones, *Trans. Chem. Soc*, 1914, 105, 2310

[8] Baker, *Trans. Chem. Soc.*, 1894, 65, 611

[9] Russell, *loc. cit.*

[10] Baker, *Trans. Chem. Soc.*, 1894, 65, 432.

[11] H. B. Baker, *Phil. Trans.*, 1888, [A], 179, 571

[12] Shenstone and Cundall, *Trans. Chem. Soc.*, 1887, 51, 610; Baker, *ibid*, 1894, 65, 611.

[13] Friend, *J. Iron Steel Inst.*, 1909, II., 172.

[14] Dixon, Strange, and Graham, *Trans. Chem. Soc.*, 1896, 59, 759.

**Influence of Desiccation upon the Physical Properties of Substances.**—Liquids that have been thoroughly desiccated by exposure to phosphorus pentoxide for several years manifest a decided elevation in boiling-point, ranging in extent from 30° to 60° C. This is well illustrated by the following data :[1]

| Liquid. | Period of Drying. (Years.) | Original Boiling-point, ° C. | New Boiling-point, ° C. | Elevation. |
|---|---|---|---|---|
| Benzene . . | 8·5 | 80 | 106 | 26 |
| Bromine. . . | 8 | 63 | 118 | 55 |
| Carbon disulphide . | 28 | 49·5 | 80 | 30 |
| Carbon tetrachloride | 9 | 78 | $>$ 112 | 34 |
| Ethyl alcohol . . | 9 | 78·5 | 138 | 60 |
| Ethyl ether . . | 9 | 35 | 83 | 48 |
| Mercury . . . | 9 | 358 | 420–425 | 62 |

Similarly the melting-point of sulphur after nine years of desiccation has been found to rise from 112·5° to 117·5° C., and that of iodine under similar treatment from 114° to 116° C. The hypothesis that naturally suggests itself is that increased association takes place as desiccation becomes more perfect, and this appears to receive support from preliminary determinations of the surface tensions of the dried liquids.[2]

**Physiological Effect.**—Pure or distilled water, on account of its freedom from dissolved solids, has a tendency to cause the saline constituents to diffuse from living cells, and so exerts a decidedly harmful influence on healthy protoplasm.[3]

It is quite possible, however, that many cases of the supposedly harmful action of distilled water on living organisms are in reality due to minute traces of foreign metals, such as copper derived from the still in which the water was prepared.

**Dissociation of Steam.**—From physico-chemical considerations it is probable that even under ordinary conditions liquid water contains an exceedingly minute though definite proportion of uncombined hydrogen and oxygen in equilibrium with the compound molecules. This state of equilibrium is outside the scope of experimental detection unless disturbed in some way, as by the influence of ultra-violet light, when the decomposition may become appreciable.

It is more easily observed at higher temperature, because with rise of temperature the position of the equilibrium moves in favour of a higher proportion of dissociated molecules. In 1847[4] Grove noticed the formation of some free hydrogen and oxygen when platinum, heated almost to fusion, was dropped into water, the experiment being repeated by Deville[5] a little later, with an even more decisive result. The main difficulties in detecting the thermal dissociation are the smallness of its extent, and especially the tendency of the gases to recombine on cooling. The latter can be obviated by cooling the gases very rapidly; for example, by passing a current of steam over a white-hot platinum wire or over a gap between sparking electrodes [1] in such a manner that the gas is removed so rapidly from the heated area that a portion of the products fails to recombine. A similar effect was achieved by Deville [2] by means of his " hot and cold " tube, in which steam was passed through the space between an externally heated porcelain tube and a water-cooled inner silver tube; hydrogen and oxygen produced by dissociation at the hot surface become cooled below the temperature of rapid recombination by the inner cold surface. The difference in the velocity of diffusion of hydrogen and oxygen can also be applied (Deville) by passing steam through a heated unglazed tube when, on account of the more rapid passage of the hydrogen, an excess of oxygen is to be found in the vapour issuing from the tube.

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[1] Baker, *Trans Chem. Soc*, 1922, **121**, 568. See also Smits, *Zeitsch. physikal Chem.*, 1922, **100**, 477.

[2] Baker, *loc. cit.*

[3] Loeb, *Pflügers Archiv*, 1903, **97**, 394.

[4] Grove, *Phil. Mag*, 1847, [3], **31**, 20, 91.

[5] Deville, *Compt. rend.*, 1857, **45**, 857.

Löwenstein's [3] method consisted in passing a slow current of water-vapour through a tube heated to various temperatures, and containing a closed platinum vessel, P, attached to a manometer, M (fig. 45). The water-vapour dissociated, and hydrogen passed through the platinum, causing a rise in pressure, which became constant for any one temperature. Since platinum functions as a semipermeable membrane in that it is impermeable to oxygen and water-vapour, it was easy to calculate from the pressure registered by the manometer the extent of dissociation of the steam.

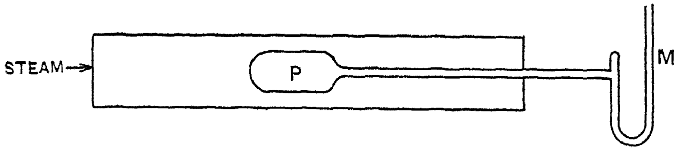

FIG. 45.—Lowenstein's apparatus for determining the dissociation of steam.

Holt [4] in his later experiments used a glass globe of 4 litres capacity containing a short length of platinum wire which was electrically heated. The globe was evacuated and then connected with a vessel containing water, the vapour from which passed into the globe and underwent partial dissociation in contact with the wire. When equilibrium was attained for the particular temperature chosen, the vessel was cooled, the gases pumped off and measured after the water-vapour had been frozen out. From these data the dissociation pressure was calculated.

Holt also endeavoured to determine the lowest temperature at which water-vapour appreciably decomposed in contact with heated platinum wire. Minute quantities of gas were collected at about 750° C. No doubt, had it not been for the solubility of the gases in the condensed vapour at the conclusion of the experiments, traces would have been detected at even lower temperatures.

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[1] Holt and Hopkinson, *Phil. Mag.*, 1908, [6], 16, 92; Chapman and Ledbury, *Trans. Chem. Soc.*, 1902, 81, 1301.

[2] Deville, *Compt. rend.*, 1857, 45, 857; 1863, 56, 195, 322.

[3] Lowenstein, *Zeitsch. physikal. Chem.*, 1906, 54, 715.

[4] Holt, *Phil. Mag.*, 1909, [6], 17, 715. See also Holt and Hopkinson, *ibid.*, 1908, 16, 92, Holt, *ibid.*, 1907, 13, 630.

Bjerrum[1] employed an explosion method and obtained the following results for 1 atmosphere pressure :

| | | | | | | |
|---|---|---|---|---|---|---|
| Temperature abs . . | 1705 | 2257 | 2642 | 2761 | 2834 | 2929 |
| Percentage dissociation . | 0·108 | 1·79 | 4·3 | 6·6 | 9·8 | 11·1 |

Nernst and Wartenberg have given several formulæ, based on thermo-dynamic considerations, whereby the percentage degree of dissociation, $x$, of steam at any temperature may be calculated. The first one[2] was used in a somewhat simplified form both by Langmuir[3] and by Holt,[4] namely :

$$\log \frac{2(100x)^3}{(2+x)(1-x)^2}=\mathrm{K}-\frac{25030}{\mathrm{T}}+2{\cdot}65 \log \frac{\mathrm{T}}{1000}-0{\cdot}00055(\mathrm{T}-1000).$$

By neglecting $x$ compared to 1 and dividing by 3,

$$\log x=k-\frac{8343}{\mathrm{T}}+0{\cdot}88 \log \frac{\mathrm{T}}{1000}-0{\cdot}00018(\mathrm{T}-1000),$$

where T is the absolute temperature. The value for $k$ given by Nernst and Wartenberg is 3·83. Calculated from the experimental data of Langmuir, $k=3{\cdot}79$ ; a slightly higher value is found by Holt, namely, 3·806, whilst Lowenstein's results yield the value, 3·80 (up to 1968° T). This latter may therefore be accepted as the most probable value for the equilibrium constant of water-vapour, oxygen, and hydrogen.

In the following table are given the percentage degrees of dissociation of water-vapour at temperatures ranging from 1000° to 3500° abs., and under pressures varying from 0·1 to 100 atmospheres.

## PERCENTAGE DEGREE OF DISSOCIATION OF WATER-VAPOUR AT VARIOUS TEMPERATURES AND PRESSURES.[5]

| Absolute Temperature. | 0·1 Atm. | 1·0 Atm. | 10 Atm. | 100 Atm. |
|---|---|---|---|---|
| 1000 | $0{\cdot}0_4556$ | $0{\cdot}0_4258$ | $0{\cdot}0_4120$ | $0{\cdot}0_5556$ |
| 1500 | 0·0433 | 0·0202 | 0·00935 | 0·00433 |
| 2000 | 1·25 | 0·582 | 0·270 | 0·125 |
| 2500 | 8·84 | 4·21 | 1·98 | 0·927 |
| 3000 | 28·4 | 14·4 | 7·04 | 3·33 |
| 3500 | 53·1 | 30·9 | 16·1 | 7·79 |

Steam is slightly decomposed when subjected to an electric discharge, hydrogen and oxygen being liberated, curiously enough, sometimes at one terminal and sometimes at the other. The nature of the spark appears to be the determining factor.[1] With long sparks the hydrogen appears at the negative and the oxygen at the positive pole ; with short sparks the positions are reversed, and the process is opposite to that taking place in the ordinary electrolysis of liquid water.

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[1] Bjerrum, *Zeitsch. physikal. Chem.*, 1912, 79, 513.

[2] See Nernst and Wartenberg, *Göttingen Nachrichten*, 1905. Two later formulæ were published, *Zeitsch. physikal. Chem.*, 1906, 56, 534.

[3] Langmuir, *J. Amer. Chem. Soc.*, 1906, 28, 1357.

[4] Holt, *Phil. Mag.*, 1909, [6], 17, 715.

[5] Taken from the summary given by Nernst, *Theoretische Chemie* (Stuttgart), 10th ed., 1921, p. 765.

**Steam as an Oxidising Agent.**—When a current of steam is made to pass over many substances, whether metals or non-metals, oxidation frequently takes place, particularly at elevated temperatures. Thus, at temperatures above 100° C. sulphur is both oxidised and reduced : [2]

$$2H_2O+3S=2H_2S+SO_2.$$

With phosphorus at 250° C :

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

When steam is allowed to impinge upon incandescent coke, hydrogen is liberated and oxides of carbon are formed. At relatively low temperatures, such as 500° to 600° C., the main products are hydrogen and carbon dioxide. Thus :

$$\text{(i)} \qquad C+2H_2O\rightleftharpoons CO_2+2H_2-18{,}900 \text{ calories.}$$

At 1000° C. and upwards a mixture of hydrogen and carbon monoxide—the so-called *water-gas*—is formed, the two gases being present in equal volumes. Thus :

$$\text{(ii)} \qquad C+H_2O\rightleftharpoons CO+H_2-29{,}100 \text{ calories.}$$

At temperatures intermediate between the foregoing a mixture of hydrogen and oxides of carbon is obtained, the percentage of carbon monoxide increasing with the temperature, that of the carbon dioxide decreasing.

From the equation

$$\text{(iii)} \qquad CO+H_2O\rightleftharpoons CO_2+H_2+10{,}200 \text{ calories}^3$$

it is evident that any variation in the pressure on the system as a whole would be without any influence upon the equilibrium, inasmuch as no change in volume is introduced by any movement of the equilibrium from right to left or in the reverse direction. Hence the value for K in the expression

$$\frac{CO+H_2O}{CO_2+H_2}=K \quad \text{or} \quad \frac{p_{CO}}{p_{CO_2}}=K\frac{p_{H_2}}{p_{H_2O}}$$

is independent of the pressure.

Since an increase in temperature tends to shift the state of equilibrium represented in equation (iii) from right to left, it follows that the value for K will rise. This has been experimentally confirmed for temperatures between 786° and 1405° C.,[4] the results being as follow :

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[1] J. J. Thomson, *Recent Researches in Electricity and Magnetism* (Clarendon Press, 1893), p. 559.

[2] See Lewis and Randall, *J. Amer Chem Soc.*, 1918, 40, 362 ; Randall and Bichowsky, *ibid.*, p. 368 ; Ruff and Graf, *Ber*, 1907, 40, 4199 ; Cross and Higgin, *Trans. Chem. Soc.*, 1879, 35, 249.

[3] This reaction begins at about 600° C., and at 900° C. some ten per cent. of the CO is oxidised to $CO_2$ (Naumann and Pistor, *Ber.*, 1885, 18, 2894). Buff and Hofmann (*J. Chem. Soc.*, 1860, 12, 282) discovered the fact that steam oxidises CO when induction sparks are passed through the mixed gases

[4] Hahn, *Zeitsch. physikal. Chem.*, 1902, 42, 705 ; 1903, 44, 513 ; 1904, 48, 735.

| Temperature, ° C. | $K=\frac{CO+H_2O}{CO_2+H_2}$. |
|---|---|
| 786 | 0·81 |
| 886 | 1·19 |
| 986 | 1·54 |
| 1086 | 1·95 |
| 1205 | 2·10 |
| 1405 | 2·49 |

In the commercial preparation of hydrogen, since carbon dioxide is more easily removed than the monoxide, the aim will clearly be to work at a low temperature and thus reduce the fraction $p_{co}/p_{co_2}$ to a minimum. For the production of water-gas, on the other hand, with a maximum combustible efficiency, the percentage of carbon dioxide must be reduced to a minimum, and high temperatures are essential.

The reaction between steam and carbon is facilitated by the presence of certain inorganic salts, such as the carbonates of sodium and potassium, which function as catalysts.[1]

Steam reacts slowly with silicon at red heat, hydrogen being evolved, whilst the residue consists of silica.

When electrolytic iron foil is heated in steam to about 330° C., tarnishing begins to take place. At 400° C. a small but measurable quantity of hydrogen is formed, and the velocity of the reaction increases rapidly with further rise of temperature The reaction appears to take place in three stages, involving [2]

1. Dissociation of the steam,

$$H_2O \rightleftharpoons H_2+O.$$

2. Formation of ferrous oxide,

$$Fe+O \rightleftharpoons FeO.$$

3 Oxidation to ferroso-ferric oxide,

$$3FeO+O \rightleftharpoons Fe_3O_4.$$

For ordinary iron shavings, the lowest temperature at which hydrogen is evolved is about 300° C., and the optimum yield is obtained at 800° C.[3]

If the reaction is allowed to take place in an enclosed space, it does not proceed to completion. Equilibrium is set up, and the reaction obeys the law of Mass Action.[4] The initial and final stages of the equilibrium may be represented as follows :

$$3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2.$$

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[1] Taylor and Neville, *J. Amer. Chem. Soc.*, 1921, 43, 2055.

[2] Friend, *J. West Scotland Iron Steel Inst.*, 1910, 17, 66 ; *J. Iron Steel Inst.*, 1909, II., 172 ; see this series, Vol. IX., Part II., p. 48.

[3] Lettermann, *Chem. Zentr.*, 1896, I., 952.

[4] This was first proved by Deville (*Annalen*, 1871, 157, 71 ; *Compt. rend.*, 1870, 70, 1105, 1201 ; 1870, 71, 30) and Chaudron (*Compt. rend*, 1914, 159, 237), and subsequently confirmed by Preuner (*Zeitsch physikal. Chem.*, 1904, 47, 385), and Schreiner and Grimnes, *Zeitsch anorg Chem.*, 1920, 110, 311. See also L. Wohler and Prager, *Zeitsch. Elektrochem.*, 1917, 23, 199.

Designating the pressure of water-vapour as $p_1$ when equilibrium has been reached, and the hydrogen pressure as $p_2$, Preuner obtained the following mean values for the ratio $p_1/p_2$:

| Temperature, ° C. | $p_1/p_2$. |
|---|---|
| 900 | 0·69 |
| 1025 | 0·78 |
| 1150 | 0·86 |

The superficial oxidation of iron with steam is used technically as a means of protecting the metal against corrosion. This is the principle of the Bower-Barff process.

When steam is passed over molybdenum at high temperatures, hydrogen and molybdenum dioxide are formed. The reaction is reversible, and has been studied from the equilibrium point of view over the temperature range 700° to 1100° C.

$$2H_2O+Mo \rightleftharpoons MoO_2+2H_2.$$

It is found that the values for the equilibrium constant,[1] namely,

$$K=p_{H_2O}/p_{H_2},$$

obtained by the oxidation of the metal agrees closely with that from reduction of the dioxide in hydrogen[2] Steam has no action on copper or cuprous oxide, but cupric oxide dissociates in steam yielding cuprous oxide. Magnesium readily ignites in steam yielding magnesium oxide and free hydrogen. At red heat nickel slowly decomposes steam, and cobalt becomes superficially oxidised. Tin decomposes steam at red heat yielding the dioxide, $SnO_2$.

Metallic sulphides are decomposed by steam at high temperatures. At incipient red heat ferrous sulphide yields magnetic oxide as follows:[3]

$$3FeS+4H_2O=Fe_3O_4+3H_2S+H_2.$$

At higher temperatures sulphur dioxide and sulphur are produced.

Lead sulphide at bright red heat yields the free metal:[3]

$$3PbS+2H_2O=3Pb+2H_2S+SO_2$$
$$2H_2S+SO_2=2H_2O+3S,$$

and, probably, to a small extent,

$$PbS+2SO_2=PbSO_4+2S,$$

for a little lead sulphate is generally produced simultaneously. At white heat cuprous sulphide is converted into metallic copper:[3]

$$Cu_2S+2H_2O=2Cu+SO_2+2H_2.$$

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[1] Chaudron, *Compt rend.*, 1920, 170, 182.

[2] The action of steam on tungsten has been studied in a similar manner by von Liempt, *Zeitsch. anorg. Chem.*, 1921, 120, 267.

[3] Gautier, *Compt. rend.*, 1906, 142, 1465.

**Detection and Estimation.**—The presence of water in a gas is easily recognised by the increase in weight suffered by desiccating agents, such as phosphoric oxide, sulphuric acid, anhydrous calcium chloride, and anhydrous copper sulphate when exposed in the gas. In neutral organic liquids, *e.g.* ether, chloroform, acetone, etc., calcium carbide supplies an easily applicable reagent, which can also be extended to the estimation of water of crystallisation, the volume of acetylene liberated being proportional to the water present.[1] On account of its change in colour on hydration, anhydrous copper sulphate can be used to detect the presence of moisture in organic liquids; potassium lead iodide has also been recommended[2] as an especially sensitive indicator in such cases, the colour of strips of paper coated with this changing from white to yellow when immersed in a liquid containing even minute traces of water.[3]

The estimation of water in a substance is almost invariably effected by drying; gases are passed through the desiccating agent, and the increase in the weight of the latter is recorded. Solids are placed in a confined space also enclosing the desiccating agent, or may even be merely heated in the open atmosphere, the amount of moisture being measured in either case by the loss in weight.[3]

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[1] Masson, *Trans. Chem. Soc*, 1910, 97, 851.

[2] Biltz, *Ber.*, 1907, 40, 2182.

[3] See Huntly and Coste, *J. Soc Chem. Ind*, 1913, 32, 62. For the special methods of "hygrometry" see Chap. VI.

# CHAPTER X.

# COMPOSITION AND MOLECULAR COMPLEXITY OF WATER.

## COMPOSITION OF WATER.

WATER was, according to Aristotelean philosophy, an elementary substance, representative of the property of moistness and liquidity. In 1781 Cavendish showed that water could be obtained by passing electric sparks between terminals surrounded by a mixture of air and hydrogen, and satisfied himself that the liquid obtained under these conditions was not always acid. His experiments indicated that the proportions by volume of hydrogen and oxygen used up in producing water were approximately as 2 : 1.

In 1783 Lavoisier allowed water to drop into a gunbarrel heated to redness, and, by collecting the hydrogen and undecomposed steam, came to the conclusion that water contains hydrogen and oxygen in the volumetric proportions of 1·9 to 1.

Monge in 1783[1] adopted the then new principle of measuring the volumes of the reacting gases and calculating by means of the densities of the gases from the volume ratio to the mass ratio. The value obtained for the former ratio was approximately 2 : 1, but his data for the relative densities of the gases were far from accurate.

From the idea, originally suggested by Priestley, that the percentage of oxygen in the atmosphere varied considerably, and that the measurement of the proportion of oxygen was equivalent to a determination of the "goodness" of the air, the apparatus used for the determination of oxygen was termed a "*eudiometer.*" The first "explosion eudiometer" was that of Volta.[2] Since that time it has become customary to apply the term "eudiometer" to all modifications of gas analysis apparatus, the principle of which is based on the explosion of gas in a graduated vessel or tube.

Another investigation of historical importance was that of Berzelius and Dulong[3] in 1820; their method was improved by Dumas[4] in 1843, who estimated the mass ratio of hydrogen to oxygen by passing purified hydrogen over heated copper oxide; the weight of water produced was found by direct weighing, that of the oxygen by the loss in weight of the copper oxide and that of the hydrogen by difference. Dumas' mean result was oxygen : hydrogen=7 98 : 1, and until 1888 this was the most reliable work done.

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[1] Monge, *Mem. Acad. Sci. Paris*, 1783, p. 78.

[2] Volta, *Annali di Chimica*, 1790, **1**, 171, 1791, **2**, 261; **3**, 36.

[3] Berzelius and Dulong, *Ann. Chim. Phys.*, 1820, **15**, 386.

[4] Dumas, *ibid.*, 1843, 8, 189.

These early experiments are of importance as marking distinct advances in our knowledge of the methods for demonstrating the composition of compounds. However, in common with Lavoisier's proof (1783) of the composition of water by decomposing steam with heated iron, the methods have been improved both by modification and substitution. Thus the method of Dumas is not capable of such accuracy as was at one time believed, whilst the standard investigations of Scott, Morley, and Burt and Edgar may be regarded as a later stage of development of the researches of Cavendish and of Monge.[1]

The ratio of the amounts of hydrogen and oxygen in water is a number which in the past was perhaps of even greater importance than now, because hydrogen is no longer generally accepted as the standard for atomic weights. With hydrogen as standard, each increase in the accuracy with which the above ratio was determined involved the alteration of the atomic weight of a considerable number of elements, because hydrogen is not suited to direct comparison with many other elements. The majority of modern determinations of the composition of water have been made by synthetic experiments, but by so many different principles and with such a variety of forms of apparatus as to justify absolute confidence in the acceptance of a value between 8 : 1·0065 and 8 : 1·0085 for the ratio of the quantities of the two constituents; the generally accepted value is 8 : 1·008. The exemplary investigations of Morley and of Scott have been of great value in providing trustworthy figures. Morley, by weighing hydrogen in the adsorbed condition in palladium and oxygen in two large glass globes, and subsequently allowing these to combine in a special glass combustion apparatus in which the water produced was subsequently weighed, obtained the ratio $O : 2H = 7{\cdot}9396$ and $H_2O : 2H = 8{\cdot}9392$. Also by exploding mixtures of the two gases and measuring the residual volume of the excess of either, he arrived at the figures 1 : 2·00269 as the relative volumes entering into combination, and then making use of the relative density of the pure gases 15·9002 : 1 which he had determined with extreme accuracy, obtained by calculation a second independent value 7·9395 : 1 for the mass ratio $O : 2H$.[2]

The method of Scott somewhat resembled the latter procedure of Morley. Hydrogen and oxygen of a high degree of purity were exploded together, and the relative volumes disappearing were found to be in the proportion 1 : 2·00245 at 14° C. or 1 : 2 00285 at 0° C. Lord Rayleigh's earlier determination of the relative densities of the gases had yielded the figure 15 882 : 1 (or 15·900 : 1 corrected to 0° C.), and using this to convert his volume ratio into a mass ratio, Scott arrived at the value $O : 2H = 7{\cdot}931 : 1$.[3]

The accuracy attained by these two investigators has received strong confirmation by a recent very careful redetermination of the volume ratio, the value found being 1 : 2·00288 at 0° C. and 760 mm.[4]

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[1] For other important investigations on the composition of water, see Cooke and Richards, *Amer. Chem. J.*, 1888, 10, 191; Keiser, *ibid.*, 1898, 20, 733; Erdmann and Marchand, *Ann. Chim. Phys.*, 1843, [3], 8, 212; Noyes, *Amer. Chem. J.*, 1889, 11, 441; 1891, 13, 354; Leduc, *Compt. rend.*, 1892, 115, 41.

[2] Morley, *Zeitsch. physikal. Chem*, 1896, 20, 68, 242, 417; *Amer Chem. J*, 1888, 10, 21; 1895, 17, 267. See also Noyes and Johnson, *J. Amer. Chem. Soc*, 1916, 38, 1017.

