·A DICTIONARY

OF

APPLIED CHEMISTRY

BY

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ASSISTED BY EMINENT CONTRIBUTORS

VOL. IX.

REVISED AND ENLARGED EDITION

ABBREVIATIONS
OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim.	Annales de Chimie.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Ann. Physik.	Annalen der Physik.
Ann. Physique.	Annales de Physique.
Ann. Report	Annual Reports of the Chemical Society.
Annali Chim. Appl.	Annali di Chimica Applicata.
Apoth. Zeit.	Apotheker-Zeitung.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Astrophys. J.	Astrophysical Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Bentl. a. Trim.	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Brewers J.	Brewer's Journal.
Brit. Assoc. Rep.	Report of the British Association for the Advancement of Science
Brit. Med. J.	British Medical Journal.
Brit. Pat.	British Patent.
Bull. Acad. roy. Belg.	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Asso. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. chim. Biol.	Bulletin de la Société de chimie biologique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Chem.and Met.Eng.	Chemical and Metallurgical Engineering.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Umschau.	Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
D. R. P.	Deutsches Reichs-Patent.
Färber-Zeit.	Färber-Zeitung.
Flück. a. Hanb.	Flückiger and Hanbury. Pharmacographia.
Frdl.	Friedländer's Fortschritte der Teerfarbenfabrikation.
Gazz. Chim. Ital.	Gazzetta Chimica Italiana.
Helv. Chim. Acta	Helvetica Chimica Acta.
J.	Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Japan J. Phys.	Japanese Journal of Physics.

J. Agric. Res.	Journal of Agricultural Resear
J. Agric. Sci.	Journal of Agricultural Science
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Bact.	Journal of Bacteriology.
J. Bd. Agric.	Journal of the Board of Agriculture.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan.
J. Chim. Phys.	Journal de Chimie Physique.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan.
J. Phys. Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
J. Tokyo Chem. Soc.	Journal of the Tokyo Chemical Society.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Kolloid Zeitsch.	Kolloid-Zeitschrift.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Met. & Chem. Eng.	Metallurgical and Chemical Engineering.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
P.	Proceedings of the Chemical Society.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmaceutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Physikal. Z.	Physikalische Zeitschrift.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Sci. Proc. R. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitz.	Sitzungsberichte der K. Akademie zu Wien.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Swiss Pat.	Swiss Patent.
T.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
U.S. Pat.	United States Patent.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. ges. Brauw.	Zeitschrift für das gesamte Brauwesen.
Z. Kryst.	Zeitschrift für Kristallographie.
Z. Kryst. Min.	Zeitschrift für Kristallographie und Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Physik.	Zeitschrift für Physik.
Zeitsch. öffentl. chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Sepler's Zeitschrift für physiologische Chemie.

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APPLIED CHEMISTRY.

OXYGEN. Sym. O. At.wt. 16.

The first recognition of the *rôle* of oxygen in nature would seem to date from the eighth century. The Chinese philosopher Mao-Khóa then promulgated a theory based on his experiments, that all matter was composed of two fundamental elements, Yang (the strong or primary) and Yin (the weak or secondary). In air both these elements were present combined with elemental fire. The Yang (or more complete air) could be obtained purer by burning in air certain of the metals, sulphur or charcoal, which robbed the air of some of its Yin; whilst Yin, never occurring pure in the air, could be obtained by heating certain minerals (the identity of which is not clear) and especially Hhò-siaõ (probably nitre). Mao-Khóa recognised that the Yin of the air was also present in water, though here it was so closely bound to Yang that its separation was difficult. The important part taken by Yin in combustion and respiration was recognised. Leonardo da Vinci was the first European to recognise, towards the end of the fifteenth century, the non-elemental character of the air and to state that only one part of it was concerned in combustion and respiration. Robert Hooke, in Micrographia, published in London in 1665, recognised the same fact, and that the same constituent, or at least a very similar one, was present in nitre. Mayow in 1674 recognised that the *active* constituent of air which supports combustion forms only part of the atmosphere, and that the same substance is present in nitre, and is given off when nitre is h ited strongly. Mayow termed this gaseous constituent of air and nitre *spiritus vitalis*, *spiritus nitro-aëreus*, and *pabulum igneo-aëreum*. Borch (1678) carried the work of Mayow further, and Hales (1727) obtained oxygen by heating nitre, and collected the gas over water in nearly theoretical quantity, but failed to recognise its character. Priestley obtained the gas on August 1, 1774, by heating mercuric oxide in a glass vessel by the heat of the sun's rays concentrated on the oxide by means of a burning glass, and gave it the name *dephlogisticated air*. The gas was isolated independently, and almost simultaneously (probably in 1771, though the publication of this result was only made several years later), by the Swedish chemist Scheele,

who applied to it the term *empyreal* or *fire-air*. Condorcet soon after suggested the name *vital air*. Lavoisier regarded it as an essential constituent of all acids, and hence gave it its present name *oxygen* (from ὀξύς, acid, and γεννάω, I form). The later discovery that hydrochloric and the other halogen acids contained no oxygen showed that this substance is not necessarily present in acids, but the name has been retained. The discovery of oxygen was the means of leading Lavoisier to the true theory of combustion (*see* Jörgensen, Die Entdeckung des Saurstoffes, Stuttgart, 1909).

Occurrence.—Oxygen is the most abundant and the most widely distributed element in nature. In the free state it occurs, mixed with nitrogen, in the atmosphere, of which it forms about 21 p.c. by volume, and more than 23 p.c. by weight. In the combined state it forms eight-ninths by weight of all the water on the globe, and nearly half of the three chief constituents of the earth's crust, viz. silicious rocks, chalk, and alumina. Most minerals—the chief exceptions being rock salt, fluorspar, blende, galena, and pyrites—contain oxygen in considerable proportions. It is an essential constituent of all animal and vegetable tissues and fluids. It is absorbed in large quantities from the atmosphere by animals and vegetables during respiration, but this abstraction is practically counterbalanced by the oxygen evolved by green foliage under the influence of sunlight.

Preparation.—A. *On the laboratory scale.* Oxygen may be obtained by the action of heat on the oxides of mercury, silver, gold, and platinum; the peroxides of hydrogen, the alkalis, barium, lead, and manganese; the chlorates, bromates, iodates, nitrates, and dichromates of potassium and other bases; it is evolved during some chemical reactions, and during the electrolysis of many substances, notably of water.

Of the modes of preparation most convenient for use in the laboratory, or of interest from historical or theoretical considerations, the following are the principal :—

1. By heating red oxide of mercury it splits up into vapour of mercury (which condenses) and oxygen: $2HgO = 2Hg + O_2$. This reaction

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is of interest as being that by which Priestley first obtained oxygen.

2. By heating manganese dioxide to a bright-red heat it gives up one-third of its oxygen: $3MnO_2 = Mn_3O_4 + O_2$. The oxide is best heated in an iron bottle placed in a furnace, as glass vessels will not stand the high temperature required. 100 parts by weight of the pure peroxide yield 12·3 parts by weight of oxygen.

Manganese dioxide occurs in large quantities in nature as the mineral *pyrolusite*, and thus forms a cheap source for the preparation of quantities of a few hundred cubic feet of oxygen, but the high temperature required makes the process somewhat inconvenient. Pyrolusite usually contains about 70 p.c. of the dioxide, and therefore gives a lower yield of oxygen than that indicated by the equation.

3. Potassium chlorate is a very convenient and economical source for small quantities of oxygen for lecture and laboratory purposes. When gradually heated in a hard glass retort or flask, this salt melts at about 360°–370°, and at about 370°–380° evolution of oxygen commences. After some time the fused mass thickens from the formation of the perchlorate, which, at a still higher temperature, is also decomposed. Ultimately, therefore, potassium chloride alone remains in the generating flask, the whole of the oxygen having been given off according to the equation: $2KClO_3 = 2KCl + 3O_2$. 100 parts by weight of chlorate yield 39·16 parts by weight of oxygen, or 1 oz. of chlorate gives 1·8 gallons of the gas. The oxygen obtained is very pure.

The temperature required in this decomposition is too high for convenient use, as the glass vessels employed in the preparation of the gas often soften under the great heat, and yield to the pressure of the contained gas. When metallic vessels are used the heating must be very carefully watched, since the decomposition being exothermic (i.e. heat being evolved during the reaction), when once decomposition has set in, the evolution of gas is liable to become very violent. If the potassium chlorate be mixed with about one-eighth its weight of some non-fusible oxide, such as oxide of copper, oxide of iron, or manganese dioxide, the evolution of oxygen takes place at about 240°, or considerably below that at which the salt fuses, and is much more regular. The addition of a little spongy platinum answers the same purpose.

