14

Oxygen

14.1 The Element

14.1.1 Introduction

Oxygen is the most abundant element on the earth's surface: it occurs both as the free element and combined in innumerable compounds, and comprises 23% of the atmosphere by weight, 46% of the lithosphere and more than 85% of the hydrosphere ($\sim$85.8% of the oceans and 88.81% of pure water). It is also, perhaps paradoxically, by far the most abundant element on the surface of the moon where, on average, 3 out of every 5 atoms are oxygen (44.6% by weight).

The "discovery" of oxygen is generally credited to C. W. Scheele and J. Priestley (independently) in 1773–4, though several earlier investigators had made pertinent observations without actually isolating and characterizing the gas.[1-4] Indeed, it is difficult to ascribe a precise meaning to the word "discovery" when applied to a substance so ubiquitously present

as oxygen; particularly when (a) experiments on combustion and respiration were interpreted in terms of the phlogiston theory, (b) there was no clear consensus on what constituted "an element", and (c) the birth of Dalton's atomic theory was still far in the future. Moreover, the technical difficulties before the mid-eighteenth century of isolating and manipulating gases compounded the problem still further, and it seems certain that several investigators had previously prepared oxygen without actually collecting it or recognizing it as a constituent of "common air". Scheele, a pharmacist in Uppsala, Sweden, prepared oxygen at various times between 1771–3 by heating KNO_3, $Mg(NO_3)_2$, Ag_2CO_3, HgO and a mixture of H_3AsO_4 and

[1] J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 1, pp. 344–51, Longmans, Green, 1922. History of the discovery of oxygen.

[2] M. E. Weeks, *Discovery of the Elements*, 6th edn., pp. 209–23, Journal of Chemical Education, Easton, Pa, 1956. (Oxygen.)

[3] J. R. PARTINGTON, *A History of Chemistry*, Vol. 3, Macmillan, London, 1962; Scheele and the discovery of oxygen (pp. 219–22); Priestley and the discovery of oxygen (pp. 256–63); Lavoisier and the rediscovery of oxygen (pp. 402–10).

[4] *Gmelin's Handbuch der Anorganischen Chemie*, 8th edn., pp. 1–82. "Sauerstoff" System No. 3, Vol. 1, Verlag Chemie, 1943. (Historical.)

MnO_2. He called the gas "vitriol air" and reported that it was colourless, odourless and tasteless, and supported combustion better than common air, but the results did not appear until 1777 because of his publisher's negligence. Priestley's classic experiment of using a "burning glass" to calcine HgO confined in a cylinder inverted over liquid mercury was first performed in Colne, England, on 1 August 1774; he related this to A. L. Lavoisier and others at a dinner party in Paris in October 1774 and published the results in 1775 after he had shown that the gas was different from nitrous oxide. Priestley's ingenious experiments undoubtedly established oxygen as a separate substance ("dephlogisticated air") but it was Lavoisier's deep insight which recognized the new gas as an element and as the key to our present understanding of the nature of combustion. This led to the overthrow of the phlogiston theory and laid the foundations