[3] Scott, *Phil. Trans.*, 1893, 184, 43; Rayleigh, *Chem. News*, 1892, 65, 200.

[4] Burt and Edgar, *Phil. Trans.*, 1916, [A], 216, 393.

To sum up, therefore, water contains [1]

(*a*) 16 parts of oxygen to $1{\cdot}00762 \times 2$ parts of hydrogen ;

or (*b*) 1 volume of oxygen to 2·00288 volumes of hydrogen.

## THE MOLECULAR COMPLEXITY OF WATER.

**1. Ice.**—From a study of X-ray photographs of ice, Dennison [2] concludes that the molecular formula for ordinary ice is $(H_2O)_2$. The general opinion of chemists, however, based on surface tension and other physical measurements of liquid water, favours the view that ice is more complex than this, and consists of molecules none of which are less complex than trihydrol, $(H_2O)_3$.

**2. Liquid Water.**—The great importance of liquid water as a solvent renders a study of its molecular complexity one of singular interest.

That water in the liquid state is associated to an appreciable extent has been recognised for many years, although it is not even yet possible to determine the quantitative extent of association with any accuracy.

Thus Brühl [3] concluded, as the result of an investigation of the molecular refractivity of water, that water is an unsaturated compound containing tetravalent oxygen. This view is in entire harmony with the results described below, and supplies an explanation for the readiness of water to form additive compounds, especially with salts, in which case the added water is commonly known as water of crystallisation.[4]

As a general rule, it may be said that the effect of molecular association of a liquid is to reduce its vapour pressure. Van der Waals [5] has shown, from theoretical considerations, that

$$\log p_c - \log p = k\frac{T_c - T}{T}$$

where $p$ is the vapour pressure of a liquid at the absolute temperature T, $p_c$ and $T_c$ the critical pressure and temperature respectively, and $k$ a constant within certain limits. Now Young [6] has found that for all non-associated liquids, the value for $k$ approximates to 3, the actual mean value for sixteen liquids investigated by him being 3·06.[7] Water, however, gives the value 3·20 to 3·24, indicative of appreciable association.

Since association reduces the vapour pressure of a liquid, it follows that the boiling-point will be raised simultaneously. Now van't Hoff [8] has shown that the boiling-point is proportional to the molecular volume, and calculates that for the simple molecule the boiling-point of water under atmospheric pressure should be 65° abs. The fact that the boiling-point is actually 373° abs. clearly indicates appreciable association.

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[1] For full details of modern determinations of the composition of water and the atomic weight of hydrogen, see this series, Vol II, Chap. II

[2] Dennison, *Chem. News*, 1921, **122**, 54; using Hull's method, *Phys Review*, 1917, 9, 85.

[3] Bruhl, *Ber.*, 1895, **28**, 2866.

[4] Compare Rosenstiehl, *Compt. rend.*, 1911, **152**, 598

[5] Van der Waals, *Kontinuitat des gasförmigen und flussigen Zustandes* (Leipsig), 1st ed., 1881. See also Nernst, *Theoretische Chemie* (Stuttgart), 10th ed., 1921, p. 247.

[6] Young, *Phil. Mag.*, 1892, [5], **34**, 507.

[7] See Ramsay, *Proc. Roy. Soc.*, 1894, **56**, 174.

[8] van't Hoff, *Lectures on Theoretical and Physical Chemistry*, translated by Lehfeldt (Arnold, 1899), Part III., p. 51.

When the boiling-points of the hydrides of sulphur, selenium, and tellurium are compared,[1] it is evident that the boiling-point rises steadily with the molecular weight.

| Substance . . . | $H_2S$ | $H_2Se$ | $H_2Te$ | $H_2O$ |
|---|---|---|---|---|
| Boiling-point, ° C. . | −62 | −42 | 0 | +100. |

Water, therefore, if it conforms to the general rule, must have a molecular weight greater than that of tellurium hydride, viz. 129·5. This suggests very appreciable association.

Walden[2] has directed attention to another fact of a similar nature. Methyl sulphide boils at a temperature 60 degrees higher than methyl ether, and ethyl sulphide 56 degrees higher than ethyl ether. Thus

| | Boiling-point | | Boiling-point. |
|---|---|---|---|
| $(CH_4)_2S$ . . | 37° C. | $(C_2H_5)_2S$ . . | 91° C. |
| $(CH_4)_2O$ . . | −23 | $(C_2H_5)O$ . . | 35 |
| Difference . | 60 | Difference . | 56. |

Hence the replacement of oxygen by sulphur raises the boiling-point on the average by about 59 degrees. Now, applying this rule to water and hydrogen sulphide, since the boiling-point of the latter is −61° C. that of water should be 59 degrees lower, namely, −120° C. The fact that the boiling-point is actually +100° C. shows that considerable association exists at the boiling-point. Further evidence of the association of water at the boiling-point is afforded by an examination of its latent heat of evaporation. Trouton's Law,[3] usually expressed in mathematical form, is

$$Ml/T = \text{constant},$$

where M is the molecular weight, T the absolute temperature of the boiling-point under atmospheric pressure, and $l$ the latent heat per gram.

Now Walden[4] concludes, as the result of a large number of measurements of normal substances, that the mean value to be assigned to the constant in the case of non-associated liquids is 20·7. If the observed value is appreciably higher than this, association in the liquid is to be presumed. For water the value 25·9 is found, which again confirms the view that water is associated at the boiling-point.

Evidence of the molecular complexity of water is also afforded by the results of viscosity measurements. Experiment shows that, for non-associated liquids of analogous composition,

$$\frac{\eta}{\mathrm{Mv}} \times 10^6 = \text{constant},$$

where $\eta$ is the viscosity coefficient and Mv the molecular volume.[5]

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[1] Vernon, *Chem. News*, 1891, 64, 54

[2] Walden, *Zeitsch. physikal. Chem.*, 1906, 55, 683.

[3] See this series, Vol. I., 3rd ed., p. 157.

[4] Walden, *Zeitsch. physikal. Chem*, 1909, 65, 129, 257, 547.

[5] Dunstan and Wilson, *Trans. Chem. Soc.*, 1907, 91, 83; Dunstan, *Zeitsch. physikal. Chem*, 1905, 51, 732; Dunstan and Thole, *Proc. Chem. Soc.*, 1907, 23, 19.

For the majority of substances the value for the constant ranges from 25 to about 70. In the case of associated liquids, however, the value of the expression is greatly increased. For water it is more than twelve times as great as for the alkyl chlorides—suggestive of very appreciable association.

In 1855 Kopp[1] showed that the molecular volume[2] of a liquid may be regarded as an additive property, being the sum of the atomic volumes of the constituent elements—with certain reservations.[3] The observed molecular volume for water, however, is larger than that calculated on an assumption of a molecular weight of 18—indicative of abnormality.

From thermo-chemical considerations Thomsen[4] was led to infer the presence of polymerised molecules in water, because the heat exchange during the hydration of certain salts could be explained most satisfactorily on the assumption that water entered into combination in the form of double molecules, $(H_2O)_2$.

All the foregoing methods, however, are qualitative in character.

A useful method of determining the quantitative molecular complexity of a pure liquid lies in measuring its surface tension and calculating the molecular weight in accordance with the method explained in Volume I. (3rd ed., 1919, p. 154) from the equation

$$\sigma(M'v)^{\frac{2}{3}}=k(\tau-d),$$

where $\sigma$ represents the surface tension, $M'$ the molecular weight, $v$ the specific volume, and $k$ a constant, the mean value for which has been determined as 2·12. $\tau$ is the temperature measured downwards from the critical temperature at which the surface tension has been measured, and $d$ has a value approximating to 6. The *degree of association*, $x$, is given, in the case of water, by the expression

$$x=M'/M=M'/18,$$

assuming monohydrol or $H_2O$ to be the normal unassociated molecule, M.

The values obtained for $x$ at temperatures ranging from 0 to 120° C., as given by Ramsay and Shields, are detailed in the fifth column of the table on p. 299. It will be observed that at low temperatures the water appears to approximate to the tetrahydrol $(H_2O)_4$ molecule. As the temperature rises, the mean molecular weight falls owing to increasing depolymerisation.

It has already been mentioned, however, that the values for the surface tension as determined by Ramsay and Shields are more than 2 per cent. too low in consequence of a systematic error throughout the series. Assuming the above relationship between $\sigma$ and M to be strictly true, it follows that the degree of association of the water is lower than that calculated.

Another method of calculating the molecular complexity from surface tension is that given by Dutoit and Mojoiu,[5] who employ the formula

$$M'=0{\cdot}6T(4{\cdot}8-\log p)/a^2,$$

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[1] Kopp, *Annalen*, 1855, 96, 153, 303

[2] Molecular weight divided by density.

[3] See Horstmann, *Ber.*, 1887, 20, 766; Traube, *Annalen*, 1896, 290, 43, 89, 410; *Ber.*, 1895, 28, 410, 2722, 2728, 2924, 3292, 3924; 1896, 29, 1203, 2732; D. Berthelot, *Compt. rend.*, 1899, 128, 606

[4] Thomsen, *Ber.*, 1885, 18, 1088.

[5] Dutoit and Mojoiu, *J. Chim. phys.*, 1909, 7, 187.

where $a^2$ is the *specific cohesion*, defined by $a^2 = hr$, $h$ being the height to which a liquid ascends in a capillary tube of radius $r$, and $p$ the vapour pressure, which, however, must not exceed 2 atmospheres. This latter restriction places an upper limit upon the temperature and prevents the formula from being used to determine the molecular aggregation of water at the critical point. The degrees of association, $x_1$, as calculated by this formula at various temperatures, are given in the following table, together with those ($x_2$) calculated by Ramsay and Shields, and also ($x_3$) by the Ramsay and Rose Innes formula,

$$x_3^{\frac{2}{3}} = \frac{2{\cdot}12}{k}(1 + at).$$

It will be observed that both $x_1$ and $x_3$ are very much less than $x_2$.

## DEGREE OF ASSOCIATION OF WATER.

| Temperature, ° C. | Specific Cohesion, $a^2$. | Vapour Pressure, mm. | $x_1$ (Dutoit and Mojoiu). | $x_2$ (Ramsay and Shields). | $x_3$ (Ramsay and Rose Innes). |
|---|---|---|---|---|---|
| 0 | 14·92 | 4·58 | 2·52 | 3·81 | 1·71 |
| 20 | 14·41 | 17·4 | 2·41 | 3·55 | 1·64 |
| 40 | 13·86 | 55 | 2·30 | 3·18 | 1·58 |
| 60 | 13·31 | 149 | 2·18 | 3·00 | 1·52 |
| 80 | 12·75 | 355 | 2·07 | 2·83 | 1·46 |
| 100 | 11·13 | 760 | 1·96 | 2·66 | 1·40 |
| 120 | 11·50 | 1491 | 1·85 | 2·47 | 1·35 |

The very serious divergence between the values for $x_1$, $x_2$, and $x_3$ calls for explanation. Attention has been very usefully directed by Dutoit and Mojoiu to the fact that molecular weights, as determined by surface tension phenomena, are most probably, in the case of associated liquids, only the particular molecular weights of the surface layers of the liquids. If the liquid is not associated, there will, of course, be no difference between the bulk and the surface, and the molecular weights calculated from the above formulæ may be expected to be correct. But where association takes place, it is highly improbable that the surface layers will possess the same state of aggregation as the interior. The probability is that the association will be accentuated in the surface, so that the calculated molecular weights will be too high.

The only conclusion that can be safely drawn from the above data is that water at all temperatures between 0° and 120° C. manifests an appreciable degree of association.

Walden [1] has adapted Trouton's Rule to a quantitative study of the molecular complexity of substances at the melting-point. Examination of a considerable number of normal, unassociated liquids shows that the expression

$$\mathrm{M}l_m/\mathrm{T}_m = 13{\cdot}5$$

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[1] Walden, *Zeitsch. Elektrochem.*, 1908, 14, 715.

may be regarded as generally true, M being the molecular weight, $l_m$ the latent heat of fusion, and $T_m$ the melting-point on the absolute scale. In the case of water, $l_m=79{\cdot}7$, $T_m=273$, whence $M=46{\cdot}2$, the degree of association, $x$, being $46{\cdot}2/18=2{\cdot}57$. This result agrees extremely well with that calculated by the method of Dutoit and Mojoiu at 0° C.

From a study of the depression of the freezing-point of various solvents on addition of water, the mean degree of association of the latter has been determined as follows: [1]

### MOLECULAR WEIGHT AND DEGREE OF ASSOCIATION OF WATER. (Oddo.)

| Solvent. | Molecular Weight | Mean Degree of Association |
|---|---|---|
| Phenol . . . . | 21 2 | 1·18 |
| *p*-Toluidine . . . | 33·4 to 38·8 | 2 00 |
| Chloracetic acid . . | 21·1 to 29·1 | 1·40 |
| Cyanamide . . . | 26·1 to 33·0 | 1·64 |
| Acetic acid . . . | 22·3 to 39·9 | 1·73 |

**3. Molecular Association at the Critical Point.**—The formulæ already considered cannot be applied to determine the molecular aggregation of water at the critical point. To meet this difficulty Guye [2] has calculated that

$$\frac{M^1}{28{\cdot}87}=\frac{1146d_cT_c}{P_c(T_c+1070)}$$

where $d_c$ is the critical density, that is, the mass in grams of 1 c.c. of a substance at the critical point. Unfortunately the usefulness of this formula is marred by the difficulty of determining the value for $d_c$ with accuracy.

In the case of water the results given on p. 301 are obtained according to the values assigned to the critical constants.

The foregoing results exhibit considerable variation, the degree of association ranging from 0·77 to 1·47 according to the values chosen for the critical constants. The final result in the table is, however, probably the most correct, the critical density having been calculated from the equation on p. 279, using the most accurate figures available (namely, those of Holborn and Baumann) for the critical temperature. The result clearly indicates that water at this temperature is not appreciably associated.

On the other hand, it should be mentioned that other methods of calculation do not lead to quite the same result. Thus Guye [3] has shown that

$$T_c/p_c=F'MR$$

---

[1] Oddo, *Gazzetta*, 1916, 46, i., 172.

[2] Guye, *Ann. Chim. Phys.*, 1892, [6], 26, 97

[3] Guye, *ibid.*, 1890, [6], 21, 206, 211

where M is the molecular weight, R the specific refraction, and F′ a constant. As the mean of a large number of calculations, Guye arrives at the value 1·8 for 1/F′. In the case of water, however, 1/F′ is of the order of 1·1, indicating association.

| Critical Pressure, $p_c$. | Critical Temperature, $T_c$ (abs.) | Critical Density, $d_c$. | Molecular Weight, $M^1$. | Degree of Association, $x$ |
|---|---|---|---|---|
| 200·5 [1] | 273+365 [1] | 0·429 [2] | 26·4 | 1·47 |
| 194·6 [3] | 273+364·3 [3] | 0·208 [3] | 13·2 | 0·77 |
| 217·5 [4] | 273+374·3 [4] | 0·329 [5] | 18·9 | 1·05 |
| 217·5 [4] | 273+374·3 [4] | 0·322 [6] | 18·5 | 1·03 |

**4. Water-Vapour.**—The problem of the molecular state of water vapour is one of considerable dispute. The vapour density of water vapour corresponds *approximately* to a molecular weight of 18.

As early as 1880 attention had been directed by Winkelmann [7] to the fact that the density of water-vapour in equilibrium with liquid water is higher than that calculated on the assumption of a molecular weight of 18·016. If the vapour conforms to the requirements of Avogadro's hypothesis, the obvious inference is that a small portion is associated.

In 1908 Kornatz [8] published the results of a further series of determinations of the vapour density of water at various temperatures, which supported earlier work.

Bose [9] showed that if water-vapour be regarded as an equilibrium mixture of many hydrol molecules with a few dihydrol, thus

$$2H_2O \rightleftharpoons (H_2O)_2,$$

then the percentage of the latter could be calculated from the data given by Kornatz by means of the expression

$$d^1=d-\frac{k^1}{p}\left(\sqrt{1+\frac{dp}{k^1}}-1\right)$$

where $p$ is the observed vapour pressure, $d^1$ the observed vapour density, and $d$ the density of pure dihydrol vapour, that of air being taken as unity. $d$ was taken as numerically equal to 1·2432, and the constant $k^1$ was calculated from the equation

$$\log k^1=-4857{\cdot}1/T+21455.$$

The percentage association is as follows :

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[1] Cailletet and Collardeau, *Compt. rend.*, 1888, 106, 1489.

[2] Nadejdine, *Wied. Annalen, Beiblätter*, 1885, 9, 721.

[3] Battelli, *Mem. R. Accad. Torino*, 1890, [2], 41.

[4] Holborn and Baumann, *Ann. Physik*, 1910, 31, 945.

[5] Davis, *Phys. Review*, 1909, 29, 81.

[6] The value for the critical density 0·329 given by Davis (reference 8) is based on the assumption of a critical temperature of 365° C. (see p. 279). To be logical, it should be calculated for the above purpose assuming a critical temperature of 374° C. Its value then becomes 0·322.

[7] Winkelmann, *Wied. Annalen*, 1880, 9, 208.

[8] Kornatz, *Dissertation*, Konigsberg, 1908.

[9] Bose, *Zeitsch. Elektrochem.*, 1908, 14, 269.

## PERCENTAGE ASSOCIATION OF WATER-VAPOUR.

| Temperature, ° C | Vapour Pressure, mm. | Per cent. associated to $(H_2O)_2$ Molecules |
|---|---|---|
| 0 | 4·579 | 6·6 |
| 50 | 92·17 | 8·2 |
| 100 | 760·00 | 8·9 |
| 150 | 3581 | 9·0 |
| 200 | 11688 | 8·7 |

The rise in vapour pressure accompanying increased temperature appears to counterbalance the dissociating influence of the latter, with the result that the extent of polymerisation remains fairly constant over a wide range.

Oddo,[1] in 1915, was led to similar conclusions as to the existence of an equilibrium mixture of mono- and di-hydrol molecules in water-vapour, but concluded that at 32° C. the amount of association is *nil*, the molecular weight of water-vapour corresponding exactly to 18·016. With rise of temperature association takes place, reaching the high value of 41·41 per cent. at 270° C. Fall of temperature below 32° C. is accompanied by diminution of the molecular weight in consequence of ionic dissociation.

As Kendall[3] has pointed out, however, the weak point in all these calculations lies in the assumption that saturated vapours follow the gas laws with exactness, more particularly Avogadro's Law. Such is most probably not the case. Whilst, therefore, water molecules may be slightly associated in the vapour phase, the present data do not justify our arriving at any other conclusion than that the extent of such association is probably small.

Such a conclusion, be it remarked, is nevertheless quite in harmony with the conclusion previously drawn that liquid water is appreciably associated (see p. 300), for, as Guye[3] has emphasised, "it is sufficient for the polymerisation in the gaseous state to be of the order of 1/10,000 for it to be appreciable in the liquid phase."

## THE CONSTITUTION OF WATER.

The problem now arises as to the constitution to be assigned to water. The results of the surface tension measurements clearly indicate that water is associated, but the extent of association cannot be calculated from the mean value alone. Thus, for example, if the mean degree of association is 2·5 at 0° C., taking by way of illustration the figure arrived at by Dutoit and Mojoiu, then, on the assumption that only two forms of water are present,[4] the equilibrium may be represented by

$$n(H_2O)_x \rightleftharpoons m(H_2O)_y.$$

---

[1] Oddo, *Gazzetta*, 1915, 45, i., 319 See also Mostovitsch, *J. Russ. Phys. Chem Soc.*, 1915, 47, 1144.

[2] Kendall, *J. Amer. Chem. Soc.*, 1920, 42, 2477; *Chem. News*, 1921, 122, 30; also Menzies, *J Amer. Chem. Soc*, 1921, 43, 851

[3] Guye, *Trans Faraday Soc*, 1910, 6, 84.

[4] The possibility that a molecule $(H_2O)_{2\cdot5}$ can exist is regarded as too remote.

If $x$ and $y$ are 2 and 3 respectively, clearly $n=m$, and 50 per cent. of dihydrol is in equilibrium with 50 per cent. of trihydrol. If, however, $y>3$, the value for $m$ must fall if $x$ remains constant. Unless, therefore, the numerical values to be assigned to $x$ and $y$ are known, those for $n$ and $m$ cannot be deduced, and *vice versa*. Further, the system becomes even more complicated if more than two forms of water are present.

The irregularities in the specific heats and densities of water at various temperatures, particularly the contraction observed when water is warmed from 0° to 4° C., led Rontgen[1] to suggest in 1892 that liquid water is a mixture of two sets of molecules in equilibrium, namely, ice molecules and water molecules. Thus:

$$(H_2O)_{\text{ice}} \rightleftharpoons (H_2O)_{\text{water}}.$$

The former were presumed to have a more complex structure but to be less dense than the latter. Hence, when water at 0° C. is warmed, the equilibrium at 0° is disturbed in the direction of left to right, some ice molecules melting to the more dense water molecules, and the contraction thereby resulting more than counteracts the normal thermal expansion of the liquid with rise of temperature.

This idea has been further developed by Sutherland,[2] who concludes that ordinary water vapour is monohydrol, $H_2O$; liquid water is an equilibrium mixture of trihydrol, $(H_2O)_3$, and dihydrol, $(H_2O)_2$; whilst ice consists entirely of trihydrol. The high value found for the latent heat of fusion of ice thus receives explanation, for it is not due merely to the heat absorption consequent upon physical change of solid to liquid; it is enhanced by the heat required to effect the simultaneous dissociation or depolymerisation of a large proportion of trihydrol molecules to the dihydrol form, as indicated by the thermal equation which Sutherland writes as:

$$3(H_2O)_2 \rightleftharpoons 2(H_2O)_3 + 6 \times 18 \times 177 \text{ calories.}$$

A similar explanation may be offered for the high values observed for the latent heat of steam. Thus, the thermal dissociation of dihydrol molecules is accompanied by an absorption of $189 \times 18 \times 2$ calories, or, expressed as an equation:

$$2H_2O \rightleftharpoons (H_2O)_2 + 2 \times 18 \times 189 \text{ calories.}$$

For dihydrol and trihydrol Sutherland calculates the following physical data (p. 304).

According to Sutherland, the percentage amount of trihydrol in water at any temperature is given by the equation:

$$37{\cdot}5(\tfrac{1}{2}+q),$$

where $q$ is defined as equal to

$$\frac{0{\cdot}8222}{1+0{\cdot}010627t}-0{\cdot}3207.$$

---

[1] Rontgen, *Wied. Annalen*, 1892, 45, 91. See also Piccard, *Compt. rend.*, 1912, 155, 1497; Chéneveau, *ibid.*, 1913, 156, 1972; Duclaux, *ibid.*, 1911, 152, 1387.

[2] Sutherland, *Phil. Mag.*, 1900, [5], 50, 460. See also Hudson, *Phys. Review*, 1905, 21, 16.

From these equations the following data have been calculated :

| Temperature, °C. | 0 | 20 | 40 | 60 | 80 | 100 |
|---|---|---|---|---|---|---|
| $q$ | 0·5 | 0·357 | 0·256 | 0·181 | 0·123 | 0·08 |
| Percentage of trihydrol | 37·5 | 32·1 | 28·4 | 25·5 | 23·4 | 21·7 |

## PHYSICAL PROPERTIES OF DIHYDROL AND TRIHYDROL (SUTHERLAND, 1900).

| | Dihydrol $(H_2O)_2$ | Trihydrol $(H_2O)_3$. |
|---|---|---|
| Density at 0° C. | 1·08942 | 0·88 |
| Compressibility per atmosphere at 0° C. | 0·000016 | 0·000010 ? |
| Surface tension at 0° C. | 78·3 | 73·32 |
| Critical temperature | 368° C. | 538° C. |
| Specific heat at 0° C. | 0·8 calorie | 0·6 calorie |
| Latent heat of fusion | .. | 16 calories |
| Latent heat of evaporation at 100° C. | 257 calories | 250 calories (approx.) |
| Viscosity at 0° C. | 0·0030 | 0·0381 |

It will be observed that the proportion of trihydrol steadily falls as the temperature is raised. At the critical temperature, 374° C., it is still about 13 per cent.—assuming the formula to be trustworthy up to this point.

But even if the water at its critical temperature consisted of nearly pure dihydrol, without any trihydrol molecules, it would still be far more highly associated than calculation from Guye's formula would indicate. As shown on p. 300, when the most recent critical data are employed in the calculation, the molecular weight of water at the critical temperature works out at 18·5, and corresponds to almost absolutely pure monohydrol.