The gas prepared in this way almost invariably contains traces of chlorine, which are removed, when necessary, by passing the gas through a solution of caustic soda.

Commercial manganese dioxide (pyrolusite) is sometimes adulterated with coal-dust. If such dioxide is heated with potassium chlorate the coal-dust burns—often with explosive violence—at the expense of the oxygen of the chlorate, and this has been the cause of fatal accidents. It is, therefore, advisable to test the dioxide before use by heating a small quantity in a test tube with some chlorate.

The action of these oxides in facilitating the decomposition of the potassium chlorate is probably due to the transient formation of higher oxides of extreme instability. The oxides which show this action most markedly are those which form unstable higher oxides. The action of spongy platinum is less clear, but is probably connected with the tendency of that substance to condense oxygen on its surface.

4. By heating a concentrated solution of bleaching powder (or any hypochlorite) to which a small quantity of oxide of cobalt has been added, it is resolved into calcium chloride and oxygen: $2CaOCl_2 + 4CoO = 2CaCl_2 + 2Co_2O_3$ and $2Co_2O_3 = 4CoO + O_2$. The decomposition is shown in two stages to exhibit the action of the oxide of cobalt. It is not necessary to use pre-formed oxide of cobalt, as any salt of cobalt will answer the same purpose. The oxides of copper and nickel are similar in their action. Instead of a solution a thick paste of bleaching-powder and water may be used if a small quantity of paraffin oil is added. The oil, floating on the surface of the pasty liquid, prevents the frothing which would otherwise take place. The best temperature for the evolution of gas is about 70°–80°, at which a steady stream may be obtained. For a study of the conditions determining the velocity of evolution of oxygen from bleaching powder, *see* Bell, Zeitsch. anorg. Chem. 1913, 82, 145.

Another modification of this method is to pass a stream of chlorine into boiling milk of lime to which a small quantity of a salt of copper, cobalt, or nickel has been added. Oxygen gas is given off according to the equation $2Cl_2 + 2Ca(OH)_2 = 2CaCl_2 + 2H_2O + O_2$.

5. From various peroxides—

(a) When an intimate mixture of 3 mols. barium peroxide (2 parts by weight) and 1 mol. potassium dichromate (1 part by weight) is treated with dilute sulphuric acid, oxygen is abundantly evolved at ordinary temperatures (Robbins, Pharm. J. [ii.] 5, 436).

(b) If 500 c.c. of commercial hydrogen peroxide (10 p.c. solution) are introduced into a suitable generating flask, and a solution of 25 grms. of potassium permanganate in 500 c.c. of water, mixed with 25 c.c. concentrated sulphuric acid, is allowed to flow gradually into the mixture from a dropping funnel, oxygen will be rapidly evolved without the application of heat, the amount of oxygen obtained from these quantities being about 10 litres.

(c) Baumann recommends (Zeitsch. anorg. Chem. 1890, 79) charging a Kipp apparatus with pieces of pyrolusite of 2–4 mm. diameter and using as the activating liquid commercial hydrogen peroxide to which, while well cooled, 150 c.c. of strong sulphuric acid has been added per litre. The evolution of the oxygen is steady and continuous. Neumann recommends the use of cubes made from 2 parts barium peroxide, 1 part pyrolusite, and 1 part gypsum with hydrochloric acid of sp.gr. 1·12 as activating liquid, but the oxygen evolved by this method contains traces of chlorine.

(d) If water is dropped on to broken pieces of fused potassium, sodium or potassium-sodium peroxide, a steady stream of oxygen is evolved. Walter recommends fusing 100 grms. sodium peroxide, 100 grms. potassium nitrate and 25 grms. magnesia; hydrochloric acid is then dropped on to the cold broken-up mass.
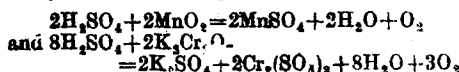
(e) If a mixture of equal parts of sodium peroxide and a salt containing water of crystallisation, such as sodium sulphate, is gently heated, oxygen is evolved in a steady stream.

6. On passing a mixture of steam and

chlorine through a red-hot porcelain tube, filled with fragments of porcelain to increase the heating surface, the chlorine combines with the hydrogen of the water and oxygen is liberated : $2H_2O + 2Cl_2 = 4HCl + O_2$.

7. By the electrolysis of a solution of sodium hydroxide or of water slightly acidulated with sulphuric acid, the water is resolved into hydrogen and oxygen, the latter appearing at the positive pole : $2H_2O = 2H_2 + O_2$. This forms a convenient method of obtaining small quantities of pure oxygen, such as are required in gas analysis.

8. Oxygen may be prepared from such highly oxidised compounds as peroxides of lead and manganese, potassium dichromate and permanganate, &c., by the action of sulphuric acid. These are, however, seldom used as sources of gaseous oxygen, but are very useful as oxidising agents. Thus hydrochloric acid, when treated with sulphuric acid and potassium permanganate, is oxidised to hypochlorous acid, and alcohol treated with sulphuric acid and manganese dioxide yields aldehyde and water. The following equations represent the changes which take place when manganese dioxide and potassium dichromate are respectively treated with sulphuric acid :

$$2H_2SO_4 + 2MnO_2 = 2MnSO_4 + 2H_2O + O_2$$
and $8H_2SO_4 + 2K_2Cr_2O_7$
$$= 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

The change is rendered visible in t latter case by the formation of a deep green salt of chromium, the solution being previously of a red colour.

9. When fresh leaves, such as mint or parsley, are exposed to the influence of sunlight in an inverted cylinder filled with water saturated with carbon dioxide and standing in a basin of the same liquid, oxygen appears after a time in minute bubbles on the leaves, and collects in the upper part of the jar. This method of liberating oxygen is of interest as being that which occurs in nature, by means of which the loss of atmospheric oxygen continually taking place from combustion and respiration is replaced.

B. *On the industrial scale.* 1. The first method proposed for obtaining oxygen on the large scale was the ignition of nitre, and this method, in various modifications, has formed the basis of several patents. The first oxygen patent occurring in the records of our Patent Office, is No. 12536, S. White, 1849. But the oxygen so obtained was contaminated with oxides of nitrogen, and this method has not proved advantageous. It deserves mention, however, as being the means by which Priestley first obtained impure oxygen in 1771. He then believed the gas to be 'fixed air' (carbon dioxide), and only recognised his mistake 3 years afterwards, when he obtained oxygen from mercuric oxide.

2. By heating manganese dioxide. This was formerly one of the cheapest methods of preparing oxygen on the commercial scale.

3. By heating a mixture of potassium chlorate and about one-eighth of its weight of manganese dioxide. Though more costly than the last-named, this method is more easily carried out, and was, until within the last 30 years, almost exclusively employed in the preparation

of the considerable quantities of oxygen used for lime-light purposes.

4. By the decomposition of sulphuric acid by heat: $2H_2SO_4 = 2SO_2 + 2H_2O + O_2$. The sulphuric acid is allowed to drop on red-hot surfaces, and is thus decomposed. If the oxygen alone is wanted, the emergent gaseous mixture is passed over media suitable for the absorption of the water and sulphur dioxide. As a method for the preparation of oxygen only this process has not found much favour, but it has been used in the preparation of sulphur trioxide, where, the water being removed by a desiccating agent, a mixture of sulphur dioxide and oxygen in the desired proportions is at once obtained. It is the process suggested by Squire in his patent for the manufacture of sulphur trioxide (Eng. Pat. 3278, 1875).

5. By the dialysis of air. Many attempts have been made to utilise the laws of diffusion of gases through porous septa, discovered by Graham, or the property of caoutchouc when in thin layers to allow oxygen to pass through it more readily than nitrogen. Several patents have been taken out for processes of this kind, but with no practical success, and the phenomena do not seem likely to lend themselves to the production of oxygen on the large scale.