Oxygen: Some Important Dates

15th century	Leonardo da Vinci noted that air has several constituents, one of which supports combustion.
1773–4	C. W. Scheele and J. Priestley independently discovered oxygen, prepared it by several routes, and studied its properties.
1775–7	A. L. Lavoisier recognized oxygen as an element, developed the modern theory of combustion, and demolished the phlogiston theory.
1777	A. L. Lavoisier coined the name "oxygen" (acid former).
1781	Composition of water as a compound of oxygen and hydrogen established by H. Cavendish.
1800	W. Nicholson and A. Carlisle decomposed water electrolytically into hydrogen and oxygen which they then recombined by explosion to resynthesize water.
1818	Hydrogen peroxide discovered by L.-J. Thenard.
1840	C. F. Schönbein detected and named ozone from its smell (see 1857).
1848	M. Faraday noted that oxygen was paramagnetic, correctly ascribed to the triplet $^3\Sigma_g^-$ ground state by R. S. Mulliken (in 1928).
1857	W. Siemens constructed the first machine to use the ozonator-discharge principle to generate ozone.
1877	Oxygen first liquefied by L. Cailletet and R. Pictet (independently).
1881	Oxygen gas first produced industrially (from BaO_2) by A. Brin and L. W. Brin's Oxygen Company.
1896	First production of liquid oxygen on a technical scale (C. von Linde).
1903	Ozonolysis of alkenes discovered and developed by C. D. Harries.
1921–3	The water molecule, previously thought to be linear, shown to be bent.
1929	Isotopes ^{17}O and ^{18}O discovered by W. F. Giauque and H. L. Johnston (see 1961).
1931	Singlet state of O_2, $^1\Sigma_g^+$, discovered by W. H. J. Childe and R. Mecke.
1934	A lower lying singlet state $^1\Delta_g$ discovered by G. Herzberg.
1931–9	H. Kautsky showed the significance of singlet O_2 in organic reactions; his views were discounted at the time but the great importance of singlet O_2 was rediscovered in 1964 by (a) C. S. Foote and S. Wexler, and (b) E . J. Corey and W. C. Taylor.
1941	^{18}O-tracer experiments by S. Ruben and M. D. Kamen showed that the oxygen atoms in photosynthetically produced O_2 both come from H_2O and not CO_2; confirmed in 1975 by A. Stemler.
1951	First detection of ^{17}O nmr signal by H. E. Weaver, B. M. Tolbert and R. C. La Force.
1952	Introduction (in Austria) of the "basic oxygen process", now by far the most common process for making steel.
1961	Dual atomic-weight scales based on oxygen $= 16$ (chemical) and $^{16}O = 16$ (physical) abandoned in favour of the present unified scale based on $^{12}C = 12$.
1963	First successful launch of a rocket propelled by liquid H_2/liquid O_2 (Cape Kennedy, USA).
1963	Reversible formation of a dioxygen complex by direct reaction of O_2 with trans-$[Ir(CO)Cl(PPh_3)_2]$ discovered by L. Vaska.
1967	Many crown ethers synthesized by C. J. Pederson (Nobel Prize for Chemistry, 1987) who also studied their use as complexing agents for alkali metal and other cations.
1974	F. S. Rowland and M. Molina showed that man-made chlorofluorocarbons, CFCs, could catalytically destroy ozone in the stratosphere (Nobel Prize for Chemistry, with P. Crutzen, 1995).
1985	J. C. Farman discovered the "ozone hole" (substantial seasonal depletion of ozone) over Halley Bay, Antarctica.

of modern chemistry.[5] Lavoisier named the element "oxygéne" in 1777 in the erroneous belief that it was an essential constituent of all acids (Greek ὀξύς, *oxys*, sharp, sour; γείνομαι, *geinomai*, I produce; i.e. acid forming). Some other important dates in oxygen chemistry are in the Panel.

14.1.2 Occurrence

Oxygen occurs in the atmosphere in vast quantities as the free element O_2 (and O_3, p. 607) and there are also substantial amounts dissolved in the oceans and surface waters of the world. Virtually all of this oxygen is of biological origin having been generated by green-plant photosynthesis from water (and carbon dioxide).[6,7] The net reaction can be represented by:

$$H_2O + CO_2 + h\nu \xrightarrow[\text{enzymes}]{\text{chlorophyl}} O_2 + \{CH_2O\}$$