For these, and other reasons, it would appear that liquid water is more complex than a binary mixture, and the suggestion first hinted at by Callendar,[1] and later developed by Bousfield and Lowry,[2] namely, that water is a ternary mixture has much to recommend it. According to this theory liquid water contains ice-, water-, and steam-molecules in equilibrium. In other words its composition is represented by the scheme :

$$(H_2O)_3 \rightleftharpoons (H_2O)_2 \rightleftharpoons H_2O.$$

Whilst this theory renders the problem considerably more complex than Röntgen's binary theory, it enables explanations of a more satisfactory character to be given for the abnormalities in density, specific heat, etc. It is, further, quite in harmony with accepted views on molecular equilibria in general. If ice molecules can exist in water at the lower temperatures, there is no apparent reason why steam molecules should be excluded from liquid water at the higher temperatures.

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[1] Callendar, *Phil. Trans.*, 1902, [A], 199, 147

[2] Bousfield and Lowry, *Trans. Faraday Soc.*, 1910, 6, 85.

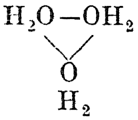
Assuming, then, that water consists of three types of molecule, namely, $H_2O$, $(H_2O)_2$, and $(H_2O)_3$, the question arises as to the manner in which the atoms are linked together. By assuming oxygen to be tetravalent, it is not difficult to construct formulæ for the associated molecules. What difficulty exists lies in choosing which formula is to be regarded as correct, inasmuch as the associated molecules may theoretically assume several isomeric forms.

Armstrong[1] has considered the structure of water molecules from the point of view of their chemical activities in promoting solution, and suggests that liquid water is to be regarded as a complex mixture of active and inactive molecules. The latter are regarded as having a closed structure, thus:

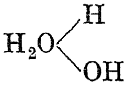
Dihydrone.

$H_2O : OH_2$

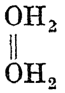
Trihydrone



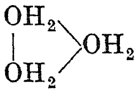
whilst the active molecules consist of *hydrone*, $H_2O$, or of *hydronol*,



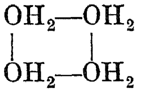
Armstrong[2] has considered the possibility of even higher complexes such as tetrahydrone and pentahydrone. These bear comparison with the methylene series, pentahydrone being, by analogy, the most stable hydrone and possessing the highest boiling-point—as is the case with pentamethylene. Thus:



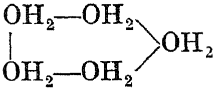
Dihydrone.



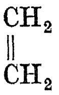
Trihydrone.



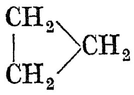
Tetrahydrone.



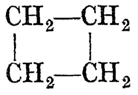
Pentahydrone.



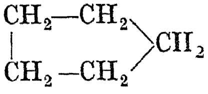
Ethylene
B.Pt. −104° C.



Trimethylene
B.Pt. −35° C.



Tetramethylene
B.Pt +11 5° C.



Pentamethylene.
B.Pt +50° C

A steric formula for a molecule of water has been proposed.[3]

---

[1] Armstrong, *Proc. Roy. Soc.*, 1908, [A], 81, 80. *Nature*, 1923, 111, 689.

[2] Armstrong, *Chem. News*, 1911, 113, 97.

[3] Piccard, *Helv. Chim Acta*, 1922, 5, 72.

# CHAPTER XI.

## WATER AS A SOLVENT. WATER ANALYSIS.

WATER is characterised by powerful solvent action, particularly as regards many inorganic substances.

**A. Solubility of Gases.**[1]—This is usually expressed in one of two ways, namely, as Bunsen's *Absorption Coefficient*, $\beta$, or as Ostwald's *Solubility expression*, $l$. These terms have already been defined (p. 36).

Gases may be divided broadly into two classes, namely, those that combine with water, such as ammonia, hydrogen chloride, sulphur dioxide, and the like; and those that are chemically inert. Amongst the latter class may be placed oxygen, nitrogen, etc. The former group usually possess high absorption coefficients, whilst the latter are frequently so slightly soluble, that for many chemical purposes they may be regarded as insoluble and may be collected and even stored over water. Xenon lies between the two groups, its solubility being greater than that of any other chemically neutral gas.

| Gas. | 0°. | 5°. | 10°. | 15° | 20°. | 25°. | 30°. |
|---|---|---|---|---|---|---|---|
| Hydrogen [2] . | 0·0214 | 0·0204 | 0·0195 | 0·0188 | 0·0182 | 0·0175 | 0·0170 |
| Nitrogen [3] . | 0·0239 | 0·0215 | 0·0196 | 0·0179 | 0·0164 | 0·0150 | 0·0138 |
| Oxygen [3] . | 0·0496 | 0·0439 | 0·0390 | 0·0350 | 0·0317 | 0·0290 | 0·0268 |
| The rare gases (see p. 308) . | .. | .. | . | .. | .. | . | .. |
| CO [4] . . | 0·0354 | 0·0315 | 0·0282 | 0·0254 | 0·0232 | 0·0214 | 0·0200 |
| $CH_4$ [4] . . | 0·0556 | 0·0481 | 0·0418 | 0·0369 | 0·0331 | 0·0301 | 0·0276 |
| NO [4] . | 0·0738 | 0·0646 | 0·0571 | 0·0515 | 0·0471 | 0·0430 | 0·0400 |
| $N_2O$ [5] . . | .. | 1·1403 | 0·9479 | 0·7896 | 0·6654 | 0·5752 | .. |
| $CO_2$ [3] . . | 1·713 | 1·424 | 1·194 | 1·019 | 0·878 | 0·759 | 0·665 |
| Chlorine ($\beta^1$) [2] . | 4·610 | (3·232) | 3·095 | 2·635 | 2·260 | 1·985 | 1·769 |
| $H_2S$ [2] . . | 4·621 | 3·935 | 3·362 | 2·913 | 2·554 | 2·257 | 2·014 |
| $SO_2$ [2] . . | 79·79 | 67·48 | 56·65 | 47·28 | 39·37 | 32·79 | 27·16 |
| HCl [6] . . | 525·2 | 496 | 474 | 456 | 443 | 432 | .. |
| $NH_3$ [2] . . | 1299 | 1019 | 910 | 802 | 710 | 635 | .. |

The solubility of most gases falls with rise of temperature, but in the case of the inert gases minimum values exist, the solubility falling in the cases of xenon and argon as the temperature rises from 0° to 40° C. Above this point the solubility rises again. For krypton the minimum lies between 30° and 40° C.; for helium at 10° C., and for neon probably in the neighbourhood of 0° C.[1]

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[1] A useful summary is given by Coste, *J. Soc. Chem. Ind.*, 1917, 36, 846

[2] From Seidell, *Solubilities* (Crosby Lockwood, 1920).

[3] Bohr and Bock, *Wied. Annalen*, 1891, 44, 319; see also p. 37.

[4] Winkler, *Ber.*, 1901, 34, 1408.

[5] Roth, *Zeitsch. physikal. Chem.*, 1897, 24, 114.

[6] Estimated from the smoothed curve drawn from the data given by Seidell.

In the preceding table are given the solubilities of a few typical gases in water at various temperatures. Unless otherwise stated the solubility co-efficient $\beta$ is employed. $\beta^1$ signifies measurement of the gaseous volume at N.T.P., but the pressure includes the vapour pressure of the liquid also, whereas $\beta$ signifies the volume under the pressure of the gas itself of 760 mm. (see p. 36).

Winkler[2] directed attention to the fact that, in the case of many chemically inert and "permanent" gases, the percentage decrease in the solubility coefficient between 0° and 20° C. is approximately proportional to the cube root of the molecular weight of the gas. Thus:

| | Percentage decrease in $\beta$. A. | Cube Root of Molecular Weight. B. | $\frac{A}{B}$ |
|---|---|---|---|
| Hydrogen . . | 15·32 | 1·259 | 12 2 |
| Nitrogen . . . | 34·33 | 3·037 | 11·3 |
| Oxygen . . . | 36·55 | 3·175 | 11·5 |
| Carbon monoxide . | 34 44 | 3·037 | 11·3 |
| Nitric oxide . . | 36·24 | 3·107 | 11·7 |

The decrease in $\beta$ is attributed by Winkler to a fall in the viscosity of the solvent consequent upon rise of temperature. The two factors may be equated as follows:

$$\frac{\beta_0-\beta_t}{\beta_0}=\frac{\eta_0-\eta_t}{\eta_0}\cdot\frac{\sqrt[3]{M}}{k}$$

where $\eta_0$ and $\eta_t$ represent the viscosities of water at 0° and $t°$ C. respectively, and $k$ is a constant, M being the molecular weight. If $\beta_t$ is calculated from this expression, the value agrees well with that found experimentally between 0° and 60° C. The following values for $k$ have been deduced:

| | $k$. |
|---|---|
| Argon . . . . . . . . . . | 4·4 |
| Hydrogen, oxygen, and diatomic gases . . | 3·8 |
| $CO_2$ and triatomic gases . . . . . | 3·2 |

Helium is exceptional, however. As a rule, for those gases that deviate markedly from Boyle's law, the value for $k$ tends to rise with temperature.

*The Inert Gases.*—The study of the solubility of the gases of group 0 of the Periodic Table has proved very interesting. The data published by Antropoff[3] are given in the following table:

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[1] See p. 308 and fig 46.

[2] Winkler, *Zeitsch. physikal. Chem.*, 1892, 9, 171; 1906, 53, 344.

[3] Antropoff, *Proc. Roy. Soc.*, 1910, [A], 83, 474.

## SOLUBILITIES OF THE INERT GASES IN WATER.

| Temperature, ° C. | Helium [1] | Neon.[2] | Argon [1] | Krypton.[2] | | Xenon.[2] |
|---|---|---|---|---|---|---|
| | | | | Sample I. | Sample II | |
| 0 | 0·0134 | 0·0114 | 0·0561 | 0·1249 | 0·1166 | 0·2189 |
| 10 | 0·0100 | 0·0118 | 0·0438 | 0·0965 | 0·0877 | 0·1500 |
| 20 | 0·0138 | 0·0147 | 0·0379 | 0·0788 | 0·0670 | 0·1109 |
| 30 | 0·0161 | 0·0158 | 0·0348 | 0·0762 | 0·0597 | 0·0900 |
| 40 | 0·0191 | 0·0203 | 0·0338 | 0·0740 | 0·0561 | 0·0812 |
| 50 | 0·0226 | 0·0317 | 0·0343 | 0·0823 | 0·0610 | 0·0878 |

These results are shown graphically in Fig. 46. A remarkable feature of these determinations is the minimum of solubility shown by every gas.

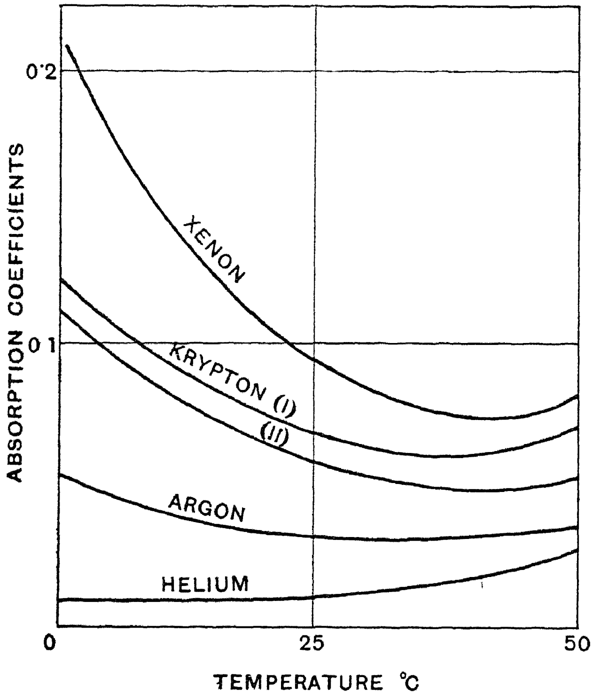

FIG. 46.—Solubilities of the inert gases in water (Antropoff, 1910).

Estreicher had already in 1899 suggested that such a minimum ought to exist, and indeed found such to be the case with helium. The minimum for xenon and argon lies at 40° C.; for krypton between 30° and 40° C.; for helium, at 10° C., and for neon probably at 0° C. As a general rule, the solubility rises with the atomic weight, helium and neon being exceptional, possibly on account of erroneous determination. It is also worthy of note that the solubility of xenon is greater than that of any other gas which does not form a compound with the solvent.

---

[1] Data obtained by Estreicher (*Zeitsch. physikal. Chem.*, 1899, 31, 176) and corrected by Antropoff Cady, Elsey, and Berger (*J. Amer. Chem. Soc.*, 1922, 44, 1456) give the solubility of helium in water between 2° and 30° C., but find no minimum value.

[2] Antropoff, *loc. cit.*

The solubility of a gas increases with the pressure; for gases chemically neutral towards water,

$$\beta \propto p,$$

since under moderate pressures Boyle's Law is obeyed with fair accuracy, it follows that a volume of water at a given temperature will absorb the same volume of gas whatever the pressure. This is **Henry's Law,**[1] enunciated in 1803. The same year Dalton observed that the amount of a gas absorbed from a gaseous mixture is directly proportional to its partial pressure. In both of these cases it is assumed that the gas does not combine with the water. If combination takes place these laws are not obeyed.

The methods employed for the determination of gases in water may be either chemical or physical. The former are useful in cases where chemically reactive gases such as oxygen, etc., are concerned. For neutral gases, like nitrogen, physical methods are essential.[2]

The presence of dissolved salts tends to reduce the solubility of neutral gases in water.[3] This is capable of explanation on the assumption that the electrolyte is hydrated, and that the water thus "fixed" is no longer able to absorb the gas. If this theory is accepted, it becomes possible to calculate the degree of hydration of the salt.[4] A solution of alcohol in water is peculiar in its behaviour towards oxygen. Although oxygen is several times more soluble in alcohol than in water, addition of alcohol to water reduces the absorption of oxygen, a minimum being reached with about 30 per cent. of alcohol. Further addition of this liquid raises the absorption coefficient.[5]

**B. Solubility of Liquids.**—Liquids sometimes dissolve in water in all proportions without separating out into two phases. Such is the case with methyl and ethyl alcohols, and it is easy to pass from what may be termed a solution of alcohol in water, by successive additions of alcohol, to a solution of water in alcohol, the latter liquid being so much in excess as to merit the term solvent, the water being the solute.

The majority of liquids, however, do not mix in all proportions with water at the ordinary temperature. When phenol is added to water, two layers are produced; the upper one consisting of a solution of phenol in water; the lower, of water in phenol. On gently warming and shaking the liquid becomes opalescent at about 68° C., and at 68·3° C.—the *critical solution temperature*—the two liquids become entirely miscible. This is shown in Fig. 47.

---

[1] Henry, *Phil. Trans.*, 1803, pp. 29, 274.

[2] See p. 36.

[3] This is well illustrated by the data given on p. 41 of the solubilities of oxygen in different concentrations of various salts in water

[4] Philip, *Trans. Faraday Soc.*, 1907, 3, 140; *Trans. Chem. Soc.*, 1907, 91, 711.

[5] See p. 43.

The mutual solubilities of carbon disulphide and water are as follow .

| Temperature, ° C. . . . | 0 | 10 | 20 | 25 | 27 | 30 |
|---|---|---|---|---|---|---|
| Grams $CS_2$ per 100 grams[1] $H_2O$ | 0 258 | 0 239 | 0 217 | . | | 0 195 |
| Grams $H_2O$ per 100 grams[2] $CS_2$ | .. | | .. | 0 010 | 0 012 | . |

In carbon tetrachloride:

| Temperature, ° C. . . . | 0 | 10 | 20 | 24 | 28 5 | 30 |
|---|---|---|---|---|---|---|
| Grams $CCl_4$ per 100 grams[1] $H_2O$ | 0 097 | 0 083 | 0·080 | . | .. | 0 085 |
| Grams $H_2O$ per 100 grams[2] $CCl_4$ | .. | .. | .. | 0 010 | 0 013 | .. |

In chloroform, $CHCl_3$:

| Temperature, ° C. . . . | 0 | 10 | 20 | 24·5 | 27·8 | 30 |
|---|---|---|---|---|---|---|
| Grams $CHCl_3$ per 100 grams[1] $H_2O$ | 1·062 | 0 895 | 0 822 | . | . | 0 776 |
| Grams $H_2O$ per 100 grams[2] $CHCl_3$ | .. | .. | .. | 0 084 | 0 107 | .. |

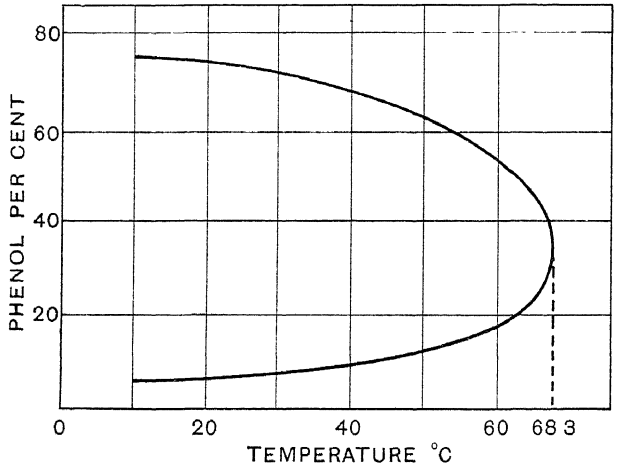

FIG. 47.—Solubility curves for water and phenol

It will be observed that, as with gases, the solubilities of the three foregoing liquids in water fall with rise of temperature, although the solubilities of water in these liquids rises with temperature. Rex[3] has made the interesting observation in connection with a considerable number of liquids that the value for *k*, in Winkler's formula for gases given above, increases regularly with the molecular weight in the case of such substances as contain a given number of atoms; it also increases with the temperature. There is thus a close analogy between the solubilities of neutral liquids in water and the absorption of neutral gases by water.

The solubility of water in benzene is as follows:[4]

| Temperature, ° C . . | 3 | 23 | 40 | 55 | 66 | 77 |
|---|---|---|---|---|---|---|
| Grams of water in 100 grams $C_6H_6$ | 0 030 | 0 061 | 0 114 | 0 184 | 0·255 | 0 337 |

The steady rise in solubility is noteworthy.

**C. Solubility of Solids.**[5]—The majority of normal inorganic salts are readily soluble in water. This is the case for all nitrates, and most chlorides and sulphides, notable exceptions being the chlorides of silver, lead, and monovalent mercury, and the sulphates of lead, calcium, strontium, and barium. Even these substances are slightly soluble in water; indeed, it is doubtful if any substances are absolutely insoluble, so that the terms soluble and insoluble must be regarded as relative. Basic salts are generally insoluble; acid salts, on the other hand, are usually soluble. The solubility of a salt in water is influenced by several factors such as temperature, pressure, and the dimensions of the particles constituting the solid phase.

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[1] Rex, *Zeitsch physikal. Chem.*, 1906, 55, 355.

[2] Clifford, *J. Ind. Eng. Chem.*, 1921, 13, 631.

[3] Rex, *loc. cit.*

[4] Groschuff, *Zeitsch. Elektrochem.*, 1911, 17, 348.

[5] For an account of the various theories of ionisation and hydration in aqueous solution see this series, Vol. I.

1. *The Influence of Temperature.*—This is well illustrated by the various solubility curves shown in Figs. 48 to 50.

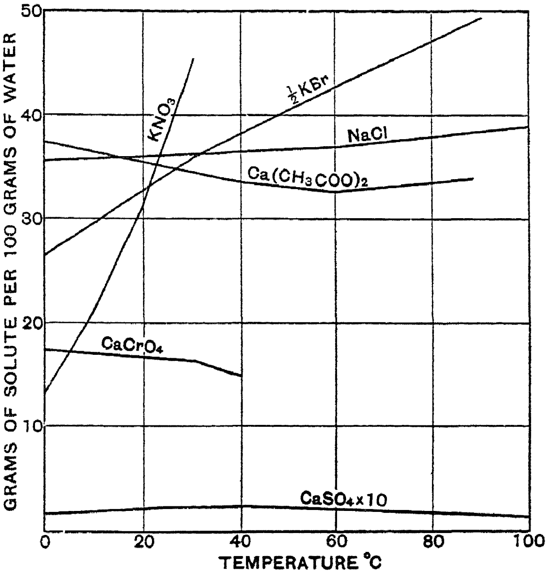

FIG. 48.—Solubility of salts in water.

A. *Continuous curves.*—These may be roughly classified into the following types:

(*a*) The solubility remains fairly constant at all temperatures—sodium chloride.
(*b*) The solubility rises steadily with the temperature—potassium bromide.
(*c*) The solubility rises rapidly with the temperature—potassium nitrate.
(*d*) The solubility falls steadily—calcium chromate.
(*e*) The solubility rises to a maximum and then falls—calcium sulphate.
(*f*) The solubility decreases to a minimum and then rises, as exemplified by calcium acetate and propionate[1] and by anhydrous sodium sulphate, the minimum in the latter case occurring at about 120° C.[2]

---

[1] Lumsden, *Trans. Chem. Soc.*, 1902, 81, 350.

[2] Tilden and Shenstone, *loc. cit.*

B. *The curve exhibits sharp breaks.*—Two possible causes, namely, a change of polymorphic form or a change of hydration,[1] will give rise to a sudden break in the curve. The former case is illustrated by ammonium nitrate, which is capable of existing in no fewer than four crystalline forms. Of these the β-rhombic passes into the α-rhombic variety at about 32° C.[2] At this temperature a break occurs in the solubility curve.[3]

The effect of change of degree of hydration in the case of those substances that can combine with water is shown in the solubility curve of sodium sulphate (fig. 49).[4] Below 32·8° C. the stable form of this salt crystallises with ten molecules of water, but above this temperature the anhydrous salt is stable. This transition-point is sharply marked by a break in the curve. So also the points of intersection in the solubility curve of ferric chloride (fig. 50) in water correspond with the appearance of new hydrated varieties until at the last point of discontinuity there is transformation into the anhydrous substance.

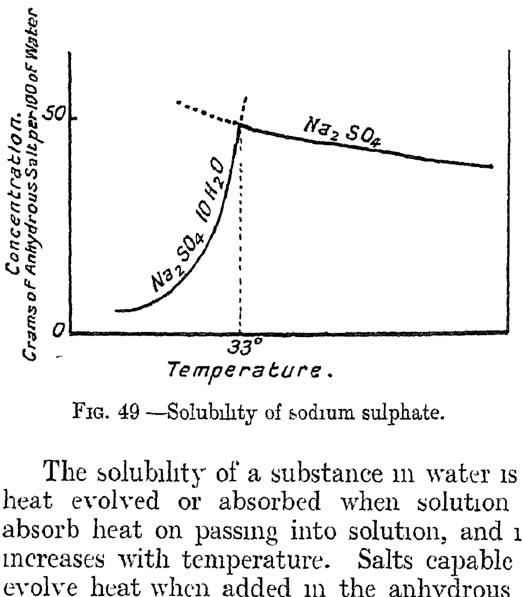

FIG. 49 —Solubility of sodium sulphate.

The solubility of a substance in water is closely connected with the heat evolved or absorbed when solution occurs. Many substances absorb heat on passing into solution, and in such cases the solubility increases with temperature. Salts capable of crystallising with water evolve heat when added in the anhydrous form, and it is found that the solubility of the anhydrous form usually decreases with rise of temperature.

Van't Hoff[5] gives two rules, which, although applying in theory only to the solution of a substance in one already practically saturated, usually hold for ordinary solution. The rules are as follow:

(i) If a substance on solution evolves heat, rise of the temperature will tend to reduce its solubility.

(ii) If the substance absorbs heat under the above condition, rise of temperature will cause an increasing amount to pass into solution.

Anhydrous ferric chloride is very deliquescent, and its solubility in water is represented by four distinct curves corresponding to the appearance of four hydrated salts, namely, $2FeCl_3.4H_2O$ (m.-pt. 73 5° C.), $2FeCl_3.5H_2O$ (m.-pt. 56° C.), $2FeCl_3.7H_2O$ (m.-pt. 32·5° C.), and

---

[1] *I.e.* an alteration in the solid phase in equilibrium with the solution

[2] See this series Vol. I., p. 66; also Vol. II., p. 120.

[3] Müller and Kaufmann, *Zeitsch. physikal. Chem.*, 1903, 42, 497.

[4] For a careful study of the changes in the solubility of sodium sulphate see de Coppet, *Ann. Chim. Phys.*, 1907, [viii.], 10, 457; H. Hartley, B M Jones, and G A. Hutchinson, *Trans Chem. Soc.*, 1908, 93, 825

[5] Van't Hoff, *Lectures on Theoretical and Physical Chemistry*, translated by Lehfeldt (Arnold), part i. pp. 37–9.