6. Better success has attended the endeavour to make use of the greater solubility of oxygen than of nitrogen in water or other solvents. Mallet, who took out a patent for this process (Eng. Pat. 2137, 1869), compressed the air over water. The coefficient of solubility of oxygen in water is about twice that of nitrogen. The oxygen was, therefore, dissolved in greater proportion than the nitrogen, and when the excess of pressure was removed and the dissolved gases extracted by the aid of a vacuum pump, the amount of oxygen in the gaseous mixture was greater than in air. This mixture was then repeatedly subjected to the same treatment, when, after about eight absorptions, nearly pure oxygen was obtained. The following table, given by Mallet (Dingl. poly. J. 199, 112), shows the composition of the gaseous mixture at each successive stage of the operation :—

Atmospheric air	Composition after successive absorptions							
	1	2	3	4	5	6	7	8
N = 79	66·7	52·5	37·5	25·0	15·0	9·0	5·0	2·7
O = 21	33·3	47·5	62·5	75·0	85·0	91·0	95·0	97·3

This process was used by Phillips in 1871–72 to obtain oxygen for his experimental lighting of part of Cologne by special oxygen-fed oil lamps, but beyond this does not appear to have been practically applied.

7. By the alternate oxidation and de-oxidation of cuprous chloride. Cuprous chloride, if exposed to air, and especially to moist air, is oxidised to cupric oxychloride, and this, when heated to dull redness, gives off oxygen, and is reconverted into cuprous chloride.

(a) $2Cu_2Cl_2 + O_2 = 2Cu_2OCl_2$
(b) $2Cu_2OCl_2 = 2Cu_2Cl_2 + O_2$
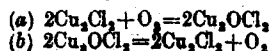
Mallet obtained patents (Eng. Pats. 2934, 1865, and 3171, 1866) for the practical utilisation of this method as a continuous process for

obtaining oxygen from the air, but it has not been found economically available on the large scale.

8. By the alternate formation and decomposition of alkaline manganates. When an oxide of manganese is mixed in suitable proportions with a caustic alkali (potash or soda), and is subjected to the action of air at a moderately high temperature, an alkaline manganate is formed. If this manganate is then heated to a bright-red heat, and a current of steam passed over it, it is resolved into its original constituents with evolution of oxygen (C. M. Tessié du Motay and C. R. Marechal, Eng. Pat. 85, 1866).

$$2MnO_2 + 4NaOH + O_2(air) = 2Na_2MnO_4 + 2H_2O$$
$$2Na_2MnO_4 + 2H_2O = Mn_2O_3 + 4NaOH + 3O$$
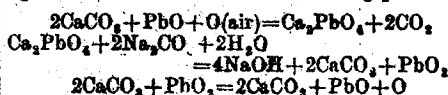$$Mn_2O_3 + 4NaOH + 3O(air) = 2Na_2MnO_4 + 2H_2O$$
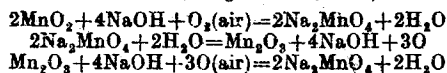
The mixture was introduced into horizontal retorts, which were heated to a dull red heat while a current of air was passed through. After oxidation was complete the supply of air was cut off, the retorts were heated to a bright red heat and a current of steam admitted, when oxygen was evolved. The retorts were then allowed to cool again to a dull red, the passage of air again commenced, and so on. The mixture was said to undergo no deterioration, and a continuous and very economical method of obtaining oxygen seemed attained. Works were erected, and the process carried out on the large scale at Paris, Lille, Brussels, Vienna, and New York, and large quantities of oxygen were made. A large part of Paris was laid with a double system of piping with the intention of lighting that city with the oxy-hydrogen light, and the New York Company carried out by the same light the lighting of the works during the building of the Brooklyn bridge. But it was found in practice that the mixture did deteriorate, the yield of oxygen rapidly diminishing, and finally almost ceasing. This was probably due to the difficulty of maintaining the intimate mixture of the easily fusible, hygroscopic and very soluble soda with the manganic oxide, the former settling to the bottom through the combined effect of the heat and steam used.

Bowman (Eng. Pat. 7851, 1890) claimed to have overcome this difficulty by making the alkaline manganate in a granular form and dusting over the granules, whilst still in a plastic condition, with oxide of copper. Parkinson (Eng. Pat. 14925, 1891) claimed improved modes of preparation of the material together with the use of a vacuum in place of steam to cause the evolution of the oxygen. The manganate material, in upright iron retorts, was heated to about 1200°, and air pumped in under pressure to effect oxidation; the pumps were then automatically reversed and the oxygen drawn off under greatly reduced pressure. Fanta's claim (Eng. Pat. 3034, 1891) mainly consisted in increased stability of the material by the use of excess of caustic soda, and Webb's resembled Bowman's, except that the pieces of manganate material were dusted over with manganese peroxide instead of with oxide of copper. In Chapman's process (Eng. Pat. 11504, 1892) 'oxide of manganese (or the like) in a powdered form is kept suspended in fused soda (or the like) so that the charge is practically in the condition of a liquid,' and the alternate

supplies of air and steam were driven into the liquid at the bottom, thereby keeping the oxide in a state of suspension. But though these modifications have been tried on the practical scale, none of them proved commercially successful.

9. Kassner (Eng. Pat. 11899, 1889) found that when an intimate mixture of lead oxide and chalk is heated to 600° in contact with the air, a calcium plumbate Ca_2PbO_4 is formed. If this plumbate is then introduced into a solution of potassium or sodium carbonate it is decomposed, an insoluble precipitate of calcium carbonate and lead peroxide is formed, and caustic potash or soda remains in solution. This is removed by decantation, and the precipitate washed. The precipitate, in which the lead peroxide is, of course, the active part, may then either be used directly as an oxidant, or it may be introduced into a decomposing vessel, dried with superheated steam, and heated to about 500°, when oxygen is evolved, the mixture of lead oxide and calcium carbonate left being then ready for regeneration. The decomposition of the plumbate may also be effected by suspending it in water and treating with carbonic acid. The following equations indicate the reactions taking place:

$$2CaCO_3 + PbO + O(air) = Ca_2PbO_4 + 2CO_2$$
$$Ca_2PbO_4 + 2Na_2CO_3 + 2H_2O$$
$$= 4NaOH + 2CaCO_3 + PbO_2$$
$$2CaCO_3 + PbO_2 = 2CaCO_3 + PbO + O$$

The complexity of the process and the large amount of labour entailed by it, offer little chance of its being practically applicable, except possibly in chemical works, where it may be used in conjunction with the manufacture of caustic alkali, and even here its economy is very doubtful.

The decomposition of the plumbate into lime and lead peroxide may also be effected in situ by means of a current of moist furnace gases at 80°-100°, and the oxygen then liberated by raising the temperature. The great changes of temperature, however, thus involved, render the method impracticable, and in addition the sulphur impurities in the furnace gases rapidly deteriorate the mixture.

Salamon (Eng. Pat. 6553, 1890) proposed to decompose the calcium plumbate without removing it from the producer in which it is formed by allowing the temperature to fall 'to a certain point,' and then introducing a current of pure carbon dioxide. The following reaction then occurs:

$$Ca_2PbO_4 + 2CO_2 = 2CaCO_3 + PbO + O$$
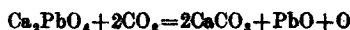
This necessitates the use of at least four times the volume of carbon dioxide as of oxygen obtained, a condition which at once puts the process out of the question as a technical and economical one. It has been suggested that the quantity of pure carbon dioxide required may be largely reduced by carrying out the earlier part of the reaction by means of the carbon dioxide in furnace gases, and using it pure only at the last. But the drawbacks so introduced neutralise any advantage.

10. By the alternate formation and decomposition of barium peroxide. In 1851 Boussingault found that when barium oxide (baryta) is heated to a dull red heat in a current of air it is converted into barium peroxide, and that at

a higher temperature this peroxide is again re-solved into barium oxide and oxygen. But his attempts to utilise this reaction as a practical and economical source of oxygen failed owing to the fact that after a few oxidations and deoxidations the baryta lost its power of re-absorbing oxygen. Many other attempts were made to overcome this difficulty, but for long without success. In 1879, however, the MM. Brin frères were more successful, and took out a patent for the process (Eng. Pat. 1416 of 1880). Further improvements were made under the auspices of the company formed to develop and work the patents, and the process was made practical and economical, and was worked on a large scale at various places.

The permanence of the baryta is mainly dependent on its physical condition, the use of reduced pressure during deoxidation, and consequent avoidance of excessively high temperatures, and the careful purification of the air used. It was found possible to dispense with change of temperature in the reaction, change of pressure being alone trusted to for determining the respective phases of oxidation and deoxidation. Neither the oxidation nor the deoxidation is as complete as when two temperatures are used, and the yield per operation is much less. But the duration of the operation was reduced from about 4 hours to 8-15 mins., and the total daily yield therefore largely increased. At the same time the operation was much simplified, the wear and tear of furnace, retorts, &c., greatly reduced, and the fuel required lessened. Labour was also economised, the multiplied reversals of cocks, &c., necessitated by the single-temperature method of working being effected automatically by reversing gear designed by K. S. Murray. The labour required was therefore little more than that needed for stoking the furnace, and oiling and supervising the pumps, &c. The oxygen obtained had a purity of about 93-96 p.c.