<div align="right">(i.e. carbohydrates, etc.)</div>
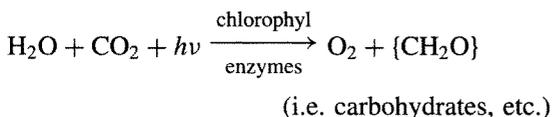
However, this is misleading since isotope-tracer experiments using ^{18}O have shown that both of the oxygen atoms in O_2 originate from H_2O, whereas those in the carbohydrates come from CO_2. The process is a complex multistage reaction involving many other species,[8] and requires $469\,kJ\,mol^{-1}$ of energy (supplied by the light). The reverse process, combustion of organic materials with oxygen, releases this energy again. Indeed, except for very small amounts of energy generated from wind or water power, or from nuclear reactors, all the

energy used by man comes ultimately from the combustion of wood or fossil fuels such as coal, peat, natural gas and oil. Photosynthesis thus converts inorganic compounds into organic material, generates atmospheric oxygen, and converts light energy (from the sun) into chemical energy. The $1.5 \times 10^9\,km^3$ of water on the earth is split by photosynthesis and reconstituted by respiration and combustion once every 2 million years or so.[9] The photosynthetically generated gas temporarily enters the atmosphere and is recycled about once every 2000 years at present rates. The carbon dioxide is partly recycled in the atmosphere and oceans after an average residence time of 300 years and is partly fixed by precipitation of $CaCO_3$, etc. (p. 273).

There was very little, if any, oxygen in the atmosphere 3000 million years ago. Green-plant photosynthesis probably began about 2500 My ago and O_2 first appeared in the atmosphere in geochemically significant amounts about 2000 My ago (this is signalled by the appearance of red beds of iron-containing minerals that have been weathered in an oxygen-containing atmosphere).[6-8] The O_2 content of the atmosphere reached ~2% of the present level some 800 My ago and ~20% of the present level about 580 My ago. This can be compared with the era of rapid sea-floor spreading to give the separated continents which occurred 110–85 My ago. The concentration of O_2 in the atmosphere has probably remained fairly constant for the past 50 My, a period of time which is still extensive when compared with the presence of *homo sapiens*, <1 My. The composition of the present atmosphere (excluding water vapour which is present in variable amounts depending on locality, season of the year, etc., is given in Table 14.1.[6] The oxygen content corresponds to 21.04 atom% and 23.15 wt% (see also ref. 10). The question of atmospheric ozone and pollution of the stratosphere is discussed on p. 608.

[5] A. L. LAVOISIER, *La Traité Elémentaire de Chimie*, Paris, 1789, translated by R. Kerr, *Elements of Chemistry*, London, 1790; facsimile reprint by Dover Publications, Inc., New York, 1965.

[6] J. C. G. WALKER, *Evolution of the Atmosphere*, pp. 318, Macmillan, New York, 1977.

[7] R. P. WAYNE, Chemistry of Atmospheres, 2nd edn. Oxford Univ. Press, Oxford, 1991, 456 pp (See especially Chap. 9).

[8] R. Govindgee, Photosynthesis, *McGraw Hill Encyclopedia of Science and Technology*, 4th edn., Vol. 10, pp. 200–10, 1977.

[9] P. CLOUD and A. GIBOR, The oxygen cycle, Article 4 in *Chemistry in the Environment*, pp. 31–41, Readings from Scientific American, W. H. Freeman, San Francisco, 1973.

[10] P. BRIMBLECOMBE, *Air Composition and Chemistry*, Cambridge Univ. Press, Cambridge, 1986, 224 pp.

Table 14.1 Composition of the atmosphere[a] (excluding H_2O, variable)