$F_2eCl_3 . 12H_2O$ (m.-pt. 37° C.) respectively. From the last point of discontinuity, namely, F in fig. 50 (66° C.), onwards the salt is anhydrous and is deposited from solution in that condition.[1]

A study of the curves in fig. 50 is particularly interesting from the point of view of the Phase Rule. AB represents the various states of equilibrium between ice and ferric chloride solutions, a minimum temperature being reached at the cryohydric point B, which is −55° C. At this point ice, solution, and the dodecahydrate of ferric chloride are in equilibrium. The number of degrees of freedom is *nil*—in other words, the system is invariant, and if heat be subtracted the liquid phase will solidify without change of temperature until the whole has become a solid mass of ice and dodecahydrate. Further abstraction of heat merely lowers the temperature of the system as a whole.

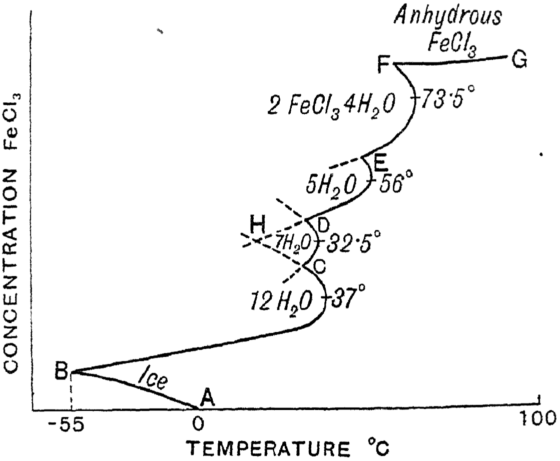

Fig. 50.—Solubility curves of ferric chloride.

If, starting at the point B, heat be added to the system, ice will melt, and more of the dodecahydrate will dissolve in accordance with the equilibrium curve BCH, which is the solubility curve of this hydrate in water. At 37° C. the dodecahydrate melts, and if anhydrous ferric chloride be added to the system, the temperature at which the dodecahydrate remains in equilibrium with the solution is lowered until the eutectic point C is reached at 27·4° C. At this point the whole solidifies to a solid mixture of the dodecahydrate and heptahydrate.

The curve has been followed in the direction of the broken line CH to +8° C., the solution being supersaturated with respect to the dodecahydrate. Similarly, the curve ED has been continued backwards until it intersects CH at H at 15° C. This is a metastable triple point or eutectic, and is capable of realisation experimentally on account of the fact that the heptahydrate is not so readily formed.

Curves EF and FG represent the solubilities of the tetrahydrate and the anhydrous salt respectively.

2. *The Influence of Pressure.*—Sorby[2] concluded that a rise of pressure increases the solubility of those substances which dissolve in a

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[1] Roozeboom, *Zeitsch. physikal. Chem.*, 1892, 10, 477 See this series, Vol. IX., Part II.

[2] Sorby, *Proc. Roy. Soc.*, 1863, 12, 538.

liquid with contraction of volume, but that it decreases the solubility of such substances as dissolve in water with an increase in volume. It was first indicated by Braun[1] that if the change of volume on solution and the thermal effect are known, the quantitative effect of alteration in pressure on the solubility may be calculated. This is in harmony with the Theorem of Le Chatelier. The following data[2] are in harmony with this:

### THE EFFECT OF PRESSURE ON SOLUBILITY.

(von Stackelberg.)

| Salt | Change of Volume on Solution in Water. | Grams of Salt in 100 Grams of Solution at 18° C., at: | | |
|---|---|---|---|---|
| | | 1 Atmos. Pressure. | 400 Atmos. Pressure. | 500 Atmos Pressure. |
| Sodium chloride . | contraction | 26·4 | .. | 27 0 |
| Ammonium chloride | expansion | 27·2 | .. | 25·8 |
| Alum . . . | contraction | 11·5 | 14·2 | .. |

Further data for sodium chloride have been published[3] which are in close harmony with those given above, but refer to 25° C.

| | | | | |
|---|---|---|---|---|
| Pressure in kilograms per sq. cm. . | 1 | 250 | 500 | 750 |
| Grams of NaCl per 100 grams solution | 26 44 | 26·58 | 26·72 | 26 82 |

3. *Physical Condition of the Solid Phase.*—As long ago as 1870 Stas observed that the solubility of silver chloride varies with its method of preparation,[4] the following results being obtained:

| | Solubility. |
|---|---|
| Flocculent silver chloride . | 0·0140 gram/litre at 20° C. |
| Powdered " " . . | 0·0060 " " 17° C. |
| Granular " " . . | 0·001 " " 15° C. |

Clearly the smaller the particles of the salt the greater the solubility. This is further supported by Hulett,[5] who investigated the solubilities of calcium and barium sulphates at 25° C. and found them to be as in table on p. 315.

Clearly, therefore, before the absolute solubility of a salt in water at any stated temperature, and under, say, atmospheric pressure, can be given, the size of the particles of the solid phase must be known. This has an intimate connection with the phenomenon of supersaturation (see p. 315), for it is clear that a saturated solution of barium sulphate prepared in contact with particles of diameter 0·1 $\mu$ is supersaturated with respect to particles of diameter $1{\cdot}8\,\mu$, and, upon introduction of such particles, the excess would be precipitated out.

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[1] Braun, *Zeitsch physikal. Chem*, 1887, I, 259.

[2] E. von Stackelberg, *ibid*, 1896, 20, 337.

[3] Sill, *J. Amer Chem. Soc*, 1916, 38, 2632. See also Cohen, Inouye, and Euwen, *Zeitsch. physikal. Chem.*, 1910, 75, 291

[4] Stas, *Œuvres*, I, 87. See Drucker, *Zeitsch Chem Ind. Kolloide*, 1909, 4, 216

[5] Hulett, *Zeitsch. physikal Chem.*, 1901, 37, 385, Hulett and Allen, *J Amer Chem Soc.*, 1902, 24, 667.

## INFLUENCE OF SIZE OF PARTICLE UPON SOLUBILITY.

| Salt. | Diameter of Particles supposed Spherical | Solubility at 25° C (Mass per Litre.) |
|---|---|---|
| Calcium sulphate . . | $2\,\mu$ | 2·085 grams |
| | $0{\cdot}3\,\mu$ | 2·476 ,, |
| Barium sulphate . . | $1{\cdot}8\,\mu$ | 2·29 mg. |
| | $0{\cdot}1\,\mu$ | 4·15 ,, |

**Supersaturated Solutions.**—When a solution of a solid in water, already saturated at a given temperature, is heated up with more of the solid until the whole of the latter has passed into solution, crystallisation or precipitation of the excess of solute does not always take place upon cooling the system to the original temperature. It is clear that the solution must now hold a greater quantity of substance than corresponds to the ordinary solubility and is said to be *supersaturated.* Such solutions can readily be prepared by heating up sodium thiosulphate, sodium acetate, or sodium sulphate with water, and allowing to cool without agitation.

Supersaturated solutions, however, are always liable to crystallise spontaneously, particularly on exposure to air. Löwell [1] was apparently the first to show, however, in the case of sodium sulphate, that crystallisation was not induced by contact with air that had been previously passed through water, sulphuric acid, caustic alkalies, glass wool, or even through a series of empty flasks. Fifteen years later Violette [2] and Gernez [3] independently threw considerable light upon the subject by showing that the spontaneous crystallisation of supersaturated solutions of sodium sulphate in contact with air is due to the presence of minute crystals of the salt in suspension in the latter [4] which serve as nuclei stimulating crystallisation. Hence by washing or filtering the air Löwell had removed these suspended nuclei, and in consequence retarded crystallisation. Lecoq de Boisbaudran [5] showed, in the following year, that not only could minute crystals of the same substance serve as nuclei, but that crystals of isomorphous bodies yield precisely the same result; and it is now known that this property is shared by many substances that are not strictly isomorphous with the dissolved salt, provided their molecular volumes are closely similar.[6] Ostwald showed that nuclei weighing only $10^{-10}$ to $10^{-8}$ grams were usually quite sufficient to induce crystallisation of supersaturated solutions. Furthermore, it appears from numerous researches[1] that mere mechanical friction is sufficient to induce crystallisation, such crystallisation taking place in the complete absence of crystalline nuclei.

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[1] Lowell, *Ann. Chim Phys.*, 1850, [iii.], 29, 62.

[2] Violette, *Compt. rend*, 1865, 60, 831.

[3] Gernez, *ibid.*, 1865, 60, 833. See also *ibid*, 1865, 60, 1027; 1866, 63, 843.

[4] Traces of sodium salts are always present in our island atmosphere, and these yield sodium sulphite and sulphate by union with the oxides of sulphur produced during the combustion of coal, etc.

[5] de Boisbaudran, *Ann Chim Phys.*, 1866, [iv.], 9, 173. See also J. M Thomson, *Zeitsch Kryst. Min.*, 1881, 6, 94; Ostwald, *Lehrbuch*, vol. ii., part 2, p. 780.

[6] See Isomorphism, this series, Vol. I., pp. 70–74.

Supersaturated solutions of liquids in liquids have only been realised in a few cases,[2] but supersaturated solutions of gases in liquids are not uncommon.

Tap water saturated with air at 7° C. can be incubated at 18° C. for six days without appreciable loss of oxygen. At this higher temperature it is, of course, supersaturated, but so long as the containing vessel is not shaken, and chemical actions such as fermentation are excluded, no appreciable loss of oxygen occurs.[3]

The addition of any powdered substance to such a solution, however, will break down the supersaturation since the gases in the pores of the powder act as nuclei. Supersaturation of this kind differs from that considered above, inasmuch as the nuclei immediately escape from the liquid, whereby their influence is severely limited.

**Combined Water or "Water of Crystallisation."**—When their concentrated aqueous solutions are cooled or allowed to evaporate many substances separate out with *combined water* or so-called *water of crystallisation*. This latter term is intended merely to imply that the actual crystalline form and not the crystalline nature of the deposit is dependent on the combined water present, because generally the anhydrous substances are also crystalline.[4] The simplest type of a substance with water of crystallisation is to be seen in the case of the crystalline compound chlorine hydrate, $Cl_2 . 8H_2O$, but the best known examples are amongst the salts, especially the "vitriols," $CuSO_4 . 5H_2O$; $ZnSO_4 . 7H_2O$; $FeSO_4 . 7H_2O$, and the alums, of which potassium alum, $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ may be regarded as typical. Generally speaking, the presence of water of crystallisation is more common amongst the salts (simple and double) of the weaker acids. The number of molecules of water which thus combine with a molecule of a substance varies[5] with the substance and even with the conditions such as the temperature of crystallisation; *e.g.* above 32·4° C., sodium sulphate crystallises from aqueous solution in the anhydrous condition, whereas below this temperature the crystals have the composition $Na_2SO_4 . 10H_2O$. Each salt containing water of crystallisation exerts a characteristic vapour pressure,[6] which increases with rise of temperature. Such hydrated compounds can therefore be deprived of their water, in part or entirely, by raising the temperature or by placing them in an atmosphere containing less water-vapour than corresponds with the vapour pressure of the hydrate. By enclosing a hydrated salt, preferably mixed with a little of the dehydrated salt, in a desiccator over a drying agent, not only does dehydration take place, but it may occur in stages revealing the existence of intermediate hydrates;[1] thus blue vitriol undergoes dehydration by the stages, $CuSO_4 . 5H_2O$; $CuSO_4 . 3H_2O$; $CuSO_4 . H_2O$; $CuSO_4$, each stage being marked by a reduction in the vapour pressure at any one temperature.

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[1] A. H. Miers and his pupils, *Trans. Chem Soc.*, 1906, 89, 413, 1013; *Proc. Roy. Soc.*, 1907, [A], 79, 322; B. M. Jones, *Trans Chem Soc.*, 1909, 95, 1672, Young, *J. Amer. Chem. Soc*, 1911, 33, 148; Young and Cross, *ibid.*, 1911, 33, 1375

[2] H. S. Davis, *J. Amer. Chem Soc.*, 1916, 38, 1166.

[3] Richards, *J. Agric. Sci.*, 1917, 8, Part 3, p. 331.

[4] Nordenskiold, *Ber.*, 1874, 7, 475; Surawicz, *ibid.*, 1894, 27, 1306

[5] From an examination of a large number of salts, Rosenstiehl (*Compt. rend.*, 1911, 152, 598, *Bull. Soc. chim*, 1911, 9, 281) arrives at the conclusion that after the first molecule of water of crystallisation further molecules of water are added, generally in groups of three, and less frequently in groups of two, and regards this result as confirmative of the existence of the molecules $(H_2O)_3$, and $(H_2O)_2$ in water; see also p. 296

[6] Wiedemann, *J. prakt. Chem*, 1874, 9, 338; Debray, *Compt. rend*, 1874, 79, 890, Roozeboom, *Zeitsch. physikal. Chem.*, 1889, 4, 31, 1892, 10, 477.

If the vapour pressure of the water of crystallisation in a substance exceeds the pressure of the atmospheric moisture, spontaneous dehydration may occur so that the substance becomes coated with a powdery layer of a less hydrated form. Glauber's salt, $Na_2SO_4 . 10H_2O$, and "washing soda," $Na_2CO_3 . 10H_2O$, are typical of this class, to which the term "*efflorescent*" is applied. On the other hand, a *hygroscopic* substance is one which absorbs moisture from the atmosphere; if the aqueous vapour tension of the atmosphere is much greater than that of the damp substance, the absorption may continue until finally a solution is obtained, the process continuing until the vapour pressure of the solution attains that of the vapour in the atmosphere. Potassium carbonate, sodium nitrate, calcium chloride, and zinc chloride are common examples of such *deliquescent* substances.

Both sunlight and ultra-violet light accelerate the escape of water of crystallisation from salts in certain cases.[2]

The transition temperature at which a hydrated salt liberates all or part of its water and passes into another less hydrated form is almost as definite as an ordinary melting-point, and can therefore be used as a standard for the calibration of thermometers; thus the transition temperature for Glauber's salt, $Na_2SO_4 . 10H_2O$, occurs at 32·383° C., whilst that of sodium bromide, $NaBr . 2H_2O$, is at 50·674° C.[3]

From the relative difficulty with which the last molecule of water of crystallisation is expelled from certain salts, *e.g.* $CuSO_4 . H_2O$ and $MgSO_4 . H_2O$, the dehydration of these salts requiring a temperature above 200° C., whereas the other water molecules in the ordinary pentahydrate and heptahydrate respectively are eliminated at a temperature a little above 100° C., it has been suggested that this last molecule is in some way more intimately associated than the others with the salt molecule and the name *water of constitution* has been applied to it.[4] By some, it is considered that this molecule may be especially associated with the acid radicle indicating, for example, in the above cases of monohydrated sulphates, that the salts are derived, not from sulphuric acid $H_2SO_4$, but from an ortho-sulphuric acid, $H_4SO_5$. On the other hand, it is equally possible that the molecule of water of constitution may be associated with the basic radicle, in which case the monohydrated salt would be regarded as a basic salt of the type $Cu(OH)SO_4H$,[5] which would thus be copper hemisulphate hemihydrol. There hardly appear to be sufficient grounds, however, for regarding water of constitution as distinct from ordinary water of crystallisation; in both cases it is probable that the molecules of water are attached to the salt molecules by additional valencies at the oxygen atoms,[1] and, as explained above, the removal of each successive molecule of water of crystallisation will be a matter of increasing difficulty.

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[1] Baker and Adlam, *Trans Chem. Soc.*, 1911, 99, 507; Cumming, *ibid.*, 1910, 97, 593.

[2] Beutel, *Chem. Zentr.*, 1916, ii., 638.

[3] Richards and Wells, *Zeitsch. physikal. Chem.*, 1903, 43, 465; 1906, 56, 348.

[4] Graham, *Annalen*, 1836, 20, 141.

[5] Erlenmeyer, *Ber.*, 1869, 2, 249. Compare Mummery, *J. Soc. Chem. Ind.*, 1913, 32, 889.

Interesting ideas as to the nature of water of crystallisation have been promulgated by A. Werner,[2] who regards six molecules of water of crystallisation as the normal quantity, and suggests that the water is combined with the basic radicle forming a complex radicle, *e.g.* $[Ca(OH_2)_6]Cl_2$ and $[Co(OH_2)_6]Cl_2$. Certainly a group of six molecules of water of crystallisation recurs frequently in hydrated salts.

In hydrated salts containing seven molecules of water, the sulphates supplying numerous examples, the seventh molecule is supposed to be attached to the acid radicle. This view receives confirmation in the frequency with which such heptahydrated sulphates form derived double sulphates containing only $6H_2O$, the additional salt being a sulphate which, when alone, crystallises in the anhydrous condition. Thus ferrous sulphate, $FeSO_4 . 7H_2O$, and zinc sulphate, $ZnSO_4 . 7H_2O$, yield such derivatives as $(NH_4)_2SO_4 . FeSO_4 . 6H_2O$, and $K_2SO_4 . ZnSO_4 . 6H_2O$ respectively. With salts containing more than seven molecules of water, the number is frequently twelve, and this is attributed to the water being combined in dihydrol molecules (see p. 298); and in accordance with this view potassium alum would be written $[Al(H_4O_2)_6](SO_4)_2K$.

The application of Bragg's X-ray spectrum analysis to hydrated crystals is throwing further light upon the manner of attachment of combined water,[3] and, in many cases, it would appear that no distinction can be made between water of crystallisation and water of constitution.

For a study of the optical behaviour of combined water, the reader is referred to the subjoined references.[4]

There is a possibility of small quantities of water being present in salts in another form than that of water of crystallisation. T. W. Richards,[5] in his attempts to prepare salts in an extremely pure condition for the determination of atomic weights, has observed indications of the presence of water in a state of solid solution in crystals.

**Water Analysis.**[6]—On account of the considerable effect of certain impurities on the value of water for drinking and other purposes, the detection and estimation of these impurities is of the greatest importance.

The water is first examined visually for *colour* or *turbidity*, and by *taste*. Thus, for example, a green colour may be due to algæ; brown, to peat or possibly to ferruginous material. Iron salts impart a distinct and bitter flavour to water, 1 part of iron per million of water being perceptible to the average person.[7] In the case of common salt, 75 grains per gallon or approximately 110 parts per 100,000 are recognisable in this manner. Hard waters are supposed to have a more refreshing or palatable taste than soft.[1] Less than 116 mg. of carbon dioxide per litre cannot be detected by the taste, whilst more than 246 mg. are distinctly perceptible at 15° to 17° C. Different persons show varying susceptibilities towards intermediate quantities. Carbon dioxide can be detected by the taste at lower concentrations in hard waters than in distilled water. In the last named, suspicion is aroused by 126 mg. per litre, but below 264 mg. of carbon dioxide, the carbonic acid is not distinctly tasted as such.

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[1] See Rhodes (*Chem. News*, 1921, 122, 85, 97), who suggests a cyclic or shell configuration for the water molecules.

[2] Werner, *New Ideas on Inorganic Chemistry*, p. 132; translated by Hedley (Longmans, 1911).

[3] See Vegard and Schjelderup, *Ann. Physik*, 1917, 54, 146; Schaefer and Schubert, *ibid.*, 1916, 50, 339; 1918, 55, 397; Niggli, *Physikal. Zeitsch.*, 1918, 19, 225

[4] Brieger, *Ann. Physik*, 1918, 57, 287.

[5] Richards, *J. Amer. Chem. Soc.*, 1911, 33, 888.

[6] As many excellent text-books deal very fully with water analysis, it is only necessary to deal with the subject in brief detail in this work.

[7] See Rideal, *Water Supplies* (Crosby Lockwood, 1914).

Any *suspended solid*, the presence of which should be regarded with suspicion, is removed by filtration. The quantity of *dissolved solid* is determined by evaporating a measured volume to dryness. From a practical view-point, the portion of the dissolved solids which affects the behaviour of a water towards lathering when treated with soap, is of especial interest, these constituents producing the so-called "*hardness*" of a water.

**Qualitative Analysis.**—Useful information as to the suitability of water for various purposes may be rapidly obtained by means of a few qualitative tests. The presence of *chlorides* is revealed by addition of a few drops of concentrated silver nitrate solution acidified with nitric acid, when a white haze or turbidity results.

*Lime* gives a white turbidity on addition of saturated ammonium oxalate solution, and *sulphates* with barium chloride acidified with hydrochloric acid. A useful reagent for *nitrites* is metaphenylene diamine, 5 grams of which are dissolved in water, acidified with dilute sulphuric acid, and made up to one litre. It may be necessary to previously decolorise the solution with charcoal. If nitrites are present in the water to be tested, on addition of the diamine, a yellow colour is produced, either immediately or upon standing. Starch-iodide solution acidified with dilute sulphuric acid may also be used, the characteristic blue colour of the starch-iodine complex indicating nitrites, but this test is not altogether satisfactory.

*Nitrates* are readily detected by adding a few drops 0·1 per cent. brucine solution to the sample of water, and then pouring concentrated sulphuric acid to the bottom of the tube in as gentle a manner as possible; a pink and yellow zone forms at the junction of the acid and water if nitrates are present.

Nessler's solution (see p. 322, note 6) gives a yellowish-brown coloration in the presence of *ammonia*. Traces of *lead* and *copper* give a dark colour with ammonium sulphide, acids being unable to destroy it. Discoloration due to copper may be removed by addition of potassium cyanide. The recognition of traces of lead by the above process, however, is sometimes impossible in the case of peaty waters, the brown colour of which entirely masks the reaction. In such cases a convenient method consists in adding permanganate to the water until it is distinctly pink. The water is then rendered alkaline with ammonia and kept for about forty-eight hours, when a precipitate will have formed, containing the whole of the lead. The supernatant liquid will be colourless unless too much permanganate has been added. The precipitate is collected on a filter, dissolved in hydrochloric acid, and, after dilution, tested with alkali sulphide in the usual manner. The composition of the precipitate has not been studied, but it appears probable that an oxide of lead is formed which is either carried down mechanically with the oxide of manganese or possibly as a compound.[1] Lead is also detected by addition of a few crystals of potassium bichromate, an immediate yellow turbidity occurring in the presence of 0·1 grain of lead per gallon (0·14 parts per 100,000). On standing for half an hour a turbidity is detectable with 0·02 grain of lead.

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[1] Friedmann, *Chem. Zentr.*, 1914, i., 1515.

The time-consuming operation of evaporating water in order to increase the concentration of lead which is necessary when the quantity is less than 0·1 mg. per litre, can be avoided by the procedure introduced by G. Frerichs.[2]

When water is filtered through pure cotton-wool, any lead is completely retained by the latter. By filtering a litre or more of the water through a plug of cotton-wool, and subsequently extracting the lead from the plug by washing it with a little hot dilute acetic acid, it is possible without loss to obtain a solution in which the proportion of lead is many times as great as in the original water. The test for lead, whether qualitative or quantitative, can then be applied in the usual manner.

The amount of lead in drinking water frequently diminishes on standing, probably in consequence of precipitation as lead carbonate.[3]

*Iron* gives a blue colour with a few drops of potassium ferro or ferri cyanide solution acidified preferably with dilute sulphuric acid. Colorimetric tests for iron are often uncertain in the presence of copper, etc., but if suitable precautions are taken this difficulty can be overcome.[4]

If the solution is rendered alkaline with ammonia, boiled and any precipitate removed by filtration, the presence of *zinc* may be demonstrated by addition of potassium ferrocyanide, when the liquid becomes turbid.

These reactions are summarised in the following table:

## QUALITATIVE TESTS FOR WATER.

| Reagent. | Result. | Conclusion | Delicacy of Test. Parts detectable per 100,000. |
|---|---|---|---|
| Silver nitrate | White haze | Chloride | 1 5 |
| | White turbidity | ,, | 6 |
| Ammonium oxalate | White turbidity | Lime | 9 |
| | White ppte. | ,, | 20 |
| Barium chloride | White turbidity | Sulphate | .. |
| Metaphenylene diamine | Yellow colour | Nitrite | .. |
| Brucine | Pink colour | Nitrate | 0·7 |
| Nessler's solution | Yellow-brown colour | Ammonia | .. |
| Ammonium sulphide | Dark colour stable towards acid | Lead or copper | .. |
| Crystal of potassium bichromate | Yellow turbidity | Lead | 0·14 (immediately)<br>0·03 (on standing) |
| Potassium ferro or ferri cyanide acidified | Blue colour | Iron | .. |

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[1] Tickle, *Analyst*, 1921, 46, 240.

[2] Frerichs, *Apoth Zeit.*, 1902, 884.

[3] Scheringa, *Pharm. Weekblad*, 1919, 56, 8.

[4] See, for details, Gregory, *Trans. Chem. Soc.*, 1908, 93, 93.