For a producer capable of delivering 10,000 cubic feet of oxygen per 24 hours the consumption of coke in the furnace was about 12-15 cwt. per day, and for plant of that or smaller size the pump power required was about 1 L.H.P. per 1000 feet of oxygen produced per day, the ratio decreasing for larger plants.

It is necessary that the barium oxide should be as hard and as porous as possible, and this is best obtained by igniting the nitrate. The nitrate fuses and decomposition soon commences with evolution of a mixture of oxygen and oxides of nitrogen. This action continues for about 2-3 hours, during which time the contents of the crucible remain in ebullition. A porous mass is then left, which is heated for another hour to complete, as far as possible, the decomposition. In this way a very hard but also very porous baryta is obtained.

This process was thoroughly practical and economical, and large numbers of plants were erected all over the world and worked successfully for many years. It was described in detail with illustrations of plant in the first edition of this dictionary (see also K. S. Murray, Proc. I. Mech. E. 1890, 131; Thorne, J. Soc. Chem. Ind. 1890, 246). In the last few years the process has been largely superseded by the still cheaper liquid air process, which also produces oxygen of greater purity (v. infra).

Cost of production.—It is very difficult to obtain data of the cost of production of oxygen under the earlier methods described, but the following figures probably approximate to the cost per 1000 cubic feet :—from chlorate 8*l*.-10*l*.; from pyrolusite 4*l*.-6*l*.; from sulphuric acid 2*l*. 10*s*.-3*l*. (probably higher when only the oxygen and not the sulphur dioxide is utilised); by the Tessié du Motay process 3*l*.-4*l*.; by the Brin process 7*s*.-12*s*. No authentic data of the cost of producing oxygen by dialysis or by solution in water are obtainable, but it would probably be *at least* as high as that by the Tessié du Motay process. In the Kassner process the cost depends largely on the amount realised by the sale of the caustic alkali, but would certainly be prohibitive for technical purposes. For cost by the liquid air and electrolysis processes, v. *infra*.

Properties.—The International Committee on Atomic Weights has adopted $O=16$ as the standard of comparison for all atomic weights, and under this scale $H=1.008$ (1.0076 Morley). Oxygen is a colourless, tasteless, and inodorous gas, of sp.gr. 1.1056 (air=1): at $0°$ and 760 mm. pressure a normal litre of gas weighs 1.42905 grms. (1.42893 at $0°$ and 760 mm., and 0.29071 grm. at $1067.4°$ and 760 mm., Jacquerod and Perrot, Compt. rend. 1905, 140, 1542; 1.42889 at $0°$, 760 mm., sea-level and latitude $45°$, Moles and Gonzalez, *ibid.* 1921, 173, 355), and at 30 ins. pressure and $15.5°$ 100 cubic ins. weigh 34.206 grs. 1 grm. of oxygen measures 0.6997 litre and 1 lb. 11.84 ft. Its absolute viscosity at $23°$ and 760 mm. pressure is $n + 10^7 = 2042.35$ (Kia-Lok Yen, Phil. Mag. 1919, [vi.] 38, 582). Oxygen also occurs in an active allotropic form called *ozone*, which is treated of in a separate article (v. OZONE).

Oxygen normally acts as a divalent element, but in many compounds, especially in certain organic compounds having somewhat basic characteristics, acts as a tetrad. When examined through very thick and highly compressed layers, gaseous oxygen has a slight blue tinge of colour. It is sparingly soluble in water. As with all gases, the quantity of oxygen dissolved by water depends on the tension of the oxygen in the atmosphere in contact with the water. Thus pure water shaken up in contact with pure oxygen will absorb nearly five times as much oxygen as it would when shaken up, at the same temperature and under the same pressure, with air—which only contains 20.9 p.c. by volume of oxygen. The following table gives the coefficients of solubility (*i.e.* the volume of oxygen absorbed by one volume of water when shaken up with pure oxygen under 760 mm. pressure) at different temperatures as determined by different observers :

Temperature	Coefficient of solubility					
	Bunsen (1855)	Dittmar	Roscoe and Lunt	Winkler (1861)	Bohr & Bock (1891)	Fox (1905)
0°C.	0.0411	—	—	0.0489	0.0496	0.0492
10°	0.0325	0.0383	0.0377	0.0380	0.0390	0.0384
20°	0.0284	0.0312	0.0308	0.0310	0.0317	0.0314
30°	—	—	—	0.0262	0.0268	0.0267
40°	—	—	—	—	0.0233	0.0233
50°	—	—	—	—	0.0207	0.0209

These numbers multiplied by 1000 give the number of c.c. oxygen absorbed by a litre of water from pure oxygen.

Winkler gives the following formula for calculating the coefficient of solubility (β) of oxygen in water at any temperature (t):

$$\beta = 0.04890 - 0.0013413t + 0.00000283t^2 - 0.00000029534t^3$$

Fox (Trans. Far. Soc. 1909, [v.] 68-81) gives the formula:

$$\beta = 0.04924 - 0.0013440t + 0.0000028752t^2 - 0.0000003024t^3$$

Rain-water is very nearly saturated with oxygen when its temperature, as collected, is below 15°. During the summer months the dissolved oxygen is always less than the saturation quantity, sometimes by as much as 25 p.c.

The coefficient of solubility of oxygen in alcohol at 0° is 0.2337; at 20° it is 0.2201 (Timofejeff), so that oxygen is much more soluble in alcohol than in water.

Nearly all natural waters contain oxygen in solution and can only be freed therefrom by prolonged boiling *in vacuo*. This dissolved oxygen, though small in amount, is the source from which fish obtain the oxygen necessary to sustain life.

The solubility of oxygen in sea water at 16° is about 78 p.c. of its solubility in pure water (Clowes and Biggs). All saline solutions dissolve less oxygen than pure water. The gas is very sparingly soluble in a strong solution of ammonium chloride.

For the solubility of oxygen in various organic solvents see Fischer and Pfleiderer, Z. anorg. Chem. 1922, 124, 61.

Oxygen, though long regarded as a permanent gas, was liquefied in 1877 by Pictet at a pressure of 320 atmospheres, and a temperature of −140°. Cailletet had previously observed the formation of a mist due to liquefaction when oxygen at −29° under a pressure of 300 atmospheres was allowed to expand suddenly. Olszewski in 1883 showed that the *critical temperature* of oxygen (i.e. the temperature above which no amount of pressure will liquefy it) is −113°, the pressure needed to liquefy it at that temperature being 50 atmospheres, and this was confirmed by Wroblewski and by Dewar in 1885. According to Cardoso (Arch. Sci. phys. nat. 1915, [iv.] 39, 400) the critical pressure is 49.30 atmos. and the critical temperature −118°. According to Kamerlingh Onnes the critical data are −118.84 and 49.713 atmospheres.

Liquid oxygen is a pale steel-blue transparent and very mobile liquid showing a clear meniscus (Dewar; Olszewski) boiling at −182.5° at 760 mm. pressure. When the pressure is reduced or removed, evaporation takes place so rapidly that a part of the oxygen is often frozen. Solidification takes place under 9 mm. pressure at −211.5° (W.), under 172 mm. at −219° (Dewar, Roy. Soc. Proc. 1911, 85, 589). This latter temperature is therefore the lowest obtainable by the evaporation of liquid oxygen. Travers, Sinter and Jacquerod (Proc. Roy. Soc. 1902, 70, 484) found the b.p. of oxygen to be −182.8° at 760 mm., −185° at 600 mm., −188.5° at 400, and −193.8° at 200 mm. The vapour

pressure of oxygen at temperatures in the neighbourhood of 57°–90° (abs.) may be expressed by the equation log $p = A/T + B + CI$ (p in atm.) with A = −419.31, B = 5.2365, C = 0.0648 (Cath.). Dewar obtained solid oxygen as a hard, doubly refracting pale blue crystalline mass by cooling liquid oxygen in a spray of liquid hydrogen. Its m.p. is −219° under a pressure of 1.12 mm. The density of liquid oxygen is 1.1181 at −182.5°, 1.1700 at −195.5°, 1.2386 at −210.5°, and that of solid oxygen 1.4256 at −252.5° (Dewar) corresponding to the general formula (for liquid and solid) $d = 1.5154 - 0.00442T°$ (where T° = absolute temperature). 781.8 volumes of oxygen at 0° and 760 mm. are contained in 1 volume of liquid oxygen at −182.5°. The latent heat of vaporisation of liquid oxygen varies with the temperature (Alt), at 760 mm. pressure (i.e. −182.5°) it is 50.97 cals., at −205° it is 55.5 cals. The specific heat between −200° and −183° is 0.347±0.014. The vapour density at −182° is normal. The refractive index of liquid oxygen is 1.2236. Liquid oxygen absorbs nitrogen readily, dissolving at −190.5° 380 times its volume, or 42 p.c. of its weight of gaseous nitrogen, the b.p. being thereby reduced to −188.8°. This was probably the cause of the discrepancies in the boiling-points given by the earlier observers. Liquid oxygen is a very perfect insulator, and is also comparatively inert in its chemical properties. Phosphorus, potassium, sodium, &c., may be immersed in it without any action taking place (Dewar).