Constituent	Vol%	Total mass/tonnes	Constituent	Vol%	Total mass/tonnes
Dry air	100.0	$5.119(8) \times 10^{15}$	CH_4	$\sim 1.5 \times 10^{-4}$	$\sim 4.3 \times 10^9$
N_2	78.084(4)	$3.866(6) \times 10^{15}$	H_2	$\sim 5 \times 10^{-5}$	$\sim 1.8 \times 10^8$
O_2	**20.948(2)**	**$1.185(2) \times 10^{15}$**	N_2O	$\sim 3 \times 10^{-5}$	$\sim 2.3 \times 10^9$
			CO	$\sim 1.2 \times 10^{-5}$	$\sim 5.9 \times 10^8$
Ar	0.934(1)	$6.59(1) \times 10^{13}$	NH_3	$\sim 1 \times 10^{-6}$	$\sim 3 \times 10^7$
CO_2	0.0315(10)	$2.45(8) \times 10^{12}$	NO_2	$\sim 1 \times 10^{-7}$	$\sim 8 \times 10^6$
Ne	$1.818(4) \times 10^{-3}$	$6.48(2) \times 10^{10}$	SO_2	$\sim 1 \times 10^{-8}$	$\sim 2 \times 10^6$
He	$5.24(5) \times 10^{-4}$	$3.71(4) \times 10^9$	H_2S	$\sim 1 \times 10^{-8}$	$\sim 1 \times 10^6$
Kr	$1.14(1) \times 10^{-4}$	$1.69(2) \times 10^{10}$	**O_3**	**Variable**	**$\sim 3.3 \times 10^9$**
Xe	$8.7(1) \times 10^{-6}$	$2.02(2) \times 10^9$			

[a]Total mass: $5.136(7) \times 10^{15}$ tonnes; H_2O $0.017(1) \times 10^{15}$ tonnes; dry atmosphere $5.119(8) \times 10^{15}$ tonnes. Figures in parentheses denote estimated uncertainty in last significant digit.

In addition to its presence as the free element in the atmosphere and dissolved in surface waters, oxygen occurs in combined form both as water, and a constituent of most rocks, minerals, and soils. The estimated abundance of oxygen in the crustal rocks of the earth is 455 000 ppm (i.e. 45.5% by weight): see *silicates*, p. 347; aluminosilicates, p. 347; carbonates, p. 109; phosphates, p. 475, etc.

14.1.3 Preparation

Oxygen is now separated from air on a vast scale (see below) and is conveniently obtained for most laboratory purposes from high-pressure stainless steel cylinders. Small traces of N_2 and the rare gases, particularly argon, are the most persistent impurities. Occasionally, small-scale laboratory preparations are required and the method chosen depends on the amount and purity required and the availability of services. Electrolysis of degassed aqueous electrolytes produces wet O_2, the purest gas being obtained from 30% potassium hydroxide solution using nickel electrodes. Another source is the catalytic decomposition of 30% aqueous hydrogen peroxide on a platinized nickel foil.

Many oxoacid salts decompose to give oxygen when heated (p. 864). A convenient source is $KClO_3$ which evolves oxygen when heated to 400–500° according to the simplified equation

$$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$$
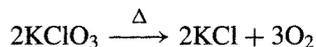
The decomposition temperature is reduced to 150° in the presence of MnO_2 but then the product is contaminated with up to 3% of ClO_2 (p. 847). Small amounts of breathable oxygen for use in emergencies (e.g. failure of normal supply in aircraft or submarines) can be generated by decomposition of $NaClO_3$ in "oxygen candles". The best method for the controlled preparation of very pure O_2 is the thermal decomposition of recrystallized, predried, degassed $KMnO_4$ in a vacuum line. Mn^{VI} and Mn^{IV} are both formed and the reaction can formally be represented as:

$$2KMnO_4 \xrightarrow{215-235°} K_2MnO_4 + MnO_2 + O_2$$

Oxygen gas and liquid oxygen are manufactured on a huge scale by the fractional distillation of liquid air at temperatures near $-183°C$. Although world production exceeds 100 million tonnes pa this is still less than one ten-millionth part of the oxygen in the atmosphere; moreover, the oxygen is continuously being replenished by photosynthesis. Further information on the industrial production and uses of oxygen are in the Panel.