If the water is first concentrated to one-fiftieth of its bulk, tests may be carried out for *magnesia* and *phosphates*. The former is precipitated as magnesium ammonium phosphate on standing for some twenty-four hours after addition of sodium phosphate solution to the water rendered alkaline with ammonium hydroxide in the presence of chloride. It is assumed that any lime has previously been removed with ammonium oxalate. Phosphates are precipitated as yellow phosphomolybdate on adding excess of ammonium molybdate solution to the water acidified with nitric acid, and warming.

**Interpretation of the Results.**—The correct interpretation of water analyses is largely a matter of experience, and can only be arrived at after a thorough knowledge of local conditions has been attained. The presence of chlorides is usually to be regarded with suspicion as indicating possible contamination with sewage. But perfectly good potable waters may contain chlorides due to proximity to the sea or salt deposits. Thus the water in the lower reaches of the Severn invariably contains sodium chloride resulting from the triassic salt springs of the neighbourhood round Droitwich. Again, chlorides may result from deep wells and mineral springs, or from waste effluents from factories. Ammonia and nitrites suggest recent contamination with animal refuse. They are gradually oxidised to nitrates. Whilst, therefore, nitrated water *may* be quite safe, owing to oxidation of all dangerous organisms, it should be regarded with suspicion until confirmatory evidence is available.

Lead in any appreciable quantity is a very dangerous constituent in potable waters, for the poisonous action of lead compounds is cumulative, so that repeated small doses may prove more serious even than one large dose. Chronic lead poisoning may result merely from drinking such water as has been conveyed in ordinary lead pipes. Waters containing 0·02 grain per gallon are dangerous.

Iron is apt to be troublesome when present in quantities of 1 part per 100,000 and upwards. The metal oxidises, and hydrated oxide (rust) precipitates out on standing; this may block the pipes conveying the water. This oxidation is assisted by certain lowly organisms known as iron bacteria.[1] Iron salts are not toxic, but have a certain medicinal value and impart a bitter taste to the water. Copper salts are frequently employed to remove algæ, 0·3 parts per 100,000 being about the minimum effective concentration of copper sulphate for this purpose. At such dilutions the salt is not prejudicial to the human organism.

The inhibiting action of copper salts upon the growth of bacilli can be detected even at such dilutions as one part of copper in ten million of water. With 0·5 parts of copper per 100,000 a marked effect is observed; zinc has a small effect, but lead and iron appear to be without effect at these concentrations.[2]

**Quantitative Analysis.**—Chlorides present in a water are estimated by titration with a dilute standard solution of silver nitrate.

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[1] Mumford (*Proc. Chem. Soc.*, 1913, 103, 645) describes an organism through the agency of which a dilute solution of ferrous ammonium sulphate was completely oxidised to ferric hydroxide in thirty-six hours at 37° C, no iron remaining in solution. See also Ellis, *Iron Bacteria* (Methuen, 1920).

[2] Atkinson and Frederick, *J. Soc. Chem. Ind.*, 1921, 40, 408 A; from *J. Roy. Naval Med. Service*, 1921.

Nitrates and nitrites in water are frequently estimated together, *e.g.* by reduction to ammonia,[1] which can be determined in the manner described below; alternative processes are based on the reduction of these salts to nitric oxide which may be measured volumetrically,[2] and on reduction of the nitrate to nitrite when the total nitrite may be estimated colorimetrically by the addition of sulphanilic acid and *α*-naphthylamine.[3] For the estimation of nitrites and nitrates separately, organic colorimetric methods are usually applied.[4]

The nitrites and nitrates in natural water generally owe their existence to the oxidation of *ammonia* or ammonium salts which have themselves been produced by the decomposition of nitrogenous organic matter. The "free" ammonia is expelled by distilling with the addition of potassium hydroxide solution, whilst the nitrogenous organic compounds are decomposed with formation of ammonia (distinguished as *albuminoid ammonia*) by boiling with an alkaline solution of potassium permanganate;[5] in both cases the amount of ammonia obtained in the distillate is measured colorimetrically with Nessler's solution.[6] As the common source of nitrogenous organic matter is animal refuse in a state of decomposition, the presence of these nitrogen compounds is suggestive of possible contamination in a water, the period which has elapsed since contamination being reflected roughly in the relation between the amounts of nitrates and nitrites, free ammonia, and albuminoid ammonia. The total quantity of oxidisable organic matter, not necessarily nitrogenous, may be determined by direct "combustion" of the residue obtained by evaporation; it is also measured by observing the extent of reduction suffered by a known volume of standard potassium permanganate solution when kept at a definite temperature (often 26·7° C.) for several hours with a measured volume of the water in the presence of sulphuric acid (Forchhammer's process);[7] an empirical factor is necessary for the calculation of the percentage of organic matter.[8]

*Sulphates*, *silica*, *iron*, *calcium*, *magnesium*, and the *alkali metals* are also sometimes estimated, as are also the *dissolved gases*, chiefly oxygen, carbon dioxide, and nitrogen.

None of the chemical tests, however, with the exception of such as reveal the presence of poisonous substances, *e.g.* *lead*, or *copper* compounds, can be regarded as final evidence of the suitability or otherwise of a water for drinking purposes, and for a definite decision on this point a bacteriological examination is necessary.[9]

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[1] Thorpe, *Trans. Chem. Soc.*, 1873, 26, 541.

[2] See Schulze and Tiemann, *Ber.*, 1873, 6, 1041; Schlosing and Reichardt, *Zeitsch. anal. Chem.*, 1870, 9, 24.

[3] Harrow, *Trans. Chem. Soc.*, 1891, 59, 320.

[4] *E.g.* Preusse-Tiemann, *Ber.*, 1879, 12, 1906; Warington, *Chem. News*, 1885. 51, 39; Frankland, *Trans. Chem. Soc.*, 1888, 53, 364.

[5] Wanklyn, Chapman, and Smith, *Trans. Chem. Soc.*, 1867, 20, 591. See also Winkler, *Zeitsch. angew. Chem.*, 1914, 27, 440.

[6] Nessler's solution is conveniently prepared by dissolving 62·5 grams of potassium iodide in 250 c.c. water and adding to a cold, saturated solution of mercuric chloride until a faint permanent precipitate is obtained. Add 150 grams of potassium hydroxide in 150 c.c. of water, and finally a sufficient quantity of mercuric chloride solution to cause a slight, permanent, yellow precipitate. Dilute to one litre.

[7] See Nikitin (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1697) for the interference of chlorides; and Kaye (*Chem. News*, 1914, 110, 13) for a modified process using potassium ferricyanide with this method.

[8] Tidy, *Trans. Chem. Soc.*, 1879, 35, 66.

[9] See Frankland, *J. Soc. Chem. Ind.*, 1911, 30, 319; *The Biology of Waterworks*, Kirkpatrick (British Museum), 2nd ed., 1917.

For the estimation of dissolved gases in water the former are generally first removed by boiling the water or by generating carbon dioxide in it; in the latter case the bubbles of this gas carry out any dissolved gas, from which the carbon dioxide is easily removed subsequently.[1] Carbon dioxide itself may be conveniently estimated by titrating a measured volume of the water with sodium carbonate solution until phenolphthalein becomes coloured, the method depending on the neutrality of sodium hydrogen carbonate towards phenolphthalein.[2]

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[1] See Winkler, *Zeitsch. angew. Chem.*, 1915, **28**, 366; also this Vol, p 36

[2] Noll, *Zeitsch angew. Chem.*, 1912, **25**, 998; Auerbach, *ibid.*, 1912, **25**, 1722.

# CHAPTER XII.

## HYDROGEN PEROXIDE, $H_2O_2$.

**History.**—Hydrogen peroxide or, as it is sometimes termed, hydrogen dioxide, was first obtained by Thénard in 1818 in an examination of the dilute aqueous solutions formed by the action of various mineral acids on barium peroxide.[1] In the early days of its investigation considerable confusion was caused by the similarity between hydrogen peroxide and ozone in aqueous solution.[2]

**Occurrence.**—Hydrogen peroxide occurs in very minute quantities in rain water and in snow,[3] but its origin here is uncertain, being variously attributed to the action of the sun's rays on atmospheric moisture and to the interaction of carbon dioxide with water-vapour under the influence of sunlight forming formaldehyde and percarbonic acid, the latter substance then decomposing with production of carbon dioxide and hydrogen peroxide.[4]

$$3H_2CO_3 = HCHO + 2H_2CO_4$$
$$2H_2CO_4 = 2CO_2 + 2H_2O_2$$

The total change in this case, therefore, amounts to a decomposition of carbonic acid into formaldehyde and hydrogen peroxide, but this explanation is not so probable as the earlier one, and the formation of hydrogen peroxide from an aqueous solution of oxygen in bright sunlight is a definite experimental fact.[5]

Although the point has been the subject of considerable controversy, hydrogen peroxide really appears to be present in the juices of some plants, but unless especial care is taken certain organic oxidation catalysts (*oxidases*) or oxidising agents, which may also be present, are likely to be mistaken for hydrogen peroxide.[6] The source of the hydrogen peroxide in plants is probably a reaction between carbon dioxide and water of the same course as that suggested above for the chemical change between these substances in sunlight.

**Formation.**—I. *From Peroxides.*—Of the various methods by which hydrogen peroxide has been artificially produced the oldest is that involving the interaction of barium peroxide and a mineral acid. As already mentioned (p. 54), peroxides (superoxides) in general exhibit this reaction.

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[1] Thénard, *Ann. Chim Phys*, 1818, 8, 306; 1819, 11, 209.

[2] See Leeds, *Chem. News*, 1884, 50, 215

[3] Schone, *Ber.*, 1874, 7, 1693, 1877, 10, 482, 561, 874, 1028, 1880, 13, 1503; 1893, 26, 3011; 1894, 27, 1233.

[4] Bach, *Ber.*, 1894, 27, 340

[5] Charitschkoff, *J. Russ. Phys. Chem. Soc*, 1910, 42, 904. Dixon (*Trans. Chem. Soc.*, 1886, 49, 108) believed hydrogen peroxide was formed during evaporation of water. Ramsay (*Proc. Chem. Soc.*, 1886, 2, 225) examined water that had evaporated in air and found a substance capable of decomposing hydrogen peroxide. Compare Smith, *Trans. Chem. Soc.*, 1906, 89, 481.

[6] Phipson, *Chem. News*, 1884, 50, 37, 288; Bach, *Compt. rend*, 1893, 16, 1145; 1894, 119, 286; Bach and Chodat, *Ber.*, 1902, 35, 2466, 3943; 1903, 36, 300, 606, 1756; 1904, 37, 36, 1342, 3785, 3985.

II. *By Electrolysis.*—In 1882 it was observed by M. Traube that during the electrolysis of dilute sulphuric acid, hydrogen peroxide may be found both at the anode and the cathode.[1] Its formation at the anode is to be ascribed to the decomposition of persulphuric acid, $H_2S_2O_8$, which is produced in some quantity. At the cathode the presence of the hydrogen peroxide is due to the reduction of dissolved oxygen, and it has been shown more recently [2] that in solution in dilute sulphuric acid under a pressure of 100 atmospheres oxygen can be so successfully reduced to hydrogen peroxide as to give a yield of more than 80 per cent. of that calculated from the current used, and solutions of 2–3 per cent. concentration can be readily obtained. That the process is merely one of chemical reduction is confirmed by the fact that the dissolved oxygen can be reduced to hydrogen peroxide also by treatment with hydrogen in the presence of the metal palladium.[3]

In the electrolysis of solutions of alkali hydroxides under suitable conditions, hydrogen peroxide is produced at the anode by the combination of the discharged hydroxyl ions.

In contradistinction to ozone, hydrogen peroxide is not produced during the electrolysis of solutions of fluorides.[4]

III. *In Processes of Autoxidation and Slow Combustion.*—As has been mentioned earlier (p. 55), the slow atmospheric oxidation of substances at the ordinary temperature (*autoxidation*) frequently gives rise to peroxidic substances of powerful oxidising properties; these substances are unstable and in their decomposition give rise to ozone, and, if water is present, also to hydrogen peroxide. The slow oxidation of phosphorus in the presence of water is stated to be accompanied by the formation of a little hydrogen peroxide.[5] In such cases the mechanism of the change probably involves the formation of an additive compound of the unstable primary peroxide compound with water, which subsequently decomposes with formation of hydrogen peroxide.

The corrosion of metals is another case of slow oxidation, and in the presence of water appreciable quantities of hydrogen peroxide may be produced; the amalgams of the metals frequently give better results than the metals themselves. If the hydrogen peroxide is removed from the solution as rapidly as it is produced (the addition of barium hydroxide, for example, will remove the hydrogen peroxide as a precipitate of barium peroxide), the yield of hydrogen peroxide may become almost quantitative, and in the case of zinc the final result of the reaction may be represented: [6]

$$Zn+O_2+2H_2O=Zn(OH)_2+H_2O_2.$$

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[1] Traube, *Ber.*, 1882, 15, 2434; 1889, 22, 1518; Richarz, *Ann. Physik*, 1885, [ii.], 24, 183; 1887, 31, 912; Richarz and Lonnes, *Zeitsch physikal. Chem.*, 1896, 20, 147; Bornemann, *Zeitsch. anorg. Chem.*, 1903, 34, 1.

[2] Fischer and Priess, *Ber.*, 1913, 46, 698.

[3] Henckell & Co., *Swiss Patent*, 1914, 63359, 63360.

[4] Pauli, *Zeitsch. Elektrochem*, 1897, 3, 474; Skirrow, *Zeitsch. anorg Chem.*, 1902, 33, 25, Prideaux, *Trans. Farad. Soc.*, 1906, 2, 34.

[5] Kingzett, *Chem. News*, 1878, 38, 243; 1879, 40, 96; 1880, 41, 76; 1881, 43, 127; Leeds, *Chem News*, 1880, 41, 163, 182; 1881, 43, 97; M'Leod, *Trans. Chem. Soc.*, 1880, 37, 118. See, however, Keiser and M'Master, *Amer. Chem J.*, 1908, 39, 96.

[6] Traube, *Ber.*, 1883, 16, 123; 1885, 18, 1887; 1893, 26, 1471; *Zeitsch. physikal. Chem.*, 1900, 32, 137; Barnes and Shearer, *J. Physical Chem.*, 1908, 12, 468; Smith, *Trans. Chem. Soc.*, 1906, 89. 481,

Other metals, *e.g.* magnesium, cadmium, and lead, can be made to yield similar results,[1] as also does palladium hydride[2] when allowed to oxidise in the presence of water containing a little sulphuric acid. It is possible, however, that, at least in the case of lead, the hydrogen peroxide owes its formation to the reduction of dissolved oxygen by nascent hydrogen produced during the corrosion.[3]

Many organic substances, such as alcohols, ethers, acetone, and especially unsaturated compounds like turpentine, are capable of slow oxidation, the action being favoured by exposure to sunlight; in the presence of moisture, hydrogen peroxide is frequently to be found amongst the products of the chemical change.[4] The disinfectant power of the "Sanitas" preparations, the basis of which is obtained by the atmospheric oxidation of wet turpentine oil, is largely due to hydrogen peroxide.

Hydrogen and oxygen, and even steam and oxygen,[5] can be made to combine at low temperatures under the influence of the silent electric discharge, and the process may be regarded as a slow oxidation of hydrogen comparable with the preceding. Also the silent electric discharge generally favours the production of unstable substances. For these two reasons, therefore, the formation of hydrogen peroxide might be expected, and the expectation is justified by experiment. By working with a well-cooled gaseous mixture, it is possible to obtain a considerable yield of hydrogen peroxide,[6] whilst at −80° C. the yield is almost quantitative and the product pure.[7]

IV. *From Water by Radioactive Substances.*—Although radium salts will decompose hydrogen peroxide, they likewise form this substance when their rays act upon water.[8] Kernbaum[9] concluded that the $\beta$ rays are the most effective agents, and suggested that the reaction takes places as follows:

$$2H_2O = H_2O_2 + H_2.$$

V. *From Hydrogen and Oxygen or from Water at High Temperatures.*—Hydrogen peroxide occurs frequently amongst the products of gaseous combustion in the presence of moisture,[10] and of the combination of hydrogen and oxygen by flame or explosion.[11] On account of the instability of hydrogen peroxide, it is advisable to cool the products as rapidly as possible, for example, by allowing the flame to impinge on the surface of cold water or ice,[12] when the condensed liquid will exhibit the reactions of hydrogen peroxide.

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[1] Dunstan, *Trans. Chem. Soc.*, 1911, 100, 1835.

[2] Leeds, *Pharm. J.*, 1881, [3], 11, 1068

[3] Lambert and Cullis, *ibid.*, 1915, 107, 217.

[4] Thénard, *Compt. rend.*, 1872, 75, 458; Houzeau, *ibid.*, 1872, 75, 349; Schaer, *Ber.*, 1873, 6, 406; Kingzett, *Trans. Chem. Soc*, 1874, 12, 511; 1875, 13, 210, Dunstan and Dymond, *ibid*, 1890, 61, 237; Richardson and Fortey, *ibid*, 1896, 69, 1352.

[5] Fischer and Ringe, *Ber.*, 1908, 41, 945.

[6] Fischer and Wolf, *ibid.*, 1911, 44, 2956, Besson, *Compt rend.*, 1911, 153, 877.

[7] Wolf, *Zeitsch. Elektrochem.*, 1914, 20, 204

[8] Kailan, *Monatsh.*, 1911, 32, 1019.

[9] Kernbaum, *Compt. rend*, 1909, 149, 116, 273 See also this Vol, p. 227.

[10] Leeds, *Chem. News*, 1884, 49, 237; Traube, *Ber*, 1885, 18, 1890; Finckh, *Zeitsch. anorg. Chem.*, 1905, 45, 118.

[11] Dixon, *Trans. Chem. Soc.*, 1886, 49, 94; Charitschkoff, *J Russ Phys. Chem. Soc.*, 1910, 42, 904

[12] Engler, *Ber.*, 1900, 33, 1109. See also Nernst, *Zeitsch. Elektrochem.*, 1905, 11, 710.

Whether the production of hydrogen peroxide in the last case is a direct process or is due to the further interaction of water vapour and oxygen at high temperature is rather uncertain. Certainly at very high temperatures oxygen and water-vapour will combine, with formation of some hydrogen peroxide which can be detected after rapid cooling.[1] Indeed, the combination of water-vapour and oxygen may be effected even at 130° C. under the influence of a silent electric discharge, and at very high temperatures even water-vapour alone, without the addition of an excess of oxygen, will undergo slight conversion into hydrogen peroxide.[2] It is therefore possible that the slight formation of hydrogen peroxide in the combustion of hydrogen, of moist carbon monoxide, or cyanogen, may be due to a purely thermal influence on the water, or water and oxygen, present. The observation that traces of hydrogen peroxide are produced when an arc discharge is formed, using very dilute sulphuric acid as a cathode,[3] may have a similar explanation.

## PREPARATION OF HYDROGEN PEROXIDE.

I. *From Metallic Peroxides.*—For the preparation of hydrogen peroxide in quantity, use is generally made of the metallic peroxides. Sodium peroxide reacts with dilute mineral acids producing hydrogen peroxide, but the considerable solubility of sodium salts renders it difficult to obtain a pure solution of the substance except by distillation.[4] Potassium hydrogen tartrate and potassium fluosilicate are sparingly soluble substances, so that dilute aqueous solutions of hydrogen peroxide may be prepared by treating potassium peroxide with dilute solutions of tartaric acid or hydrofluosilicic acid.[4] Barium peroxide, however, is the substance commonly employed.

Some of the earlier processes depending on the use of barium peroxide were inconveniently cumbrous. Thus Thénard, early in the nineteenth century, recommended a method of which the following description is merely an outline, many details being omitted.[5] Powdered barium peroxide was dissolved in dilute hydrochloric acid and the barium then precipitated by the careful addition of sulphuric acid. The resulting solution, containing hydrogen peroxide and hydrochloric acid, together with impurities from the barium peroxide and probably a little sulphuric acid, was treated with a little barium hydroxide solution or barium peroxide emulsion when any heavy metals were precipitated at the same time as the sulphuric acid; by the artifice of previously introducing a little phosphoric acid, any manganese or iron could be simultaneously removed as their respective phosphates, whereas, if allowed to remain, they would have caused rapid decomposition of the hydrogen peroxide. After this treatment the solution contained only hydrogen peroxide and barium chloride, the latter of which was removed by conversion with silver sulphate into silver chloride and barium sulphate. The clear solution of hydrogen peroxide thus obtained possessed a high degree of purity and was finally concentrated in a vacuum over sulphuric acid.

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[1] Fischer and Ringe, *Ber*, 1908, 41, 945; Fischer and Marx, *ibid.*, 1906, 39, 3631; 1907, 40, 443, 1111; Kahlbaum, *German Patent*, 1908, 197023, Findlay, *Zeitsch. Elektrochem.*, 1906, 12, 129.

[2] Fischer and Ringe, *loc. cit.*

[3] Makowetzky, *Zeitsch. Elektrochem.*, 1911, 17, 217.

[4] Merck, *German Patent*, 152173; Hoffmann, *Annalen*, 1865, 136, 188.

[5] Thénard, *Ann. Chim. Phys.*, 1832, 50, 80.

The disadvantage attaching to the direct conversion of barium peroxide into an insoluble salt by treatment with such an acid as sulphuric or carbonic acid, lies in the sparing solubility of the first-named substance which causes the reaction to be incomplete. This difficulty can be remedied by previous prolonged agitation of the anhydrous barium peroxide with water, by which treatment it becomes converted into the hydrated and more reactive compound $BaO_2 . 8H_2O$. This readily yields dilute solutions of hydrogen peroxide when treated with aqueous sulphuric,[1] hydrofluoric,[2] hydrofluosilicic, phosphoric,[3] or carbonic acid.[4] In the case of the last-named acid, it is important to use an excess.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

The resulting solution will contain saline impurities such as salts of iron and manganese derived from the barium peroxide. These can be removed by the addition of a little phosphoric acid followed by neutralisation with barium hydroxide solution when the metals are precipitated as phosphates. If necessary, further addition of barium hydroxide may be made in order to precipitate the hydrogen peroxide as pure barium peroxide, which on treatment with the correct quantity of dilute sulphuric acid will give a pure solution of hydrogen peroxide.

Purification from mineral impurities can also be effected by extracting the impure solution with ether in which hydrogen peroxide is very soluble, although less so than in water.[5] The value of the process is somewhat discounted by the possibility of formation of organic peroxidic compounds which may give rise to violent explosions during the distillation of the ether.[6] Dilute aqueous solutions may be subsequently obtained by merely shaking the ethereal solution with pure water.

II. *From Per-Acids.*—Another process suited to the economical preparation of hydrogen peroxide is based on the decomposition of permonosulphuric acid under the influence of water. The acid, prepared by the electrolysis of sulphuric acid or by the interaction of potassium persulphate and sulphuric acid, undergoes gradual hydrolysis according to the equation

$$H_2SO_5 + H_2O \rightleftharpoons H_2SO_4 + H_2O_2.$$

The hydrogen peroxide can be separated by distillation under reduced pressure.[7]

The use of other per-acid salts such as percarbonates and perborates has been suggested for a similar purpose, as also has the direct treatment of ammonium persulphate with steam.[8]

III. *From Autoxidation Processes.*—The slow oxidation of metals, such as zinc or cadmium, especially in the form of their amalgams, in the presence of water, has also been suggested as a basis for an industrial preparation of hydrogen peroxide.[1]

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[1] Thomsen, *Ber.*, 1874, 7, 73.

[2] Hanriot, *Compt. rend.*, 1885, 100, 57, 172.

[3] Lindner, *Monit. Scientif.*, 1875, [iii], 5, 818; Davis, *Chem. News*, 1879, 39, 221; Bourgougnon, *J. Amer. Chem. Soc.*, 1890, 12, 64.

[4] Duprey, *Compt. rend.*, 1862, 55, 736; Balard, *ibid.*, 1862, 55, 738; Lunge, *Zeitsch. angew. Chem.*, 1890, 4, 3; Mond, *Ber.*, 1883, 16, 980; Merck, *German Patent*, 1907, 179771, 179826.

[5] Crismer, *Bull. Soc. chim.*, 1893, 6, 24; Ossipoff and Popoff, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 637.

[6] Bruhl, *Ber.*, 1895, 28, 2847.

[7] Consortium Elektrochem. Industrie, *German Patent*, 199958 (1908).

[8] Soc l'Air Liquide, *French Patent*, 476816 (1914); Cobellis, *U.S. Patent*, 1195560 (1916).