When liquid oxygen is subjected to the action of strong light, and particularly of the ultra-violet rays, some of it is converted into ozone (Dewar) (cf. Weigert, Ber. 1913, 46, 815). It is also ozonised by α-rays. It is diathermanous, a non-conductor of electricity, but is strongly magnetic, its magnetic moment being 1 when iron is taken at 1000. The magnetic susceptibility of liquid oxygen at the freezing-point is 1.3 times as great as that of the solid. Its susceptibility is diminished or temporarily suspended by elevation of temperature. Oxygen is the least refractive of all gases; it gives a characteristic though not very strong absorption spectrum, but to obtain this it is necessary to view the source of light through great thicknesses of liquid or through the highly compressed gas. The spectrum first appears in the form of a number of fine lines, but as the pressure is increased or a layer of liquid oxygen is employed, it shows a number of broader and shaded dark bands, with almost complete absorption in the violet and ultra-violet. Six absorption bands have been observed, two in the red corresponding to the A and B Fraunhofer lines. The absorption spectrum of liquid oxygen is practically identical with that of gaseous oxygen. Oxygen shows a luminous spectrum in a Geissler tube containing a bright band in the red, two in the green, and one in the blue, but the spectrum varies under varying conditions.

The chemical activity of air depends upon the oxygen it contains, air being simply, in its chemical relations, oxygen diluted with nitrogen. Free oxygen, whether diluted with nitrogen or not, manifests considerable chemical activity, even at ordinary temperatures, this activity increasing with rise of temperature. There

..e only few elements—viz. fluorine, chlorine, bromine, iodine, silver, gold, platinum, neon, argon, and helium—which do not unite *directly* with oxygen. Most of the non-metallic elements unite with oxygen to form anhydrous acids. Of the exceptions, hydrogen forms a neutral oxide (water), whilst no oxides of fluorine, argon, neon, or helium have yet been obtained.

Phosphorus combines with oxygen at ordinary temperatures, as do also moist iron, moist lead, moist saw-dust, and many metallic compounds such as cuprous chloride, manganous hydroxide, ferrous hydroxide, &c. This oxidation at ordinary temperatures is called *autoxidation*, and substances undergoing autoxidation often induce the oxidation of other substances present which otherwise would not oxidise spontaneously. The alkali metals, especially rubidium, are especially active in this way. In many cases ozone is simultaneously produced. Light, and particularly sunlight, greatly assists oxidation by gaseous oxygen. Potassium and sodium are at once attacked by dry oxygen at ordinary temperatures, becoming coated with their respective oxides. The majority of metals remain bright under similar conditions, but many become oxidised when moisture is present. In some of the metals oxidised by exposure to air the first coating of oxide formed acts as a protective covering and prevents further oxidation, as is the case with lead. In others, however, the oxide first formed gradually becomes converted into a higher oxide and may then give up part of its oxygen to the metal in contact with it, and the oxidation is thus propagated through the mass of the metal. The rusting of iron is not a simple case of oxidation. Some metals which in their ordinary condition are comparatively inert towards oxygen combine with it readily at ordinary temperatures when they are in a finely divided state, offering a very large surface for chemical action. Thus lead or antimony when obtained by the ignition of their tartrates, and iron, nickel, cobalt, and copper, when reduced from their precipitated oxides in a current of hydrogen at a low temperature, all ignite spontaneously in contact with air or oxygen, and when in this finely divided state are therefore often termed *pyrophori*. Silver, gold, and platinum are not acted on directly by oxygen at any temperature. Some metals in a molten state absorb considerable quantities of oxygen which is given out again wholly or in part when the metal solidifies. 10 grms. of molten silver at 1020° absorb about 20 c.c. oxygen (*v.* Donnan and Shaw, J. Soc. Chem. Ind. 1910, 987).

Molten platinum and palladium also absorb oxygen. Heated at 450° silver gradually absorbs (*occludes*) about 5 times its volume of oxygen, gold 35–45, platinum 65–75, and palladium about 500 (7 p.c. by weight). Platinum black absorbs about 100 times its volume of oxygen and palladium sponge 1000, of which the whole is not given up again below a red heat. Wood charcoal absorbs oxygen at ordinary temperatures—about 18 times its volume (Goldstein)—but this absorptive power increases enormously at very low temperatures. At −185° 1 c.c. absorbs 230 c.c. of oxygen with the evolution of 34 cals., and this action may be employed to produce an oxygen vacuum, the pressure being reduced to that of a Geissler tube (Dewar).

The activity of oxygen is increased greatly by increase of temperature, and with most substances (except under the conditions already mentioned) an initial heating is necessary to start free oxidation, the heat evolved during oxidation being then sufficient to maintain it. Thus iron heated to bright redness in an atmosphere or stream of oxygen takes fire and burns brightly. A mixture of oxygen and hydrogen may be kept at ordinary temperatures for any length of time without change, but if the temperature of any part of the mixture be raised to bright redness—either by the electric spark, by the presentation of a flame or by other means—ignition at once takes place with explosive force throughout the whole mass. Under certain circumstances, however, this combination may be effected at ordinary temperatures. Thus, if a piece of clean platinum foil be hung in the mixture, combination takes place gradually at ordinary temperatures. This appears to be due to the power possessed by palladium, platinum, and some other substances of condensing gases and especially hydrogen on their surfaces, the activity of the gases so condensed being thereby greatly increased. If platinum or palladium black or sponge is used instead of foil, the action is so much increased that the heat evolved in the combination soon raises the temperature of the metal to the ignition-point of the gaseous mixture, and ordinary combustion ensues. This effect has been taken advantage of in the *Döbereiner* lamp (named after the investigator who first noticed this property of platinum) wherein a piece of spongy platinum is suspended over a jet connected with an automatic hydrogen-generating vessel. When the tap is turned on, the jet of hydrogen becoming mixed with air and at the same time impinging on the spongy platinum, oxidation takes place rapidly, the platinum soon becomes red hot and ignites the jet of hydrogen. Similar effects are produced with oxygen (or air) and gaseous hydrocarbons.

Various substances which expose large surfaces to air (or oxygen) become gradually heated through slow oxidation or combustion, and, if the heat cannot get away, ignition eventually occurs. Thus oily or greasy woollen and cotton rags and refuse are capable of absorbing oxygen fairly rapidly, and if present in any quantity the heat produced may accumulate and cause spontaneous combustion, and this action is a not infrequent cause of fires in factories. A similar generation of heat and eventual 'spontaneous combustion' often arises from the storing of moist hay in hayricks, and from the storage of damp coal in ships or heaps. The allegation that the ignition of coal is due to the oxidation of pyrites has been disproved by the work of Richters and Lewes, who have shown that the heat is generated by the absorption of oxygen and its action on the bituminous constituents of the coal.

Dixon, Baker, Traube, and others have shown that even at high temperatures the presence of a trace of moisture is necessary for free oxidation (combustion), and that in *absolutely* dry oxygen, sulphur and phosphorus can be distilled, and carbon made red-hot without

combustion taking place. A jet of burning dry carbon monoxide is even extinguished when introduced into pure and absolutely dry oxygen. The presence of the minutest trace of moisture is, however, sufficient to restore to oxygen its activity.