**Concentration of Solutions.**—In dilute solutions such as are obtained as the first product in most of the methods of preparation, hydrogen peroxide is fairly stable. Very dilute solutions can be concentrated by careful evaporation on a water bath, but it is not usually advantageous to concentrate in this way beyond 50 per cent. because of the increase in the rate of decomposition. Another method of concentrating a dilute solution is to submit it to partial freezing, when the mother liquors are enriched in hydrogen peroxide; by repeating the treatment with the mother liquors several times it is possible to attain a concentration of 30 per cent. with little trouble.[2] The low temperature involved in this method introduces the advantage of reducing the tendency of the solution to undergo spontaneous decomposition. For the preparation of pure hydrogen peroxide, fractional distillation is the most convenient process,[3] the distillation being effected under reduced pressure in order that the temperature may be as low as possible; water, being the more volatile, distils first. The danger of explosive decomposition during distillation [4] appears to be much greater with solutions which have already been concentrated by extraction with ether (see p. 332).

Exceptionally pure hydrogen peroxide was obtained by Maass and Hatcher [5] from a 3 per cent. solution prepared in the usual way from commercial barium hydroxide. This was first concentrated to 30 per cent., using a special type of sulphuric acid concentrator,[6] but this product required very careful handling as all the non-volatile impurities had also been concentrated in the process. The liquid was now distilled at 65° C. under a pressure of 10 mm. of mercury maintained with a sulphuric acid pump. Qualitative analysis of the distillate showed the absence of all non-volatile impurities; sulphuric acid was also absent, but in those cases where the original peroxide solution contained large amounts of chloride, some hydrochloric acid was present in the distillate unless the original solution was first made alkaline. The distillate was now exceedingly pure and contained on the average 85 per cent. of peroxide, the remainder being water. This was concentrated to 90 per cent. peroxide over sulphuric acid in the special concentrator referred to above. It now remained to remove, in so far as possible, the remaining 10 per cent. of water. This was effected by systematic fractional crystallisation, a product containing 99·93 per cent.[7] of peroxide being ultimately obtained.[8] The most concentrated commercial solution of hydrogen peroxide, containing about 30 per cent. $H_2O_2$ is known as *perhydrol* (see p. 336).

**Preservation.**—On account of its instability and even explosive tendency it is advisable to use hydrogen peroxide in the form of a solution, a concentration of 30 per cent. being sufficient for most purposes, whilst much more dilute solutions will often satisfy the needs of experiments. Small traces of alkali, such as may be dissolved from glass,[1] and of such impurities as iron oxide and even dust will greatly accelerate the decomposition of the substance, the stability of the solutions decreasing with concentration. In order to avoid contact with glass, the bottles are frequently lined and stoppered with paraffin wax. A very small quantity of an acid is frequently added as a preservative, sulphuric acid being commonly chosen, but other acids are effective, and certain organic substances [2] have been found to exert a marked preservative action, one of the most effective being acetanilide (see p. 339).

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[1] Lustig, *Dingl. Poly J.*, 1887, 266, 375.

[2] Hanriot, *Compt. rend.*, 1885, 100, 57, 172. See also Ahrle, *J. prakt. Chem.*, 1909, 79, 129.

[3] Wolffenstein, *Ber*, 1894, 27, 3307.

[4] Spring, *Zeitsch. anorg. Chem.*, 1895, 8, 424.

[5] Maass and Hatcher, *J. Amer. Chem. Soc.*, 1920, 42, 2548.

[6] Maass, *ibid.*, p. 2571.

[7] Mean of four estimations with permanganate.

[8] The highest concentration obtained by Brühl (*Ber.*, 1895, 28, 2854) was 99·2 per cent.

It is stated that pure anhydrous hydrogen peroxide does not decompose at 0° C.[3]

## PHYSICAL PROPERTIES OF HYDROGEN PEROXIDE.

Anhydrous hydrogen peroxide is an almost colourless syrupy liquid,[4] which in bulk is seen to have a faint greenish-blue colour rather more marked than that of water.[5] The odour of the pure substance is stated to recall that of nitric acid,[6] but the dilute solutions are without odour.

Pure hydrogen peroxide readily assumes an undercooled condition and may refuse to crystallise even at temperatures as low as $-30°$ C., although its melting-point is $-1·70°$ C.[7] If, however, a small quantity be solidified by strongly cooling, *e.g.* with a mixture of solid carbon dioxide and ether, the product can be used as a nucleus to induce crystallisation at temperatures just below the melting-point. The solid then separates in prismatic crystals, and fractional crystallisation may be applied as an effective method of final purification.[8] Slow evaporation of the liquid can occur at the ordinary temperature,[9] and, under reduced pressure, distillation may be effected with only slight decomposition, the boiling-point under 26 mm. of mercury being 69·2° C.[10] Hydrogen peroxide is denser than water, the following data being given for the anhydrous liquid [11] (99·93 per cent.):

| Temperature, ° C. | $-12·13$ | $-6·23$ | $+0·10$ | 3·00 | 5·55 | 8·30 | 12·60 | 15·30 | 19·90 |
|---|---|---|---|---|---|---|---|---|---|
| Density of $H_2O_2$ | 1·4774 | 1·4705 | 1·4631 | 1·4579 | 1·4570 | 1·4541 | 1·4490 | 1·4465 | 1·4419 |

The variation in density with dilution is shown in the following table [11] (p. 331).

Water is miscible with hydrogen peroxide in all proportions, a slight evolution of heat accompanying the process; although dilute solutions are neutral in reaction, pure hydrogen peroxide appears to be feebly acidic.[12] The aqueous solutions have a characteristic unpleasant taste and, if fairly concentrated, attack the skin, causing a prickling sensation and the formation of opaque white patches which slowly fade. Ether, alcohol, and acetic acid are also good solvents for hydrogen peroxide.

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[1] Drechsel, *J. prakt. Chem.*, 1878, [ii], 18, 303.

[2] Walton and Judd, *Zeitsch. physikal. Chem.*, 1913, 83, 315; Clover, *Amer. J. Pharm.*, 1913, 85, 538; Merck, *German Patent*, 1915, 275499; Fischer, *Pharm. Central-h.*, 1907, 48, 57; *Abstr. J. Chem. Soc.*, 1907, 92, ii, 161. See also Bruhl, *Ber.*, 1895, 28, 2854; Staedel, *Zeitsch. angew. Chem.*, 1902, 15, 642; Kingzett, *J. Soc. Chem. Ind.*, 1890, 9, 3

[3] Maass and Hatcher, *J. Amer. Chem. Soc.*, 1920, 42, 2548.

[4] Wolffenstein, *Ber.*, 1894, 27, 3311.

[5] Spring, *Zeitsch. anorg. Chem.*, 1895, 8, 424.

[6] Hanriot, *Compt. rend.*, 1885, 100, 172

[7] Maas and Hatcher, *loc. cit.*

[8] Staedel, *Zeitsch. angew. Chem.*, 1902, 15, 642; Ahrle, *J. prakt. Chem.*, 1909, 79, 129.

[9] Traube, *Ber.*, 1889, 22, 1528; Wolffenstein, *loc. cit.* See also Clayton, *Trans. Faraday Soc.*, 1916, 11, 164

[10] Bruhl, *loc. cit.*

[11] Maass and Hatcher, *J. Amer. Chem. Soc.*, 1920, 42, 2548

[12] Wolffenstein, *loc. cit.* See also Carrara and Bringhenti, *Gazzetta*, 1903, 33, 362

### DENSITY OF AQUEOUS HYDROGEN PEROXIDE.

(Maass and Hatcher.)

| $H_2O_2$ per cent. | Density at 0° C. | Density at 18° C. |
|---|---|---|
| 0·00 | 0·99987 | 0·99862 |
| 10·57 | 1·0419 | 1·0372 |
| 22·33 | 1·0894 | 1·0815 |
| 40·14 | 1·1655 | 1·1552 |
| 56·70 | 1·2404 | 1·2270 |
| 61·20 | 1·2610 | 1·2465 |
| 73·44 | 1·3235 | 1·3071 |
| 84·86 | 1·3839 | 1·3662 |
| 90·42 | 1·4144 | 1·3955 |
| 98·89 | 1·4596[1] | 1·4404 |
| 99·93 | 1·4632 | .. |

In the following table are given the more important physical constants of hydrogen peroxide as compared with water, compiled from the data supplied by Maass and Hatcher. These may be taken as entirely replacing the earlier data of Bruhl and others.[2]

### PHYSICAL PROPERTIES OF HYDROGEN PEROXIDE.

| Physical Constant. | Hydrogen Peroxide (100 per Cent.). | Water. |
|---|---|---|
| Melting-point . . . | −1·70° C. | 0° C. |
| Density of liquid at 0° C. . | 1·4633 | 0·99987 |
| Mean coefficient of expansion (−10° to +20° C.) . . | 0·00107 | 0·0000 |
| Density of solid . . . | 1·644 | 0·9168 |
| Specific heat of liquid . . | 0·579 | 1·000 |
| Latent heat of fusion of solid . | 74 calories [5] | 79·7 calories |
| Specific heat of solid . . | 0·470 [5] | 0·5057 |
| Surface tension at 0° C. . . | 78·76 dynes | 75·5 [6] |
| Molecular association[3] at 0° C.. | 3·48 | 3·58 [6] |
| Viscosity at 0° . . . | 0·01828 dynes | 0·01793 dynes |
| Refractive index D 22° . . | 1·4139 | 1·3330 [6] |
| Do.[4] D 20° . . | 1·40624 | .. |

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[1] Bruhl's value, 1·4584 for 99·2 per cent peroxide is in fairly close agreement with this figure (Bruhl, *Ber.*, 1895, 28, 2854).

[2] Spring, *Zeitsch. anorg. Chem.*, 1895, 8, 424, 1895, 9, 205; Calvert, *Ann. Physik*, 1900, 1, 483.

[3] Calculated from Ramsay and Young's formula

[4] Bruhl, *loc cit.* Probably at the time of measurement Bruhl's sample only contained 98 per cent. of peroxide.

[5] Believed correct to within 4 per cent.

[6] As given by Maass and Hatcher.

A study of the freezing-point curve of solutions of hydrogen peroxide in water indicates the existence of a definite hydrate $H_2O_2 . 2H_2O$, melting at −51° C.[1]

In aqueous solution, hydrogen peroxide possesses only a very feeble electrical conductivity comparable with that of water, and cannot be regarded as an electrolyte.[2] As a solvent, however, it exhibits certain characteristics similar to water; thus it favours the dissociation of the solute, especially of acids, whilst with salts it tends to form compounds in a manner corresponding with the hydration of substances in aqueous solution [3] (p. 333). The absorption spectrum of hydrogen peroxide for ultra-violet light has been examined.[4]

Hydrogen peroxide is diamagnetic, and that to a greater extent than water. Representing magnetic susceptibility by K, the values for air, water and peroxide at 10° C. are as follow:[5]

$$K_{\text{air}},\ 0{\cdot}25 \times 10^{-7}; \quad K_{\text{water}},\ 7{\cdot}2\ \times 10^{-7}; \quad K_{H_2O_2},\ 8{\cdot}8 \times 10^{-7}.$$

This high value for hydrogen peroxide is in harmony with the observation of Henrichson,[6] that as a general rule unsaturation gives a diamagnetic tendency to a molecule.

## Chemical Properties of Hydrogen Peroxide.

Pure hydrogen peroxide is an extremely unstable substance, and, if suddenly raised in temperature, will explode. The reason is that although indirect determination shows the formation from its elements to be an exothermic process,[7]

$$(H_2)+(O_2)=H_2O_2+46{,}000 \text{ calories},$$

hydrogen peroxide is endothermic with respect to water and oxygen, so that its decomposition into these substances is accompanied by a very considerable evolution of heat:

$$H_2O_2=(H_2O)+\tfrac{1}{2}(O_2)+23{,}000 \text{ calories.}^8$$

Any tendency to decompose on account of local overheating will therefore be accentuated by the heat developed in the decomposition, so that the latter will tend to become explosive.

Hydrogen peroxide does not volatilise appreciably from its aqueous solutions at 50° to 60° C., and its rate of decomposition at these temperatures is not accelerated by stirring.[9]

Although its dilute aqueous solutions are neutral, various indications have been observed of a feeble acidic tendency in some of the reactions of hydrogen peroxide. At the ordinary temperature barium hydroxide reacts with a solution of hydrogen peroxide, giving a precipitate of hydrated barium peroxide, $BaO_2 . 8H_2O$, but at lower temperatures an unstable compound, $BaO_2 . H_2O_2$, is also obtainable.[1] Calcium peroxide in several stages of hydration has been prepared,[2] notably $CaO_2 . 8H_2O$ and $CaO_2 . 2H_2O$ or $Ca(OH)_2 . H_2O_2$. In the presence of ammonia, hydrogen peroxide converts calcium chloride into the peroxide, which is precipitated out from solution.[3] With alkali hydroxides various unstable, highly oxidised products have been obtained, and it is possible that such compounds are involved in the catalytic decomposition of hydrogen peroxide by alkalies.

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[1] Maass and Herzberg, *J Amer. Chem. Soc.*, 1920, 42, 2569. No evidence was obtained of the monohydrate $H_2O_2 . H_2O$, described by Wolffenstein, *Ber*, 1894, 27, 3307.

[2] Calvert, *loc. cit.*; Dewar and Fleming, *Proc. Roy. Soc*, 1897, 62, 250; Jones, Barnes, and Hyde, *Amer. Chem J.*, 1902, 27, 22; Joyner, *Zeitsch anorg. Chem*, 1912, 77, 103.

[3] Jones and Carroll, *Amer. Chem. J.*, 1902, 28, 284; Jones and Murray, *ibid.*, 1903, 30, 205. See also Bredig and Calvert, *Zeitsch. physikal. Chem.*, 1901, 38, 513, for the action of hydrogen peroxide on solutions of alkalies

[4] Rosanoff, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 1146.

[5] Maass and Hatcher, *J Amer. Chem. Soc.*, 1922, 44, 2472.

[6] Henrichson, *Wied. Annalen*, 1884, 22, 121, 1888, 34, 180

[7] Berthelot, *Compt. rend*, 1880, 90, 331, 897; Thomsen, *Thermochemistry*, translated by Burke (Longmans, 1908), p. 193; de Forcrand, *ibid.*, 1900, 130, 1620.

[8] Tanatar, *Ber.*, 1903, 36, 1873.

[9] Clayton, *Trans. Faraday Soc.*, 1916, 11, 164.

On addition of 30 per cent. peroxide to sodium hydroxide or ethoxide a precipitate of *sodium perhydroxide* is obtained to which the formula[4] $2NaHO_2 . H_2O_2$ is given. This possesses marked basic properties, and on saturation with carbon dioxide yields the acid percarbonate,[5] $NaHCO_4$. The same compound is formed when hydrogen peroxide is added to sodyl hydroxide,[4] $NaO . OH$. This latter substance was first prepared by Tafel[6] by the action of sodium peroxide upon well-cooled absolute alcohol.

With potassium hydroxide two compounds have been obtained, namely, $2KHO_2 . H_2O_2$[7] and $2KHO_2 . 3H_2O_2$.[4]

On passing dry ammonia into a solution of pure hydrogen peroxide in absolute ether[8] at −10° C., or into pure anhydrous peroxide[9] at 0° C., ammonium perhydroxide, $NH_4O . OH$, or $NH_3 . H_2O_2$, crystallises out. Further addition of ammonia is stated[10] to convert this into an oily mass which solidifies at about −40° C. and has the composition $(NH_4)_2O_2$, and is therefore ammonium peroxide, the analogue of sodium peroxide.[8] The crystals of ammonium perhydroxide melt at 24·5° C. to an oily liquid, which is stable in the entire absence of water.[9]

The frequent occurrence of additive compounds of hydrogen peroxide with basic organic compounds[11] also appears indicative of an acidic tendency, although it is quite possible that in such compounds the hydrogen peroxide is playing a similar rôle to water in the so-called water of crystallisation; indeed, many salts do give rise to additive compounds with hydrogen peroxide, a solution of ammonium sulphate in 30 per cent. hydrogen peroxide on evaporation in a vacuum depositing crystals of the composition, $(NH_4)_2SO_4 . H_2O_2$, and analogous compounds with other salts are producible in a similar manner.[1] In such compounds the hydrogen peroxide is only feebly combined and is removable by the addition of water or by extraction with ether.[2] Quite frequently it happens that the hydrogen peroxide "of crystallisation" is accompanied by water of crystallisation, the sodium salt,[3] $2Na_2SO_4 . 2H_2O . H_2O_2$, corresponding with the above ammonium salt being a case in point.

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[1] Schone, *Annalen*, 1878, 192, 257; 1878, 193, 241; Berthelot, *Compt. rend.*, 1880, 90, 334.

[2] Foregger and Philipp, *J Soc. Chem. Ind.*, 1906, 25, 298.

[3] Macri, *Boll. chim farm.*, 1917, 56, 417.

[4] d'Ans and Friederich, *Zeitsch. anorg. Chem.*, 1912, 73, 325.

[5] Wolffenstein, *German Patent*, 196369 (1908); Wolffenstein and Peltner, *Ber.*, 1908, 41, 280; Wolffenstein gives the substance the formula NaOOH, which makes it isomeric with Tafel's sodyl hydroxide.

[6] Tafel, *Ber.*, 1894, 27, 816, 2297.

[7] Schone, *Annalen*, 1878, 193, 276, 289; d'Ans and Friederich, *loc. cit.*

[8] d'Ans and Wedig, *Ber.*, 1913, 46, 3075 Compare the data of Melikoff and Pissarjevski, *Ber.*, 1897, 30, 3144; 1898, 31, 152, 446.

[9] Maass and Hatcher, *J. Amer. Chem. Soc*, 1922, 44, 2472.

[10] d'Ans and Wedig, *loc cit.* This is disputed by Maass and Hatcher, *loc. cit.*

[11] Marcuse and Wolffenstein, *Ber.*, 1901, 34, 2430; Tanatar, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 376; von Girsewald, *Ber*, 1912, 45, 2571; Vanino and Schinner, *ibid.*, 1914, 47, 699, Stoltzenberg, *ibid*, 1916, 49, 1545; Bamberger and Nussbaum, *Monatsh.*, 1919, 40, 411.

When a mixture of hydrogen peroxide and hydrochloric acid is evaporated in a platinum dish, a certain amount of chlorplatinic acid is formed.[4] Hydrogen peroxide is capable of displacing acids, notably the halogen acids,[5] in certain circumstances. Addition of saturated copper nitrate solution to the peroxide results in the precipitation of brown hydrated copper oxide with simultaneous evolution of oxygen. A similar precipitate is obtained when copper foil is introduced into a solution of hydrogen peroxide containing alkali nitrates or sulphates. The reaction is presumed[6] to take place in several stages; thus, in the case of sodium sulphate solution

$$\begin{gathered} Na_2SO_4+H_2O_2=Na_2O_2+H_2SO_4; \\ Na_2O_2+H_2O=2NaOH+H_2O_2; \\ Cu+H_2SO_4+H_2O_2=CuSO_4+2H_2O; \\ CuSO_4+2NaOH=Na_2SO_4+CuO . H_2O. \end{gathered}$$

Hydrogen peroxide vapour affects a photographic plate in the same way as exposure to light,[7] the sensitised film detecting the presence of as little as $3 \times 10^{-9}$ grams of vapour per cubic centimetre;[8] in this power is probably to be found the explanation of the photographic action of some oxidisable metals.[9] The effect is a chemical one,[10] probably analogous to the action of hydrogen peroxide on silver oxide (see later).

Towards protoplasm hydrogen peroxide exerts a decidedly poisonous action,[11] and so causes the death of organic ferments such as yeast, although it does not necessarily affect the activity of the enzymes. Cases have been observed of seeds, moulds, and phagocytes the growth of which was favoured by very dilute solutions of hydrogen peroxide,[12] but it is possible that such results may be due to the presence in the organism of some organic catalyst (catalase) which causes the decomposition of the peroxide and so prevents its usual action.[13] In dilute aqueous solution hydrogen peroxide forms an excellent antiseptic wash for open sores and wounds.[1]

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[1] Tanatar, *Zeitsch. anorg. Chem.*, 1901, 28, 255; *Ber.*, 1899, 32, 1544; Rudenko, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 1209, Melikoff, *ibid.*, 1902, 34, 207; Kazanecki, *ibid.*, 1914, 46, 1110. Maass and Hatcher, *loc. cit.*

[2] Petrenko, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 204, 391.

[3] Willstätter, *Ber*, 1903, 36, 1828.

[4] Macri, *Boll. chim. farm.*, 1917, 56, 417.

[5] Sperber, *Chem. Zentr.*, 1914, i., 738, 2139; 1913, ii., 1195; 1913, i, 502, 1490.

[6] Sperber, *ibid*, 1916, i., 453.

[7] Dony-Hénault, *ibid.*, 1906, ii., 203; Russell, *Proc. Roy. Soc*, 1899, 64, 409; Dony-Hénault, *Bull. Soc. chim. Belg.*, 1908, 22, 224.

[8] van Aubel, *Compt. rend.*, 1904, 138, 961; Precht and Otsuki, *Zeitsch physikal Chem.*, 1905, 62, 236.

[9] Saeland, *Ann. Physik*, 1908, 26, 899.

[10] And not due to radiation as suggested by Graetz, *Physikal. Zeitsch*, 1904, 5, 688, Merckens, *Zeitsch. angew. Chem*, 1905, 18, 489.

[11] Bert and Regnard, *Compt. rend*, 1882, 94, 1383; Hamlet, *Trans. Chem. Soc.*, 1881, 39, 326.

[12] Demoussy, *Compt rend.*, 1916, 162, 435; Chodat and Bach, *Ber.*, 1902, 35, 1275; Hamburger, *Intern. Zeitsch. phys.-chem. Biol.*, 1915, 2, 255.

[13] Loew, *Ber.*, 1902, 35, 1275.

Some of the most striking properties of the substance are connected with its ready decomposition and the closely related oxidising power which have proved very attractive fields for physico-chemical investigations.

**Catalytic Decomposition.**—Hydrogen peroxide can be regarded as stable only in cold dilute aqueous solutions free from even traces of alkali, compounds of the heavy metals, and suspended solid matter, and when protected from exposure to bright illumination. Thus in solution in tap water decomposition occurs fifty times as rapidly as in conductivity water.[2] Minute quantities of alkalis markedly accelerate the rate of decomposition,[3] possibly by the intermediate formation of unstable " salts " of the peroxide (see p. 333), the activity of the catalyst being dependent upon concentration of the hydroxyl ion which it yields.[4] Exposure to ultra-violet radiation also induces the rapid decomposition of hydrogen peroxide, the reaction in this case being unimolecular,[5] and also differing from the spontaneous or purely thermal decomposition of the solutions in being accelerated both by alkalis and acids.[6]

On account of the extreme sensitiveness of hydrogen peroxide to external influences, it is almost impossible to consider the decomposition process apart from the effect of catalysts because the minute traces of foreign matter inevitably present in a " pure " substance and the walls of the containing vessel are capable in this case of producing a disproportionate effect on the stability of the compound. Even water exerts a distinct catalytic effect.[7] Ordinary pure hydrogen peroxide and its solutions, as is to be expected, decompose more rapidly when the temperature is raised,[8] but, as has already been stated, the decomposition is sufficiently gradual to permit distillation under reduced pressure. The thermal decomposition is a bimolecular process, and in the case of the pure compound the heat generated during the chemical change tends to make this become explosive. With pure hydrogen peroxide the oxygen liberated measured at 14° and 760° mm. is 475 times the volume of the original hydrogen peroxide; with solutions of the substance the volume of oxygen (at N.T.P.) producible by the decomposition of unit volume of the solution supplies a convenient method of expressing the concentration; solutions are therefore frequently sold not as of a certain percentage concentration but as " ten volume," " twenty volume," etc.:

$$2H_2O_2=2H_2O+O_2.$$

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[1] Bonjean, *Compt. rend.*, 1905, 140, 50. For the action of hydrogen peroxide on the living organism, see Capranica and Colasanti, *Ber*, 1883, 16, 1105.

[2] Clayton, *Trans Faraday Soc*, 1916, 11, 164.

[3] Schone, *Annalen*, 1878, 192, 257: Berthelot, *Compt. rend.*, 1880, 90, 334; Tammann, *Zeitsch. physikal. Chem*, 1889, 4, 441; Lemoine, *Compt. rend*, 1915, 161, 47.

[4] Schenck, Vorlander, and Dux, *Zeitsch. angew. Chem*, 1914, 27, 291.

[5] Tian, *Compt. rend.*, 1910, 151, 1040, *Thesis*, 1915; see *Abstr. J. Chem. Soc.*, 1915, 108, ii., 828; Mathews and Curtis, *J. Physical Chem.*, 1914, 18, 166, 521; Kornfeld, *Zeitsch. wiss. Photochem.*, 1921, 21, 66.

[6] D'Arcy, *Phil. Mag.*, 1902, 3, 42, Thiele, *Ber*, 1907, 40, 4914.

[7] Lemoine, *Compt. rend.*, 1912, 155, 9.