In ordinarily dry oxygen all substances which burn in air burn with much greater brilliancy, and many substances which do not burn in air burn vividly in oxygen. Thus iron, zinc, &c., if the ignition is started by a portion being raised to a white heat in an atmosphere of oxygen, continue to burn with great brilliancy and with the production of much heat. The actual amount of heat given out during the complete oxidation of any substance is the same whether the combustion is slow or rapid, and is carried on in air or in oxygen. But it is quite different in regard to the temperature developed, this depending on the concentration of the heat, and so being higher the more rapid the combustion and the less extraneous matter is present to absorb the heat. Thus, when phosphorus is burned in oxygen, the temperature produced is very high, and the combustion takes place with dazzling brilliancy. The temperature of a hydrogen or a coal-gas flame burning in oxygen is very much higher than that of a similar flame burning in air. The temperature of a flame of hydrogen burning in oxygen is 2800°; of carbon monoxide 2600°; and of acetylene 3000°. These facts have been utilised in the construction of the oxy-hydrogen and oxy-acetylene blowpipes for obtaining very high temperatures (v. *infra*). If coal-gas is substituted for the hydrogen, a very hot flame is still obtained, but the temperature is not as great as when hydrogen is employed. 16 grms. of oxygen combining with hydrogen to form water evolve 68,400 cals.

Oxygen is the only gas capable of supporting respiration, and forms the life-maintaining constituent of air. In the pure state it may be inhaled for a time with impunity, and acts as a mild tonic or exhilarant. But its long-continued respiration is harmful, feverishness and weakness being produced; and it becomes poisonous if breathed under pressure. Dr. Richardson kept a rabbit in an atmosphere of pure oxygen at a temperature of 23·9° for 3 weeks. It ate voraciously all the time, but became so emaciated from inability to assimilate new material fast enough to supply waste that it was found necessary to discontinue the experiment. At 7·2° the rabbit became speedily narcotised, and would have died had it not been removed. Richardson found that cold-blooded animals were very little affected by being introduced into an atmosphere of oxygen, whilst most warm-blooded animals (dogs, cats, guinea-pigs, &c., but not the rabbit) speedily showed strong febrile symptoms (Asclepiad 1887–89). Some observers had noticed very decided narcotic effects produced on animals under these conditions, but Richardson ascertained that this is due to the oxygen becoming vitiated by repeated inhalations. He found that when the same oxygen was used over and over again, although purified from carbonic acid, &c., by passage over caustic potash, sulphuric acid, &c., the animals became speedily narcotised, but that when a continuous stream of fresh oxygen was employed this was not the case. This 'de-

vitalising' of the oxygen appears to be due to traces in the exhaled gases of some compound which is not removed by the ordinary methods of purification. The electric discharge very quickly re-vitalised the vitiated oxygen. Flesh was found to decompose more readily in devitalised than in pure oxygen. At low temperatures, and at very high ones, however, oxygen is decidedly narcotic in its effect.

But although in health the continued inhalation of nearly pure oxygen is detrimental, its use where the action of the lungs and heart is sluggish, as in cases of partial suffocation, of collapse in cholera, pneumonia, and other illnesses, is very valuable, and has been the means of saving many lives. Its use in cases of cyanosis, gout, diabetes, &c., has also been found advantageous. Wounds and sores are said to heal more rapidly in an atmosphere of oxygen than in air, and it has been largely used in this connection.

Methods of testing and estimation.—The readiest test is the property possessed by oxygen of moderate purity of re-kindling a glowing splint of wood, a property only possessed by one other gas—viz. nitrous oxide. A mixture of air and oxygen containing less than 30 p.c. by volume of oxygen does not ignite a glowing splint. When mixed with colourless nitric oxide gas, oxygen produces deep reddish-brown fumes of nitric peroxide, whilst nitrous oxide does not. Nitrous oxide is also much more soluble in water than oxygen. Ferrous sulphate and catechol mixed in an alkaline solution rapidly absorb oxygen and with the production of a deep red colour.

White indigo absorbs oxygen rapidly, at the same time turning blue. For general purposes of estimation, however, one of the three following methods is generally used:—

1. A solution of cuprous chloride in hydrochloric acid (which is colourless) absorbs oxygen readily with formation of cupric oxy-chloride. The greenish-brown solution of this salt may be again reduced by keeping copper foil in it.

2. An alkaline solution of pyrogallol absorbs oxygen freely, forming a dark-brown liquid. Carbon monoxide is evolved from the solution if the sodium hydroxide solution has a sp.gr. of less than 1·3; all sodium pyrogall oxide solutions evolve carbon monoxide if the oxygen content is more than 95 p.c. A reagent which evolves the minimum quantity of carbon monoxide is made by dissolving sodium hydroxide in its own weight of water and adding 5 parts of this solution to 2 parts of a solution containing 1 gram of pyrogallol in 3 c.c. of water (Jones and Meighan, J. Ind. Eng. Chem. 1919, 11, 311). Good results are obtained by mixing 45 c.c. of a 25 p.c. solution of pyrogallol (prepared by dissolving 60 grms. in 180 c.c. water) with 145 c.c. of 60 p.c. solution of caustic potash (prepared by dissolving 400 grms. ordinary stick potash in 300 c.c. water). 200 c.c. of this solution will absorb nearly two litres of oxygen, but it is better not to push the absorption beyond about 450 c.c. as then more or less carbon monoxide may be formed. Carbon monoxide is also sometimes formed when the percentage of oxygen in the gas being tested exceeds about 30 p.c. Clowes (J. Soc. Chem.

Ind. 15, 170, 742) recommends the use of a very large excess of potash to prevent the formation of carbon monoxide. He advises 160 grms. potash dissolved in 130 c.c. water, and 10 grms. pyrogallol added to the alkaline liquid. According to Hoffmann (Z. angew. Chem. 1922, 35, 325), the best proportion is 20 parts pyrogallol, 20 parts potash, and 60 parts water, or 40 grms. pyrogallol in 90 c.c. of water with 70 grms. of potash solution of sp.gr. 1·55. A still more active absorbent is made by suspending 11·4 grms. of powdered hydroxyquinol triacetate (prepared by the action of acetic anhydride on p-benzoquinone) in 20 c.c. of water, shaken in a hydrogen atmosphere with a concentrated alkali hydroxide containing 17·4 grms. of KOH, or the equivalent (6 mols.) of NaOH, diluted with 130 c.c. of water (Henrich, Ber. 1915, 48. 2006).

3. Clean moist copper absorbs oxygen freely, but a skin of sub-oxide is rapidly formed over the copper, which prevents further oxidation. An ammoniacal solution of ammonium carbonate, however, readily dissolves this sub-oxide again, leaving the clean copper. To utilise this reaction for analysis a suitable absorption vessel is packed with fine copper wire and then filled with a solution composed of equal volumes of ammonia of sp.gr. 0·930, and of a saturated solution of commercial ammonium carbonate. When the gas in which the oxygen is to be estimated is introduced into the vessel and displaces the liquid, a large surface of clean copper is exposed, and the oxygen is rapidly absorbed. When the residual gas is removed, the liquid again fills the vessel and dissolves the sub-oxide of copper formed, leaving the copper clean for the next analysis. 200 c.c. of this solution will dissolve the oxide formed by the absorption of about 4 litres of oxygen, but it is advisable to renew it after the absorption of about 3 litres, as otherwise a good deal of a yellowish-brown precipitate (probably an ammonia-copper compound) forms which renders the renewal more troublesome. A little fresh copper wire must be occasionally added as that in the vessel gets used up.

For all these tests Hempel's, Orsat's, or Stead's apparatus (see ANALYSIS) answers well for all but the most delicate determinations. With these an oxygen determination can easily be made in 10 mins.

If the first method is employed, the gas after absorption must be freed from hydrochloric acid by means of potash.

The property of phosphorus of absorbing oxygen at ordinary temperatures is also sometimes used for analytical purposes, but this is not a generally convenient method. A hydrochloric acid solution of chromous chloride or an alkaline solution of ferrous tartrate may also be employed.

Sheaff (J. Biol. Chem. 1922, 52, 35) describes a method in which small amounts of air or other gas containing oxygen are diluted with hydrogen and treated with excess of nitric oxide in presence of NaHO solution, and the resulting nitrite estimated colorimetrically by sulphanilic acid and α-naphthylamine in acetic acid solution, and comparison with a standard solution of sodium nitrite. Quantities of oxygen of the order of 0·1 c.mm., approximating to a weight of 1×10^{-7} grms. may be estimated with a maximum error of 4 p.c.

Applications of oxygen.—Oxygen has been used successfully to maintain the air in a respirable condition in places where it cannot be replaced, as in diving-bells, submarine vessels, &c. Its use has often been suggested in connection with the ventilation of large halls, theatres, &c., but the cost has hitherto proved too great for its adoption.

It is employed in conjunction with hydrogen or coal-gas to produce the oxy-hydrogen and oxy-coal-gas flames in which platinum can be melted, silver distilled, &c. One application of these flames is in the production of the Drummond or lime-light where the intense heat of the flame is made use of to raise a lime cylinder to a white heat and thus obtain an intensely vivid light. The oxy-hydrogen and oxy-coal-gas or acetylene blowpipe is also used for the brazing of metals, autogenous soldering, the blowing and manipulation of hard-glass apparatus, and for many other purposes where very high temperatures and local heating are required (v. also *infra*).

Oxygen is used for many purposes in the laboratory, and, as already mentioned, for some medical purposes. It has been found that the admixture of small proportions (up to 6 or 7 p.c.) of oxygen with nitrous oxide during anæsthetising with that substance prevents or reduces the tendency to convulsions experienced with pure nitrous oxide, without reducing appreciably its anæsthetic power. Johnson has shown (J. pr. Chem. [i.] 49, 148) that anæsthesia may be produced with nitrogen equally as well as with nitrous oxide, and that a mixture of nitrogen with 5–7 p.c. oxygen forms a very satisfactory anæsthetic, producing slight or no convulsions.

Oxygen has been applied in the purification of coal-gas from sulphur compounds. It is found that if from 0·5–1 p.c. of oxygen is added to the crude coal-gas before it enters the purifiers the reduction of the sulphur compounds to 8–12 grms. per 100 cubic feet of gas may be effected by lime alone, the use of oxide of iron or lime sulphide being unnecessary. If oxide of iron is used, its efficiency is increased. In any case the purifying space needed is lessened, the life of the purifying material is lengthened, and the luminosity of the purified gas is considerably increased. If lime is used for purification the fouled lime ('blue billy') has not the objectionable smell which it usually possesses (Valon, Trans. Gas. Inst. 1889, 41).

It has been found that if, during the bleaching of paper pulps and other materials with bleaching powder, oxygen in a fine state of division is introduced into the bleaching potcher, a great saving of bleaching powder is effected, the bleached fibre also being stronger in texture (Thorne, J. Soc. Chem. Ind. 1889, 83).

Pure oxygen is also advantageously employed in the oxidation and thickening of oils for varnish and linoleum purposes. The thickened oil is paler in colour than boiled oil, the danger is less, as only steam heat is needed, and the thickening, besides being much more rapid, is accompanied by increase of weight instead of by loss of weight as in the ordinary process of boiling. The use of driers is also unnecessary (Eng. Pat. 18628, 1889).

Oxygen is now sometimes used to hasten the maturing of spirits, the same effect being produced in a few hours or days by means of pure oxygen acting on the spirit in a finely divided state as occurs under the ordinary method of storage in casks in 2 or 3 years.

Proposals have been made to use a mixture of oil gas and oxygen as an illuminating gas (Tatham, Eng. Pats. 13763, 16138, and 16142, 1889). It was found that, if 15–30 p.c. of oxygen is added to an oil gas retorted at a low temperature from a heavy and crude petroleum, a gas of very high illuminating power and of good travelling properties is obtained. The gas is a perfectly safe gas, as about its own volume of oxygen must be added to a heavy oil gas before an explosive mixture is formed. The same inventor proposed (l.c.) to use carburetted oxygen as a motive gas for engines, &c. He claims that with properly constructed valves, &c., perfect safety is secured, and that the great expansive force of carburetted oxygen on ignition gives results far superior to those obtained in the ordinary steam or gas engine.

The use in the manufacture of vinegar of small quantities of oxygen to act as a stimulant on the mycoderma has been found to considerably increase the rate of acetification.

L. T. T.

The Production of Oxygen by the Liquefaction of Air.

Since 1902, the liquid air process for the production of oxygen has rapidly come to the front and with the single exception of the electrolytic method it is now the oxygen process almost exclusively employed for commercial purposes.

The separation of liquid air into its main constituents, oxygen and nitrogen, was a problem which for many years, prior to 1902, occupied the attention of physicists and chemists who have studied the practical production of extreme cold and the liquefaction of gases.

It was, however, not until 1895 that the first real step of importance was taken in the practical production of liquid air. In that year, Carl von Linde took out a patent (Eng. Pat. 12528, 1895) for an apparatus which marked a new era in the production of liquid air and probably the first serious step in the separation of its constituents.

It has been proved by Thomson (Lord Kelvin) and Joule that if compressed air were allowed to expand without doing external work there was a slight fall of temperature due to the fact that internal work must be done in such expansion. Linde first realised [1] that this cooling effect increased very rapidly as the temperature fell, and in his patent of 1895 he

[1] It is a coincidence in the history of invention that the Eng. Pat. 10165 of 1895 was applied for by an Englishman, Dr. William Hampson, a few weeks before Professor Carl von Linde took out his British Patent. Hampson's patent is held by some to anticipate Linde in this country although there is no question as to the priority of Linde elsewhere. The terms of Hampson's provisional specification are somewhat ambiguous and it is difficult to say how much credit should be attached to this publication. Full details of Linde's apparatus were made known before the completion of Hampson's patent so that unfortunately his claim to priority has to stand on his provisional specification alone.

utilised the fact to make a most practical and effective air-liquefier. He took highly compressed air at ordinary atmospheric temperature and caused it to pass through a coiled copper pipe contained in a well-insulated heat interchanger, so constructed that the air which was allowed to expand through a throttle valve at the lower end of the coil was then caused to pass back in a reversed flow through the interchanger in intimate contact with the external surface of the pipe, through which the compressed air was passing on its way to the expansion valve. The principle of regenerative cooling was thus established between the expanded and compressed air with a self-intensive cooling effect which continued to increase until the cold became so great that a portion of the incoming compressed air was liquefied and collected in the vessel. Linde employed no preliminary cooling of the air, and by this simple construction of self-intensive counter-current interchanger, there is no doubt that he originated an air liquefying apparatus of much scientific value, although not perhaps of much direct commercial utility.

But in his 1895 patent, Linde did not aim merely at providing a simple method of producing liquid air; his real object was by liquefaction and subsequent fractional evaporation to separate its constituents in order to obtain oxygen of commercial purity. To do this, Linde relied on the fact that nitrogen being more volatile than oxygen the vapour from a liquid mixture of the two was richer in nitrogen than was the liquid itself. This process of fractional evaporation did not, however, prove successful. It was found by experiment that under the most favourable conditions in order to obtain a residue containing 50 p.c. of oxygen 70 p.c. of the liquid had to be evaporated, and that the further evaporation was carried the greater became the proportion of oxygen lost in the vapours. Thus in the end when the liquid approached the ordinary commercial standard of purity in oxygen its quantity had become so minute as to be practically valueless.

The following table, prepared by Linde from his own experiments, clearly shows how the composition of the liquid changes even under the most favourable conditions, viz. during slow or quiet evaporation:

Per cent. of liquid not yet evaporated	Per cent. of oxygen in liquid	Per cent. of oxygen in vapour coming off	Per cent. of original oxygen still in liquid
100·0	23·1	7·5	100·0
50·0	37·5	15·0	80·0
30·0	50·0	23·0	65·0
20·0	60·0	34·0	52·0
15·0	67·5	42·0	43·0
10·0	77·0	52·0	33·0
5·0	88·0	70·0	19·0

Between 1895 and 1902, many patents were taken out for the production of liquid air, and the separation of its constituents. Nearly all appear to derive their inspiration from Linde,

the low temperature for liquefaction of the air being obtained in practically every case by his nozzle expansion self-intensive system, whilst fractional evaporation of the liquid was invariably the system employed for obtaining oxygen

As a matter of historical accuracy it must be admitted that for the seven years following Linde's patent of 1895 no substantial progress was made towards the industrial separation of oxygen from liquid air. It was not until 1902 (Eng. Pat. 14111, 1902) that Linde himself took the final step which solved that problem and laid the foundation for what is to-day undoubtedly the cheapest and best process for the production of oxygen.

It has already been shown that to obtain oxygen from liquid air by fractional evaporation a serious loss was entailed of the very substance that the process was designed to produce. It was this difficulty which Linde solved in his patent of 1902 and he accomplished it by adapting to the treatment of liquid air the process of rectification long known and employed in the production of alcohol (see ALCOHOL). Linde himself regarded his 1902 invention solely as an addition to the method of obtaining oxygen from liquid air by means of fractional evaporation as described in his 1895 patent, and he only claims it as such. By introducing a rectification column, however, on the top of his evaporation chamber he not only succeeded in arresting the oxygen which was formerly lost but actually employed it to form part of a continuous rectification process for the production of oxygen in a state of remarkable purity.