[8] Wolffenstein, *loc. cit.* See also Nernst, *Zeitsch physikal. Chem.*, 1904, 46, 720; *Zeitsch. Elektrochem.*, 1905, 11, 710.

A ten-volume strength corresponds approximately to a 3 per cent. solution, and a twenty-volume strength to a 6 per cent. Perhydrol (p. 329) is practically a 30 per cent. solution corresponding to a one hundred-volume strength.

Many other substances than those mentioned above possess the power of markedly influencing the rate of decomposition of hydrogen peroxide, especially in feebly alkaline solution. Carbon,[1] silver, gold, the platinum metals, and many other substances [2] in a fine state of division are exceedingly active, but if the metal exposes only a smooth polished surface, the result may be relatively inappreciable.[3] In colloidal solution the activity of the noble metals is still greater,[4] and the effect of one part of colloidal platinum in more than 100,000,000 times its weight of water exerts a distinct catalytic action. Whether the effect of such metals is due to a mere surface action or to the continuous formation and decomposition of an intermediate unstable oxide is uncertain, but the former view appears more probable, because all finely divided substances exhibit a similar although often feebler effect; silica powder, for example, has a very considerable accelerating influence on the decomposition.[5] It is a very remarkable fact that these colloidal substances lose their power in the presence of almost equally small quantities of such substances as mercuric chloride, phosphorus and arsenic hydrides, hydrocyanic acid, and hydrogen sulphide, which are therefore described as "poisons" to the catalyst.[6] Some organic substances such as alcohol act similarly.[7] The decomposition of hydrogen peroxide is usually regarded as a reaction of the first order [8] or monomolecular, whether in acid or in neutral solution. The reaction is convenient to study, since its rate can be followed by titration with permanganate, or volumetrically, by measuring the volume of evolved oxygen.

In alkaline solution the activity of the colloidal platinum increases to a maximum with increase of alkalinity, and then decreases. In this respect it behaves in an analogous manner to certain inorganic ferments.[9] Exposure to Röntgen rays retards the reaction.[10] Colloidal rhodium,[11] palladium, iridium,[12] silver, and gold behave in an analogous manner to platinum. By increasing the pressure of oxygen in contact with the decomposing solution from one to 200 atmospheres the rate of decomposition is not appreciably affected.[1]

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[1] Lemoine, *Compt. rend.*, 1916, 162, 725.

[2] Filippi, *Chem. Zentr.*, 1907, ii., 1890.

[3] Spring, *Bull. Acad. roy. Belg.*, 1895, [3], 30, 32; Teletoff, *J. Russ. Phys. Chem Soc.*, 1907, 39, 1358; Lemoine, *Compt. rend.*, 1916, 162, 657.

[4] Bredig and others, *Zeitsch physikal. Chem*, 1899, 31, 258, 1901, 37, 1, 323; *Ber.*, 1904, 37, 798; Kastle and Loevenhart, *Amer. Chem. J.*, 1901, 26, 518; 1903, 29, 397, 563; Senter, *Proc Roy. Soc.*, 1904, 74, 566; Price and Friend, *Trans. Chem. Soc*, 1904, 85, 1526; Paal and Amberger, *Ber.*, 1907, 40, 2201; Teletoff, *J. Russ. Phys. Chem. Soc.*, 1907, 39, 1358; Lebedeff, *Bull. Soc. chim.*, 1908, 3, 56; MacInnes, *J. Amer. Chem Soc.*, 1914, 36, 878; Lemoine, *loc. cit.*

[5] Lemoine, *Compt. rend.*, 1916, 162, 702.

[6] Bredig and Fortner, *Ber.*, 1904, 37, 798. See also the above references to Bredig's papers; Brossa, *Zeitsch. physikal. Chem.*, 1909, 66, 162; Maxted, *Trans. Chem. Soc.*, 1922, 121, 1760

[7] Meyerhof, *Pflugers Archiv*, 1914, 157, 307.

[8] Disputed by Rocasolano, *Anal. Fis. Quim.*, 1920, 18, 361; *Compt rend.*, 1920, 170, 1502.

[9] For further details the reader is referred to this series, Vol. IX., Part II.

[10] Schwarz and Friedrich, *Ber.*, 1922, [A], 55, 1040.

[11] Kernot and Arena, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [3], 15, 157; Zenghelis and Papaconstantinos, *Compt. rend.*, 1920, 170, 1178, 1058.

[12] Brossa, *Zeitsch. physikal. Chem*, 1909, 66, 162; Kernot and Arena, *loc. cit.*, pp. 125, 145.

Other metals, the commonest being lead,[2] bismuth, and manganese, in powder form exert a more moderate effect on the decomposition. Mercury would also fall into this class of moderate accelerators, but the catalytic action in this case is remarkable in being periodic or rhythmic. When the concentration of hydrogen ion is reduced to an almost negligible quantity by the addition of a little sodium acetate solution, a clean mercury surface in contact with hydrogen peroxide solution of approximately 10 per cent. concentration, at periodic intervals of about one second, becomes coated with a bronze film which suddenly disappears with a burst of oxygen from the contact layer of the two liquids ; the substance of the film, which is alternately formed and decomposed, is probably an unstable oxide, possibly mercurous peroxide.[3]

Copper, nickel, cobalt, and cadmium have only a feeble effect on the rate of decomposition of the substance.

Many compounds, especially various metallic oxides, also induce very rapid decomposition of hydrogen peroxide without themselves being permanently changed.[4] In addition to the solutions of the alkali hydroxides already mentioned, manganese dioxide, cobalt oxide, and lead oxide (massicot) are remarkably active, and as might be expected a colloidal solution of manganese dioxide [5] is also able to exert powerful catalytic influence.[6] The effect in such cases may be partly a surface effect, but is also probably due in part to the intermediate formation and decomposition of unstable highly oxidised derivatives.

The oxides of iron, bismuth, copper, cerium, and magnesium are capable of exerting an appreciable influence on the rate of decomposition,[7] but much depends on the physical condition of the solid, freshly precipitated iron oxide, for example, being more effective than the ignited substance ; [8] aluminium hydroxide is rather exceptional in behaving as a "negative catalyst" and retarding the decomposition.

Amongst other inorganic catalysts are to be included the iodides [9] (also bromides and chlorides but less active) and chromates or dichromates. The agent in the former case appears to be the iodide ion, the mechanism of the reaction probably involving oxidation to hypoiodite which then reacts with more hydrogen peroxide with formation of iodide, and water and free oxygen[1] (compare the reaction with hypochlorites, p. 341).

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[1] Spear, *J. Amer. Chem. Soc.*, 1908, 30, 195.

[2] See Zotier, *Bull. Soc. chim.*, 1917, 21, 241.

[3] Bredig and Weinmayr, *Zeitsch. physikal. Chem*, 1903, 42, 601 ; Bredig and Wilke, *Biochem. Zeitsch.*, 1908, 11, 67 ; von Antropoff, *Zeitsch. physikal Chem.*, 1908, 62, 513 ; *J. prakt. Chem.*, 1908, 77, 273 ; Lemoine, *Compt. rend.*, 1916, 162, 580 ; Okaya, *Proc. Phys. Math. Soc. Japan*, 1919, [3], 1, 283.

[4] See Lemoine, *Compt. rend.*, 1916, 162, 702.

[5] See Lottermoser and Lehmann, *Kolloid. Zeitsch*, 1921, 29, 250.

[6] Bredig and Marck, *Gedenkboek. aangeb. aan Bemmelen*, 1910, p. 342 ; *Abstr. Chem. Soc.*, 1911, 100, ii., 399.

[7] Thénard, *Ann. Chim. Phys.*, 1818, [2], 9, 441 ; 1819, 10, 114, 335 ; 11, 85

[8] Lemoine, *Compt. rend.*, 1916, 162, 702.

[9] Weltzien, *Ann. Chim. Phys.*, 1860, 59, 105 ; *Bull. Soc. chim*, 1866, [2], 5, 261 ; Schone, *Annalen*, 1879, 195, 228 ; *Chem News*, 1881, 43, 149, 249 ; Kingzett, *Chem. News*, 1881, 43, 161, 278 ; Berthelot, *Compt. rend.*, 1880, 90, 333 ; Pechard, *Compt. rend.*, 1900, 130, 1705 ; Orlov, *J. Russ. Phys Chem Soc.*, 1912, 44, 1598, 1623 ; Bohnson, *J. Physical Chem.*, 1920, 24, 677.

$$H_2O_2+I'=H_2O+IO';$$
$$H_2O_2+IO'=H_2O+I'+O_2.$$

The action of iodides is catalytic only in neutral solution; in alkaline solution oxidation occurs with formation of free iodine. Whilst chromates and dichromates accelerate the decomposition of hydrogen peroxide, the action is not purely catalytic because some of the chromate or dichromate undergoes permanent reduction, so that the change falls more correctly into the next section.[2]

With iodine the following reactions are believed to occur:[3]

$$\text{(i)}\quad 5H_2O_2+I_2=2HIO_3+4H_2O,$$
$$\text{(ii)}\quad 5H_2O_2+2HIO_3=5O_2+I_2+6H_2O,$$
$$\text{(iii)}\quad 2H_2O_2=2H_2O+O_2,$$

the last-named reaction being catalysed by the iodic acid—iodine couple. In ammonium hydroxide solution the reaction takes place[4] in accordance with the equation

$$2NH_3+I_2+H_2O_2=2NH_4I+O_2.$$

Manganous sulphate[5] and ferric salts in general accelerate the decomposition of hydrogen peroxide.[6] The sulphate is less active than the chloride or nitrate. With dilute solutions of the salts the effect is proportional to the concentration of the peroxide and that of the iron ions, whilst in the presence of acids it is inversely proportional to the hydrogen-ion concentration. The temperature coefficient of the reaction is 3 25 for ten degrees.[7]

If a few drops of potassium ferrocyanide solution are added to dilute hydrogen peroxide (1 per cent.), and kept in the dark, decomposition of the latter is exceedingly slow. On placing in direct sunlight for a few moments, however, brisk evolution of oxygen takes place and continues, even after removal from the light. The effect is not due to rise of temperature, but, presumably, to some catalyst generated under the influence of the light.[8]

Even carbon, in the form of charcoal, catalytically decomposes hydrogen peroxide,[9] its activity being apparently connected with its absorptive power for gases.

Certain complex organic substances are known to catalyse the decomposition of hydrogen peroxide[1]: of these "catalases" the best known is the "hæmase" present in blood,[2] in the presence of which the decomposition process is greatly accelerated and approximates to a unimolecular reaction. It is a remarkable circumstance that many of the "poisons" which destroy the catalytic power of the colloidal noble metals have a similar effect on the power of hæmase, but the list of poisons is not quite the same for the two types of catalyst.[3] In view of the marked influence of these poisons or negative catalysts it is possible that the various preservatives mentioned earlier are effective in a similar manner, namely, by checking the activity of traces of positive catalysts such as alkali.

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[1] Bredig and Walton, *Zeitsch. Elektrochem.*, 1903, 9, 114; Walton, *Zeitsch. physikal. Chem.*, 1904, 47, 185; Bredig, *Zeitsch. physikal. Chem.*, 1904, 48, 368. See also Abel, *Zeitsch. Elektrochem*, 1908, 14, 598.

[2] See Orlov, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 1576; Spitalsky, *ibid.*, 1910, 42, 1085; Riesenfeld, *Ber.*, 1911, 44, 147.

[3] Bray, *J. Amer. Chem. Soc.*, 1921, 43, 1262. See also Abel, *Zeitsch. physikal. Chem*, 1920, 96, 1; *Monatsh.*, 1920, 41, 405; Auger, *Compt. rend.*, 1911, 152, 712.

[4] Broeksmit, *Pharm. Weekblad,* 1917, 54, 1373.

[5] Porlezza and Norzi, *Atti R. Accad. Lincei*, 1913, 22, i., 238.

[6] Bohnson, *J. Physical Chem*, 1921, 25, 19; Bertalan, *Zeitsch. physikal. Chem*, 1920, 95, 328.

[7] Bertalan, *loc. cit.*

[8] Kistiakowsky, *Zeitsch. physikal. Chem.*, 1900, 35, 431; Winther, *Chem Zentr.*, 1920, i., 723.

[9] Lemoine, *Compt. rend.*, 1916, 162, 725.

It is interesting to note that metallic salts may catalytically decompose hydrogen peroxide in organic solvents such as amyl acetate and quinoline. In the latter solvent, if not more than 2 per cent. of water is present, the velocity of decomposition in the presence of manganese acetate corresponds to that required for a bimolecular reaction. But if the quinoline is saturated with water, the reaction is monomolecular.[4] On the other hand, not a few organic substances tend to stabilise hydrogen peroxide solutions. Amongst these are oxalic,[5, 7] uric and benzoic acids,[5] acetanilide[6] (see p. 330).

Concentrated solutions of sodium chloride[8] preserve the peroxide, provided a catalyst such as sodium hydroxide[5] is excluded. Dilute sulphuric acid is very effective, even 0·00066 gram of the acid per litre exerting a marked retarding effect upon the rate of decomposition[6] of 30 per cent. peroxide solution. There would appear to be no simple relationship between the retardation effect and the concentration of the sulphuric acid. A yellow bottle is preferable to a white or blue one.[8]

Although not strictly a case of catalysis, the effect of radium radiation on the rate of decomposition of hydrogen peroxide is most conveniently mentioned here; the penetrating rays are the most effective.[9]

**Decomposition with Self Reduction.**—There is a numerous class of chemical substances containing oxygen which, when placed in contact with hydrogen peroxide, cause the latter to change into water and oxygen whilst they themselves simultaneously lose oxygen. This result is again to be attributed in many cases to the primary formation of unstable more highly oxidised molecules. Many oxides of the noble metals, *e.g.* $Au_2O_3$, $PtO_2$, and HgO, exhibit this behaviour with neutral or alkaline solutions and emerge in the metallic state. Silver oxide behaves similarly and the action has been carefully investigated; apparently the change is not strictly representable by the equation

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[1] Béchamp, *Compt. rend.*, 1882, 94, 1720, Bach and Chodat, *Ber.*, 1903, 36, 600, 606, 1756; Bach, *ibid.*, 1905, 38, 1878; Waentig and Steche, *Zeitsch. physiol. Chem*, 1911, 72, 226, 1913, 83, 315; 1914, 93, 228; Waentig, *ibid*, 1912, 79, 177, 446, Phragmén, *Medd. K. Vetenskapsakad Nobel-Inst*, 1919, 5, No. 22, 1.

[2] Senter, *Zeitsch. physiol. Chem*, 1911, 74, 101; *Zeitsch. physikal. Chem.*, 1903, 44, 257, Ville and Moitessier, *Bull. Soc. chim.*, 1902, [3], 27, 1003; 1903, [3], 30, 978; Evans, *Biochem. J.*, 1907, 2, 133.

[3] Senter, *Proc. Roy. Soc*, 1905, 74, 201, 566, Bredig and Ikeda, *Zeitsch. physikal. Chem.*, 1901, 37, 1; Kastle and Loevenhart, *Amer Chem J.*, 1901, 26, 518; 1903, 29, 397.

[4] Walton and Jones, *J. Amer. Chem Soc.*, 1916, 38, 1956

[5] Porlezza and Norzi, *Atti R. Accad. Lincei*, 1913, 22, i., 238.

[6] Walton and Judd, *Zeitsch physikal. Chem.*, 1913, 83, 315.

[7] Fischer, *Pharm. Centr.-h*, 1907, 48, 57, 79. Contrast Arth, *Chem. Zeitung*, 1901, p. 568.

[8] Allain, *J. Pharm. Chim.*, 1906, 24, 162.

[9] Kailan, *Monatsh.*, 1911, 32, 1019; Fenton, *Proc. Cambr. Phil. Soc.*, 1904, [5], 12, 424.

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$$

as might be expected. More oxygen is evolved than would be generated by the hydrogen peroxide alone, but the quantity is not exactly double. The probable course of the reaction is the formation of a peroxidic derivative of silver which then decomposes into silver and oxygen, the finely divided silver produced, possibly accompanied by some oxygen derivative of silver, catalytically accelerating the independent decomposition of the hydrogen peroxide.[1]

In the majority of such reactions, however, the oxidised compound and the hydrogen peroxide appear to undergo reduction to an equivalent extent. Ozone and hydrogen peroxide react as follows:[2]

$$H_2O_2 + O_3 = H_2O + 2O_2$$

(see p. 151); this relationship holds only for the process in alkaline solution, in acid solution an excessive quantity of ozone undergoing decomposition except when a very large excess of hydrogen peroxide is present.[3] This is explained on the assumption that the interaction between ozone and hydrogen peroxide is accompanied by the spontaneous decomposition of ozone, this latter reaction being catalytically accelerated by the peroxide.

Although manganese dioxide behaves merely as a catalyst towards a neutral or alkaline solution of hydrogen peroxide, yet in acid solution reduction occurs to manganous oxide, MnO, or a corresponding salt, the hydrogen peroxide undergoing simultaneous reduction with the liberation of an equal amount of free oxygen.[4] Lead dioxide and hydrogen peroxide in acidic solution likewise undergo mutual reduction. In both cases half the liberated oxygen may be attributed to the dioxide and half to the peroxide, but it is also possible that the mechanism of the reaction may involve the transference of an oxygen atom from the metallic peroxide to the hydrogen peroxide which thereby becomes oxidised to water and oxygen. If the latter view is correct, the liberated oxygen comes entirely from the hydrogen peroxide, but with either explanation the final result is the same. As manganous oxide, MnO, and lead oxide, PbO, are oxidised by hydrogen peroxide in the presence of alkali giving the corresponding dioxides, it is quite possible that the catalytic effect of manganese dioxide and of the less active lead dioxide on an alkaline solution of hydrogen peroxide is due to the repeated oxidation and reduction of the monoxides by the hydrogen peroxide.

Already, in the consideration of methods for the preparation of oxygen, mention has been made of the interaction of hydrogen peroxide with alkaline solutions of ferricyanides[5] and with acidic solutions of hypochlorites[1] and permanganates[2] (hypochlorous and permanganic acids) with formation of the corresponding ferrocyanides, chlorides, and manganese salts. In these cases the reactions occur quantitatively, and can be represented as follows:

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[1] Thénard, *loc. cit.*; Berthelot, *Compt. rend.*, 1880, **90**, 572; 1901, **132**, 897; *Bull. Soc chim.*, 1880, [2], **34**, 135; *Ann. Chim. Phys.*, 1897, [7], **11**, 217; Bayley, *Phil. Mag.*, 1879, [5], **7**, 126.

[2] Schone, *Annalen*, 1879, **196**, 239; Inglis, *Trans. Chem. Soc.*, 1903, **83**, 1013.

[3] Rothmund, *8th Intern. Congr. Appl. Chem.*, 1912, **26**, 611; Rothmund and Burgstaller, *Monatsh.*, 1917, **38**, 295.

[4] Thénard, *Compt. rend.*, 1872, **75**, 177; Bayley, *Phil. Mag.*, 1879, [5], 126

[5] Quincke, *Zeitsch. anal. Chem.*, 1892, **31**, 1; Barralet, *Chem. News*, 1899, **79**, 136.

$$\begin{aligned}2K_3FeC_6N_6+2KOH+H_2O_2&=2K_4FeC_6N_6+2H_2O+O_2;\\ HOCl+H_2O_2&=HCl+H_2O+O_2;\\ 2HMnO_4+2H_2SO_4+5H_2O_2&=2MnSO_4+8H_2O+5O_2.\end{aligned}$$

Again, the view is held by some chemists that in the interaction of permanganic acid and hydrogen peroxide the liberated oxygen originates entirely from the latter substance, which is oxidised by the permanganic acid with production of water and free oxygen.[3] In addition to this, the observation that at temperatures below 0° C., interaction, as demonstrated by the decolorisation of the permanganate, will occur without any marked effervescence of oxygen, has led to the suggestion that a higher oxide, possibly hydrogen trioxide, $H_2O_3$,[4] or hydrogen tetroxide, $H_2O_4$,[5] is an unstable intermediate product, and that the evolution of oxygen occurs in the decomposition of this. This view has been vigorously combated,[6] and it appears highly probable that the lack of effervescence in the cold is due merely to the oxygen remaining in supersaturated solution and perhaps in part as persulphuric acid if sulphuric acid is originally present. Even below 0° C. most of the oxygen may be liberated in the gaseous condition, and the reaction is so definite in its results at the ordinary temperature as to constitute a trustworthy and convenient method for the estimation of the concentration of hydrogen peroxide solutions.

In alkaline media, chromium oxide undergoes oxidation to a chromate.[7] The importance of the medium is again seen in this case, because in acid solution a bichromate or chromic acid yields an unstable blue solution containing a labile perchromic acid which is stated to have the composition $HCrO_4$ or $H_2CrO_5$, according to the relative properties of the reagents. The blue solution soon decomposes, giving, in the presence of sulphuric acid, ordinary chromium sulphate and oxygen[8]; the blue compound can be extracted with ether in which a more stable solution is obtained. The blue coloration has for years been made use of as a convenient and delicate test for chromic acid and for hydrogen peroxide.

Potassium persulphate[9] also reacts slowly with hydrogen peroxide solutions, giving potassium hydrogen sulphate and oxygen—

$$H_2O_2+K_2S_2O_8=2KHSO_4+O_2.$$

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[1] Schone, *Annalen*, 1879, 196, 239; Fairley, *Trans Chem. Soc.*, 1877, 31, 1; Aschoff, *J. prakt Chem.*, 1860, 81, 487

[2] Thénard, *Compt. rend*, 1872, 75, 177, Berthelot, *Ann. Chim. Phys.*, 1880, [5], 21, 176; Baeyer and Villiger, *Ber.*, 1900, 33, 2488; Engel, *Bull. Soc. chim.*, 1891, 6, 17. The kinetics of this reaction has been studied by Zawidzki, *Roczniki Chemji*, 1921, 1, 135

[3] Traube; references on p. 56

[4] Berthelot, *Ann. Chim. Phys*, 1901, [7], 22, 433; also *loc cit.*

[5] Bach, *Ber.*, 1900, 33, 1506, 3111; 1902, 35, 158, 3424.

[6] Baeyer and Villiger, *loc. cit*, Armstrong, *Proc. Chem. Soc*, 1900, 16, 134; Ramsay, *Trans Chem. Soc.*, 1901, 79, 1224; Clover, *Amer. Chem. J.*, 1903, 29, 463.

[7] Lenssen, *J. prakt. Chem.*, 1860, 81, 276; Martinon, *Bull. Soc. chim*, 1886, 45, 862; Barreswil, *Compt. rend.*, 1843, 16, 1085; *Ann. Chim. Phys.*, 1847, 20, 364; Brodie, *Proc. Roy. Soc.*, 1861, 11, 442, Spitalsky, *J. Russ. Phys Chem. Soc.*, 1910, 42, 1085; *Ber.*, 1910, 43, 3187; *Zeitsch anorg Chem.*, 1907, 53, 184; 56, 72; Riesenfeld, *Zeitsch. anorg. Chem*, 1912, 74, 48; *Ber*, 1911, 44, 147.

[8] See this volume, Part III.

[9] Friend, *Trans. Chem. Soc.*, 1906, 89, 1092.

A suspension of silver chloride in potassium hydroxide solution is rapidly reduced by hydrogen peroxide in accordance with the equation [1]

$$2AgCl + H_2O_2 + 2KOH = 2Ag + 2KCl + 2H_2O + O_2.$$

**Oxidation Processes.**—Hydrogen peroxide possesses exceptional activity as an oxidising agent. Nascent hydrogen is oxidised to water, so that, on electrolysis, hydrogen peroxide solutions undergo reduction at the cathode whilst at the anode also decomposition occurs, the nascent oxygen appearing to have a similar effect to permanganic or hypochlorous acid [2]

$$H_2O_2 + 2H = 2H_2O\ ;$$
$$H_2O_2 + O = H_2O + O_2.$$

Hydrogen peroxide readily oxidises alkali nitrites to nitrates in acid solution. In alkaline or neutral solution oxidation does not take place.[3]

Silicic acid gel, when evaporated with a slight excess of 30 per cent. peroxide, yields a highly active amorphous residue which continuously evolves ozonised oxygen. It liberates chlorine from hydrochloric acid, iodine from potassium iodide, decolorises permanganate, and evolves ozone with concentrated sulphuric acid.[4] Possibly a persilicic acid is formed. Thiosulphates are at first oxidised to tetrathionates, the solution becoming alkaline : [5]

$$2Na_2S_2O_3 + H_2O_2 = Na_2S_4O_6 + 2NaOH.$$

The reaction soon becomes more complex, a fact that will account for various published discrepancies.[6]

Concentrated sulphuric acid is oxidised by hydrogen peroxide giving permonosulphuric acid, also called Caro's acid,[7]

$$H_2SO_4 + H_2O_2 \rightleftharpoons H_2SO_5 + H_2O\ ;$$

sulphurous acid yields sulphuric acid and hydrogen sulphide undergoes slow conversion into free sulphur and even into sulphuric acid,[8] the formation of the latter being easily demonstrated by heating together hydrogen sulphide, barium chloride, and hydrogen peroxide in aqueous solution.[9] Hydrogen selenide is oxidised more readily, with formation of selenium. The metallic sulphides become converted into sulphates,[10]

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O,$$

and for this reason hydrogen peroxide is frequently applied in the restoration of old paintings in which the white-lead basis of the paint has become blackened by the action of atmospheric hydrogen sulphide.