The simplest form of the Linde oxygen separator as employed to-day embodies all the essential features of his 1902 patent, so that a brief description of the actual machine with special reference to the accompanying diagrams may be taken as describing all the important characteristics of the apparatus as set forth in the specification and claim of that patent.

Fig. 1 represents diagrammatically the sectional elevation of a Linde separator capable of producing large quantities of oxygen of 98–99 p.c. purity. The circular upper portion of the casing, which is of wood, contains in its centre the rectifying column A, whilst the base constructed of wood in the form of a hexagon contains the vaporising, or distilling chamber B. All clearance spaces are packed with sheep's wool or other suitable insulating material in order to prevent the penetration of heat from outside sources. e is the counter-current interchanger constructed in the form of a large copper spiral pipe and containing three small copper pipes d, one of which is enclosed in a larger pipe e, as indicated more clearly in the sectional diagram, Fig. 2. c_1 is an extension of the main spiral pipe to the top of the rectifying column A with a gas or vapour collecting funnel F projecting within the same. e_1 is an open funnel-ended extension of the pipe e at the top of the vaporising chamber B. The pipe coil d_1, shown in the vaporising chamber, is connected at one extremity with the small pipes d, contained in the counter-current interchanger. The other extremity of this pipe is connected with the inlet of the valve G, to the outlet of which another pipe d_2 is connected as shown.

This pipe is carried upwards and enters the rectification column near the top where it is fitted as shown with a rose end, the function of which will be explained later.

With this preliminary description of the essential parts the working of the apparatus can
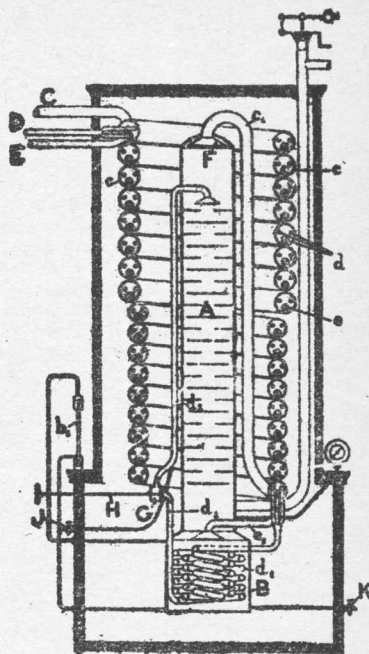

FIG. 1.

now be readily followed. There are two stages in the working. First, the preliminary cooling down and production of liquid, and second, the separation of oxygen from the liquid.

In commencing to work the machine, air at normal atmospheric temperature, or less, and at a pressure of about 2000 lbs. per sq. in. is conveyed from a gas compressor of suitable construction through the main pipe D, into the three small pipes d of the counter-current inter-changer. It passes down these pipes and through the pipe coil d_1 in the vaporiser to the inlet of the valve box G. At this point, by the adjustment of the regulating valve spindle H, the
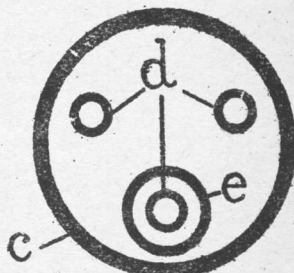

FIG. 2.

air is caused to expand from a high to a low pressure and is discharged at this low pressure through the rose ended pipe d_2 into the top of the rectification column. This expanded air fills the column and then flows through the only two possible outlets, c_1 and e_1, into the counter-current interchanger, in a reverse flow to the incoming high pressure air, leaving

the apparatus through the pipes c and e as indicated.

It is at the valve g that Linde obtains the Thomson-Joule effect to which reference has already been made and regenerative cooling occurs in the counter-current interchanger where the incoming compressed air parts with some of its heat to the outgoing air which has been rendered colder by this temperature drop on expansion. The cooling effect throughout the whole apparatus goes on cumulatively until a temperature is ultimately reached at which the expanded air begins to liquefy and collect in that state round the coils in the vaporiser B. The quantity of liquid thus collecting is registered outside the apparatus by means of an ordinary coloured liquid which is contained in a glass tube b, enclosed in a pressure equalising circuit as indicated.

When the whole apparatus has been cooled down nearly to the temperature of liquid air, the liquid begins to accumulate rapidly in the vaporiser B, and the initial pressure of the air may be gradually reduced by increasing the opening of the valve g. Until this stage is reached, any separation of oxygen and nitrogen, which may have occurred, has been due simply to fractional evaporation.

As, however, the liquid begins to accumulate round the coil in the vaporiser B, the compressed air transmits some of its latent heat to the liquid. The latter is thereby evaporated whilst the compressed air is itself liquefied in proportion to the amount of heat thus extracted. The vapours thus produced begin to flow upwards through the rectification column in which the liquid air is flowing downwards. The temperature gradient necessary for efficient rectification then rapidly becomes established in the column and the second stage is reached in which the apparatus can be employed for the production of oxygen.

In the separation of oxygen from liquid air by rectification, Linde relies for his temperature gradient on the difference between the boiling-points of nitrogen and oxygen. The former is $77 \cdot 5°$ absolute and the latter $91 \cdot 5°$ absolute. Liquid air is discharged into the top of the column at a temperature of about $81°$ absolute. Nitrogen being the more volatile component it immediately begins to boil off, and thus automatically creates the maximum cold at the top of the column. For the same reason the nitrogen present in the original liquid collected in the vaporiser is the first element to be liberated by latent heat from the compressed air; so that the temperature of the liquid in the vaporiser becomes higher as its content of oxygen increases, thus the highest temperature is also established automatically at the bottom of the column. When all the nitrogen has been expelled from the vaporiser, liquid air passing down the column over various baffle plates comes into intimate contact with rising vapours of oxygen and an exchange of material takes place. At each stage some of the rising oxygen is condensed and some of the nitrogen in the downcoming liquid is evaporated whilst the liquid gradually gains in temperature until by the time it reaches the vaporiser its composition is that of practically pure oxygen. The gas, on the other hand, which passes off from the top

of the column through the funnel F and the pipe c_1 to the counter-current interchanger, c, is mainly nitrogen at a temperature about $14°$ lower than that of the oxygen at the bottom of the column. The oxygen which rises in the column to effect the material exchange with the nitrogen of the liquid air is carried back to the vaporiser together with most of the oxygen contained in the original liquid. The excess of oxygen which thus continually gathers at the bottom of the apparatus is drawn off in a gaseous condition through the pipe e_1 into the pipe e of the counter-current interchanger. It will thus be seen that the gases drawn from the top and bottom of the apparatus are made to abstract heat completely from the incoming compressed air which is on its way to be liquefied.

The pressure at which the cold gases escape from the apparatus is from 4 to 5 lbs. per sq. in., just enough to cause them to pass freely through the counter-current interchanger. L is an emergency release valve on the low pressure system. J and K are test cocks communicating with the liquid air and liquid oxygen supplies respectively.

After the regular condition of oxygen producing has been reached the apparatus works steadily, the air supply from the compressor being kept at sufficient pressure not only to ensure its liquefaction at the temperature of the liquid oxygen bath (say $91°$ absolute), but also to ensure that the drop to the low pressure of from 4 to 5 lbs. sq. in. is sufficient to make good thermal losses due to leakage of heat from outside and to imperfect interchange in the counter-current apparatus. In practice, this pressure is found to be from 50 to 60 atmospheres.

A separate fore-cooler for the compressed air (not shown) is usually employed with the Linde apparatus. This fore-cooler is kept cold by means of a carbonic acid or an ammonia machine and is interposed between the air compressor and the separator so that the air leaving the compressor at normal atmospheric temperature becomes reduced to a temperature well below the freezing-point of water before it enters the separator. By this means, practically all the moisture which has not previously been abstracted by compression and chemical absorption gets frozen out of the air. This is a point of more importance in actual work than the slight supplementary cooling which is obtained, because unless the air is thoroughly dry before it enters the coils of the counter-current interchanger the working of the apparatus is liable to be interrupted by the formation of ice which has to be thawed out before work can be resumed. This is an operation which involves considerable delay. It is usual therefore to make both fore-coolers and separators in duplicate to ensure continuous working. In addition to the elimination of moisture it is also desirable to remove carbonic acid from the air. This is usually done by drawing the air on its way to the compressor through a purifier containing slaked lime. In practice, separators work for a week or longer without freezing up and fore-coolers for about two days.

The three essentials of Linde's process could not be more concisely or accurately described than in his own patent specification. They are