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[1] Kleinstuck, *Ber.*, 1918, 51, 108.

[2] Tanatar, *Ber.*, 1903, 36, 199. See also Lebedeff, *Bull. Soc. chim.*, 1908, 3, 56.

[3] Usher and Rao, *Trans. Chem. Soc.*, 1917, 111, 799

[4] Komarovsky, *Chem. Zeitung*, 1914, 38, 121 ; Jordis, *ibid.*, p. 221.

[5] Nabl, *Ber.*, 1900, 33, 3554 ; Tarugi and Vitali, *Gazzetta*, 1909, 39, i., 418.

[6] See Nabl, *Ber.*, 1900, 33, 3093, 3554 ; Willstätter, *Ber*, 1903, 36, 1831 ; Abel, *Monatsh.*, 1907, 28, 1239.

[7] Baeyer and Villiger, *Ber.*, 1900, 33, 126 ; 1901, 34, 353 , Caro, *Zeitsch. angew. Chem.*, 1898, p 845

[8] Particularly in alkaline solution. Passage of hydrogen sulphide through strongly alkaline perhydrol rapidly converts it into sulphuric acid This reaction may be used to estimate the gas. Klemmer, *Chem. Zeitung*, 1922, 46, 79.

[9] Fairley, *loc. cit.*

[10] Thénard, *loc. cit.* ; Raschig, *Ber.*, 1885, 18, 2743 ; Hernández, *Anal. Fis. Quim.*, 1908, 6, 476.

In alkaline solution cobalt sulphide is oxidised to cobaltic hydroxide, manganese sulphide yields the hydroxide and a deposit of sulphur, whilst zinc sulphide is converted into soluble zincates.[1]

Dilute solutions of hydrogen peroxide (6 per cent.) oxidise yellow phosphorus on warming, phosphorous and phosphoric acids resulting. Amorphous phosphorus is violently attacked by 8 per cent. peroxide, hydrogen phosphide being evolved, phosphorous and phosphoric acids remaining in solution.[2]

Metallic potassium and sodium are explosively converted into the hydroxides when brought into contact with concentrated solutions of hydrogen peroxide; many of the heavier metals such as zinc and iron, and especially aluminium,[3] are readily changed into their respective hydroxides, whilst chromium, arsenic, and molybdenum are oxidised respectively to chromic, arsenic, and molybdic acids. Colloidal tellurium yields telluric acid with very dilute solutions of peroxide[4]; the crystalline modification reacts slowly with 60 per cent. peroxide at 100° C.

Ordinary lead oxide becomes oxidised to the dioxide, and manganese oxide also to its dioxide; [5] many other oxides and hydroxides undergo similar oxidation, the products frequently being unstable peroxidic substances.

In many of these oxidation processes a considerable proportion of the hydrogen peroxide undergoes concurrent decomposition with liberation of gaseous oxidation. Thus an acidified solution of potassium iodide gives a slow formation of iodine, the change being representable as

$$2HI + H_2O_2 = 2H_2O + I_2.$$

This oxidation, and indeed many others with the same oxidising agent, are greatly accelerated by the presence of certain inorganic substances, particularly iron salts,[6] and especially when these are in the ferrous condition.[7] The addition of a very small quantity of ferrous sulphate to a dilute solution of potassium iodide containing hydrogen peroxide, acetic acid, and starch, reduces in a remarkable manner the time necessary for the production of the well-known blue coloration. Copper salts are less active, but a mixture of copper sulphate and ferrous sulphate is a much better accelerator than would be expected, the copper sulphate appearing disproportionately to augment the activity of the ferrous salt.[8] Complex organic catalysts have also been discovered.[9]

In the presence of hydrochloric acid or hydrobromic acid the oxidation of hydriodic acid may proceed further, the iodine being converted into iodic acid possibly by way of iodine trichloride or bromide. However, periodic acid is reduced to iodic acid by hydrogen peroxide and in dilute solution partial reduction even to iodine may occur.[10]

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[1] Hernández, *loc. cit.*

[2] Weyl, *Ber.*, 1906, 39, 1307.

[3] Droste, *Chem. Zeit.*, 1913, 37, 1317.

[4] Schluck, *Monatsh.*, 1916, 37, 489.

[5] For the volumetric estimation of manganese by this reaction, see Schlossberg, *Zeit. anal. Chem.*, 1902, 41, 735.

[6] Schonbein, *loc. cit.*

[7] Mummery, *J. Soc. Chem. Ind.*, 1913, 32, 889.

[8] Brode, *Zeitsch. physikal. Chem.*, 1901, 37, 257.

[9] Bach, *Ber.*, 1904, 37, 3785

[10] Auger, *Compt. rend.*, 1911, 152, 712; 153, 1005.

Iodides in general, and also to a less degree bromides and chlorides, even in small quantities, increase the rate of decomposition of hydrogen peroxide in neutral or alkaline solution. This catalytic effect has already been mentioned. Some metals will dissolve in cold, and sometimes in diluted acid solutions in the presence of hydrogen peroxide, even if almost insoluble in them under ordinary conditions. Thus glacial acetic acid containing hydrogen peroxide will attack bismuth, copper, lead, mercury, and silver in the cold; and dilute sulphuric acid charged with peroxide effects the solution of bismuth, copper, mercury, nickel, and silver.[1]

Many per-acids or salts of such acids have been prepared by the action of hydrogen peroxide on the corresponding derivative of the normal acids; thus pernitrates, perborates, percarbonates, permolybdates, pervanadates, pertitanates, and others have been rendered accessible by the strong oxidising character of this substance. Details of such compounds will be found under the heading of the respective parent elements. In this connection it is interesting to note that hydrogen peroxide actually reduces many of these per-acids as well as leading to their formation. Thus an ethereal solution of perchromic acid is gradually decomposed by hydrogen peroxide, as are also permonophosphoric and pervanadic acids.[2]

With organic substances pure hydrogen peroxide is a powerful and valuable oxidising agent [3]; it will oxidise acetyl chloride to peracetic acid, $CH_3.CO_3H$, and acetyl peroxide $(CH_3.CO)_2O_2$, volatile unstable liquids; another general method for the preparation of such organic per-acids is by the interaction of hydrogen peroxide with the acid itself in the presence of sulphuric or nitric acid as catalyst.[4]

$$CH_3.CO_2H+H_2O_2=CH_3.CO_3H+H_2O.$$

The organic per-acids of lower molecular weight are generally pungent, unstable—even explosive—liquids; those of higher molecular weight, such as perbenzoic acid, are crystalline compounds and rather more stable.

For many organic oxidation processes, a solution of ordinary 30 per cent. aqueous hydrogen peroxide in acetic acid is used, the latter solvent occasionally being essential. In such cases it is probable that the oxidation is really effected by peracetic acid.[5]

With such a solution of hydrogen peroxide, organic sulphides can be easily and conveniently oxidised to the corresponding sulphoxides and sulphones.[6]

$$RR'S \rightarrow RR'SO \rightarrow RR'SO_2$$

and azo-compounds to azoxy-compounds [7]

$$R_2N_2 \rightarrow R_2N_2O,$$

where R and R′ represent organic radicles.

---

[1] Salkowski, *Chem Zeitung*, 1916, 40, 448.

[2] Miró, *Anal. Fis Quim.*, 1920, 18, 35.

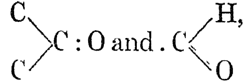
[3] See *e.g.* Perkin, *Proc. Chem. Soc.*, 1907, 23, 166; Twiss, *Trans. Chem. Soc.*, 1914, 105, 36; Clover and Houghton, *Amer. Chem. J.*, 1904, 32, 43.

[4] d'Ans and Frey, *Ber.*, 1912, 45, 1845.

[5] Hinsberg, *Ber.*, 1910, 43, 289.

[6] Gazdar and Smiles, *Trans Chem. Soc*, 1908, 93, 1833; Hinsberg, *Ber.*, 1910, 43, 289.

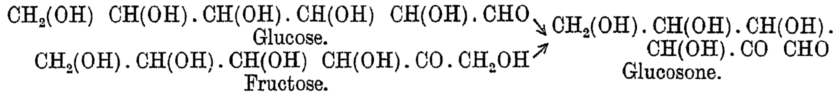
[7] Angeli, *Atti R. Accad. Lincei*, 1910, [5], 19, i., 793.

Ketones and aldehydes containing respectively the characteristic atomic groups  $\begin{matrix}C\\ C\end{matrix}\!>\!C:O$ and $.C\!<\!\begin{matrix}H,\\ O\end{matrix}$ react readily with aqueous hydrogen peroxide especially in the presence of a little hydrochloric acid; acetone, $CH_3.CO.CH_3$, for example, gives an explosive crystalline acetone peroxide of the molecular formula $(C_3H_6O_2)_2$,[1] and benzaldehyde, $C_6H_5.CHO$, yields a fairly stable substance $(C_6H_5CHO_2)_2$.[2] Carbon monoxide appears to be unaffected by hydrogen peroxide.[3]

In the presence of a small quantity of ferrous sulphate an aqueous solution of hydrogen peroxide forms a valuable reagent for the oxidation of polyhydroxy compounds such as glycerol, glycol, and mannitol, a terminal hydroxyl group being invariably converted into an aldehydic one [4] the reaction, for glycerol being representable as follows:

$$CH_2(OH).CH(OH).CH_2.OH \rightarrow CH_2(OH).CH(OH).CHO.$$

Tartaric acid with the same reagent undergoes oxidation to dihydroxymaleic acid, $CO_2H.C(OH):C(OH).CO_2H$, which readily undergoes further oxidation to dihydroxy-tartaric acid, $CO_2H.C(OH)_2.C(OH)_2.CO_2H$, which possesses especial interest on account of the very sparing solubility of its sodium salt.[5] For this reason the acid is recommended by Fenton[6] as a reagent for the quantitative estimation of sodium. The hexose sugars, glucose, fructose, etc., are oxidised by hydrogen peroxide containing the same catalyst (Fenton's reagent) with production of the corresponding osones.[7]



$$\begin{matrix}\underset{\text{Glucose.}}{CH_2(OH)\ CH(OH).CH(OH).CH(OH)\ CH(OH).CHO} \searrow \\ \underset{\text{Fructose.}}{CH_2(OH).CH(OH).CH(OH)\ CH(OH).CO.CH_2OH} \nearrow\end{matrix} \underset{\text{Glucosone.}}{\begin{matrix}CH_2(OH).CH(OH).CH(OH).\\ CH(OH).CO\ CHO\end{matrix}}$$

It is interesting to note that, whilst solutions of aniline green and magenta are not bleached by dilute hydrogen peroxide solution in the dark, yet upon exposure to the light of a quartz-mercury lamp the colours readily fade. It would appear, therefore, that under the influence of the light, the peroxide becomes increasingly active.[8]

The bleaching of litmus and of indigo solution (in the latter case with the aid of a little ferrous sulphate) is evidence of the oxidising power of hydrogen peroxide, but probably one of the most striking oxidations effected by hydrogen peroxide is that of benzene to phenol and further into quinol, pyrogallol, quinone, and other products.[9]

A remarkable property of hydrogen peroxide, which may be mentioned here, although in the result the effect is not an oxidising one, is the power of causing organic cyanides to unite with the elements of water, undergoing hydrolysis to the corresponding amides.[1] In acid solution cyanogen gives rise to oxamide, and phenyl cyanide (benzonitrile) to benzamide

---

[1] Wolffenstein, *Ber.*, 1895, 28, 2265; Twiss, *J. Soc. Chem. Ind.*, 1916, 35, 1027.

[2] Baeyer and Villiger, *Ber*, 1900, 33, 2479.

[3] Jones, *Amer. Chem. J.*, 1903, 30, 40.

[4] Fenton, *Trans. Chem. Soc.*, 1899, 75, 1, 57.

[5] Fenton, *Trans. Chem. Soc.*, 1894, 65, 899; 1895, 67, 48; 1896, 69, 546; 1905, 87, 811.

[6] Fenton, *ibid.*, 1895, 67, 48.

[7] Morrell and Crofts, *Trans Chem. Soc*, 1899, 75, 786; 1900, 77, 1219; 1902, 81, 666; 1903, 83, 1284; Morrell and Bellars, *ibid.*, 1905, 87, 280.

[8] Curtis, *J. Amer. Chem. Soc.*, 1920, 42, 720.

[9] Martinon, *Bull. Soc. chim.*, 1887, 20, 2934.

$$CN.CN+2H_2O=CO(NH_2).CO(NH_2);$$
$$C_6H_5.CN+H_2O=C_6H_5.CO.(NH_2).$$

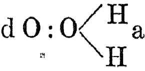
**Applications.**—Hydrogen peroxide is applied largely as a bleaching agent for materials such as feathers, hair, wood, bone, ivory, and skins where the action of chlorine or sulphur dioxide might harmfully affect the article; it has the especial advantage that, after its action, nothing more harmful than water remains; in order to accelerate the action of the hydrogen peroxide, a small quantity of a mild alkali such as magnesium oxide or ammonia is often added.[2] Treatment with hydrogen peroxide has also been suggested as a method for the removal of the excess of chlorine or sulphur dioxide in compounds which have been bleached with these agents.[3] On account of its marked disinfectant and antiseptic action, hydrogen peroxide in dilute aqueous solution is of value as a wash for open wounds and is also frequently applied as a preservative in milk.

The catalytic decomposition of hydrogen peroxide by finely divided metals has been suggested as the basis of a photographic process. An ethereal solution of the peroxide is wiped over the negative when, after the evaporation of the ether, the residual hydrogen peroxide film undergoes rapid decomposition at the dark portions of the negative. If a gelatinised but unsensitised paper is then applied to the glass, the undecomposed hydrogen peroxide is partially absorbed by the gelatinised surface of the paper from the transparent portions of the negative and, when subsequently dipped in a suitable solution, *e.g.* an ammoniacal solution of manganese sulphate, a brown " positive " print appears on the paper.[4]

The value of hydrogen peroxide as an oxidising agent for analytical and preparative purposes can easily be realised from the foregoing description of its properties and, indeed, was recognised early in its history.[5]

## COMPOSITION AND CONSTITUTION OF HYDROGEN PEROXIDE.

Hydrogen peroxide is, of all known compounds, the richest in oxygen. Its molecular weight has been shown by the freezing-points of its aqueous solutions to be represented by the formula $H_2O_2$.[6]

This formula leaves undetermined the actual structure of the molecule which needs further evidence. Two constitutions are possible, which may be described as the asymmetrical and the symmetrical, and which may be represented  $O:O{<}\begin{smallmatrix}H\\H\end{smallmatrix}$ and $(OH)_2$ respectively. The latter formula is also referred to as the *chain* formula HO . OH. If the molecular structure actually involves the coupling of two hydroxyl groups as the symmetrical or chain arrangement suggests, a synthesis from hydroxyl groups might be expected. In spite of earlier failures, it has been recently shown that, under suitable conditions, especially at temperatures near −40° C., hydrogen peroxide is produced in appreciable quantity during the electrolysis of potassium hydroxide; the electrolysis was performed with platinum electrodes and the formation of the hydrogen peroxide was due to the anodic coupling of the hydroxyl groups after the loss of their ionic charge.[1]

---

[1] Radziszewski, *Ber.*, 1887, 20, 2934; 1885, 18, 355; Dubsky, *J. prakt. Chem.*, 1916, [2], 93, 137. For the hydrolytic activity of hydrogen peroxide towards other types of organic compounds, such as albumin, gelatin, and starch, see Neuberg and Muira, *Biochem. Zeitsch.*, 1911, 36, 37.

[2] Prud'homme, *Compt. rend*, 1891, 112, 1374; Bourgougnon, *J. Amer. Chem Soc*, 1890, 12, 64; Ebell, *Chem. News*, 1882, 45, 71; Schrotter, *Ber.*, 1874, 7, 980.

[3] Lunge, *Dinglers. Poly J*, 1886, 259, 196.

[4] For an account of this " Catatype " process, see Gros, *J. Soc. Chem. Ind.*, 1903, 22, 379, 380, 963; 1904, 23, 1044.

[5] See, for example, Davis, *Chem. News*, 1879, 39, 221.

[6] Carrara, *Gazzetta*, 1880, 10, 1, 1892, 22, 341; Orndorff and White, *Amer Chem J*, 1893, 15, 347; Tammann, *Zeitsch. physikal. Chem.*, 1893, 12, 431.

$$2OH' + 2\oplus = H_2O_2$$

Sodium hydroxide, probably on account of its more powerful decomposing action on hydrogen peroxide, fails to yield an appreciable amount of this compound.

Organic derivatives of hydrogen peroxide are known, the organic per-acids already mentioned (p. 344) belonging to this class. Examples of a simpler type—the alkyl peroxides—are produced when ethyl sulphate, $(C_2H_5)_2SO_4$, is allowed to react with fairly concentrated hydrogen peroxide.[2] The products, ethyl peroxide, $C_2H_5O . OH$, and diethyl peroxide, $C_2H_5 . O . O . C_2H_5$, are explosive liquids which on reduction yield ethyl alcohol, $C_2H_5 . OH$, without any ethyl ether, $(C_2H_5)_2O$; the asymmetrical formula, $(C_2H_5)_2O:O$, thus appears to be definitely disproved, and so presumably the alkyl peroxides and hydrogen peroxide itself are of the symmetrical constitution.

On the other hand, the physico-chemical evidence appears to be almost entirely opposed to the view that the structure of hydrogen peroxide involves merely two hydroxyl groups, as indicated by the formula H . O . O . H. As has been mentioned already, the high dielectric constant and the absence of any exceptional power to absorb electric waves, likewise militate against the likelihood of the presence of hydroxyl groups (see p. 332). Also from the fact that hydrogen peroxide never appears to be formed by the oxidation of water, but that molecular oxygen on reduction by hydrogen will yield hydrogen peroxide, it has been argued that this substance may be regarded as reduced oxygen, the hydrogen atoms being only feebly bound so that they readily undergo oxidation by permanganic acid and other oxidising agents with the liberation of the whole of the oxygen from the peroxide[3]; this indicates the absence of hydroxyl groups which indeed would also be expected from the difference in stability between hydrogen peroxide and water.

From the refractive power of the substance also it has been demonstrated by Bruhl that the presence of hydroxyl groups in hydrogen peroxide is extremely unlikely.[4] One method of reconciling the chemical and physico-chemical evidence apparently is to acknowledge the symmetrical nature of the molecule whilst simultaneously conceding the point that no hydroxyl groups are present; the groups present are probably of the type O . H, which will have quite different characteristics from the . OH group, and the structural formula for the molecule will be H.O O.H, the oxygen atom being present in its quadrivalent condition (see p. 131). This constitution accords well with the facts. On the other hand, hydrogen peroxide may be regarded as an equilibrium mixture, thus:

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[1] Riesenfeld and Reinhold, *Ber*, 1909, 42, 2977.

[2] Baeyer and Villiger, *Ber.*, 1900, 33, 3387; 1901, 34, 738.

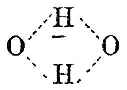
[3] Traube, *Ber.*, 1882, 15, 222, 659, 2421, 2434; 1886, 19, 1111, 1115, 1889, 22, 1496, 1515, 1893, 26, 1476

[4] Bruhl, *Ber.*, 1895, 28, 2860, 1897, 30, 162; 1900, 33, 1709. See also Spring, *Zeitsch. anorg. Chem.*, 1895, 8, 424; Kingzett, *Chem. News*, 1882, 46, 41, 183; Heyes, *Phil. Mag.*, 1888, [5], 25, 221.

$$H_2O.O \rightleftharpoons HO.OH,$$

the left-hand structure predominating in the aqueous peroxide.

Miró [1] suggests the symmetrical formula:



but whilst this may have its advantages, it attributes to hydrogen a valency of two—an assumption not generally accepted by chemists, but in harmony with Friend's views of latent valency.[2]

### Detection and Estimation of Hydrogen Peroxide.

Many of the reactions described in the preceding pages can easily be applied to the detection of hydrogen peroxide The blue coloration with chromic acid, especially with subsequent extraction of the coloured compound by ether. The oxidation of potassium iodide in a solution containing acetic acid and starch, especially in the presence of a catalyst such as ferrous sulphate [3] or molybdic acid; with the latter catalyst, there is the additional advantage that the oxidation of the iodide by atmospheric oxygen is not accelerated,[4] so that atmospheric oxidation has less likelihood of introducing a serious disturbing factor. The formation of Prussian blue on addition to a solution of ferric chloride and potassium ferricyanide. Of these three tests, which are all of considerable sensitiveness, the last possesses the additional advantage of being unaffected by nitrogen dioxide.

Numerous colour reactions depending on the oxidation of various organic compounds have been suggested; paper impregnated with cobalt naphthenate changes in colour from rose to green; [5] a dilute solution of aniline or dimethylaniline containing potassium dichromate and a little oxalic acid yields a red coloration ; [6] *m*-phenylenediamine in hot ammoniacal solution gives a blue coloration and *p*-phenylenediamine has also been used.[7] These reactions [8] are all delicate for hydrogen peroxide.

Certain inorganic reagents possess the additional advantage of being specific for hydrogen peroxide. Titanium sulphate in neutral or acid solution gives a deep yellow coloration due to the formation of a pertitanic acid, $TiO_3,xH_2O$.[1] Acid solutions of ammonium molybdate give an intense yellow coloration of permolybdic acid, $H_2MoO_5$.[2] Both these supply very sensitive tests.

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[1] Miró, *Helv. Chim. Acta*, 1920, 3, 347.

[2] Friend, *Trans Chem. Soc.*, 1921, 119, 1040.

[3] Traube, *Ber.*, 1884, 17, 1062.

[4] Rothmund and Burgstaller, *Monatsh.*, 1913, 34, 693.

[5] Charitschkoff, *Chem. Zeit.*, 1910, 34, 50.

[6] Bach, *Moniteur Scientif*, 1859, [4], 9, 184 ; Ilosva, *Ber*, 1895, 28, 2029

[7] Darlington, *J. Ind. Eng. Chem.*, 1915, 7, 676.

[8] For other similar tests, see Denigès, *Ann. Chim anal.*, 1917, 22, 193.

For the purpose of distinguishing hydrogen peroxide vapour from nitrogen dioxide or ozone, potassium permanganate and manganese dioxide are useful reagents, the former leaving only ozone unaffected whilst the latter fails only to decompose nitrogen dioxide.[3]

The liberation of iodine from an acidified solution of an iodide provides a convenient method for estimating hydrogen peroxide quantitatively, and by first allowing the solution or vapour to react with a slightly acid solution of potassium bromide, any ozone present may be previously determined quantitatively and removed in one process.[4]

The reaction of potassium permanganate or hypochlorite with hydrogen peroxide in acidified solution also can be conveniently made the basis of a volumetric determination, the volume of liberated oxygen being twice that expected from the decomposition of the peroxide into an equimolecular proportion of water. If the solution of hydrogen peroxide is sufficiently dilute, direct titration with the permanganate is possible[5] in the presence of sulphuric acid, a molecule of hydrogen peroxide decolorising two-fifths of a molecule of potassium permanganate.

In those cases where there exists a possibility of organic substances interfering with the estimation of hydrogen peroxide by treatment with a solution of potassium permanganate or potassium iodide, the use of a standard solution of stannous chloride has been proposed; the reaction follows the course

$$SnCl_2+2HCl+H_2O_2=SnCl_4+2H_2O$$

and may be applied by direct titration with methylene blue as indicator, or by the addition of an excess followed by titration of the superfluous stannous salt with iodine.[6]

---

[1] Schone, *Zeitsch anal. Chem*, 1870, 9, 41.

[2] Denigès, *Bull. Soc. chim*, 1890, [3], 3, 797

[3] Keiser and M'Master, *Amer Chem J.*, 1908, 39, 96.

[4] Rothmund and Burgstaller, *loc. cit.*

[5] For the estimation of hydrogen peroxide in the presence of a persulphate by a modification of this method, see Friend, *Trans Chem Soc*, 1904, 85, 597, 1533; 1905, 87, 1367.

[6] von Berlatan, *Chem. Zeit*, 1916, 40, 373.

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