Industrial Production and Uses of Oxygen[11]

Air can be cooled and eventually liquified by compressing it isothermally and then allowing it to expand adiabatically to obtain cooling by the Joule-Thompson effect. Although this process was developed by C. von Linde (Germany) and W. Hampson (UK) at the end of the last century, it is thermodynamically inefficient and costly in energy. Most large industrial plants now use the method developed by G. Claude (France) in which air is expanded isentropically in an engine from which mechanical work can be obtained; this produces a much greater cooling effect than that obtained by the Joule-Thompson effect alone. Because N_2 (bp $-195.8°C$) is more volatile than O_2 (bp $-183.0°C$) there is a higher concentration of N_2 in the vapour phase above boiling liquid air than in the liquid phase, whilst O_2 becomes progressively enriched in the liquid phase. Fractional distillation of the liquefied air is usually effected in an ingeniously designed double-column dual-pressure still which uses product oxygen from the upper column at a lower pressure (lower bp) to condense vapour for reflux at a higher pressure in the lower column. The most volatile constituents of air (He, H_2, Ne) do not condense but accumulate as a high-pressure gaseous mixture with N_2 at the top of the lower column. Argon, which has a volatility between those of O_2 and N_2, concentrates in the upper column from which it can be withdrawn for further purification in a separate column, whilst the least-volatile constituents (Kr, Xe) accumulate in the oxygen boiler at the foot of the upper column. Typical operating pressures are 5 atm at the top of the lower column and 0.5 atm at the bottom of the upper column. A large plant might produce 1700 tonnes per day of separated products. A rather different design is used if liquid (rather than gaseous) N_2 is required in addition to the liquid and/or gaseous O_2.

From modest beginnings at the turn of the century, oxygen has now become the third largest volume chemical produced in the USA (after H_2SO_4 and N_2 and ahead of ethylene, lime and NH_3, see p. 407). Production in 1995 was 23.3 million tonnes (USA), over 3 Mt (UK), and 100 Mt worldwide. About 20% of the USA production is as liquid O_2. This phenomenal growth derived mainly from the growing use of O_2 in steelmaking; the use of O_2 rather than air in the Bessemer process was introduced in the late 1950s and greatly increased the productivity by hastening the reactions. In many of the major industrial countries this use alone now accounts for 65–85% of the oxygen produced. Much of this is manufactured on site and is simply piped from the air-separation plant to the steel converter.

Oxygen is also used to an increasing extent in iron blast furnaces since enrichment of the blast enables heavy fuel oil to replace some of the more expensive metallurgical coke. Other furnace applications are in ferrous and non-ferrous metal smelting and in glass manufacture, where considerable benefits accrue from higher temperatures, greater productivity, and longer furnace life. Related, though smaller-scale applications, include steel cutting, oxy-gas welding, and oxygen lancing (concrete drilling).

In the chemical industry oxygen is used on a large scale in the production of TiO_2 by the chloride process (p. 959), in the direct oxidation of ethene to ethylene oxide, and in the manufacture of synthesis gas ($H_2 + CO$), propylene oxide, vinyl chloride, vinyl acetate, etc. Environmental and biomedical uses embrace sewage treatment, river revival, paper-pulp bleaching, fish farming, artificial atmospheres for diving and submarine work, oxygen tents in hospitals, etc. Much of the oxygen for these applications is transported either in bulk liquid carriers or in high-pressure steel cylinders.

A final, somewhat variable outlet for large-scale liquid oxygen is as oxidant in rocket fuels for space exploration, satellite launching and space shuttles. For example, in the Apollo mission to the moon (1979), each Saturn 5 launch rocket used 1270 m^3 (i.e. 1.25 million litres or 1450 tonnes) of liquid oxygen in Stage 1, where it oxidized the kerosene fuel (195 000 l, or about 550 tonnes) in the almost unbelievably short time of 2.5 min. Stages 2 and 3 had 315 and 76.3 m^3 of liquid O_2 respectively, and the fuel was liquid H_2.

14.1.4 Atomic and physical properties

Oxygen has 3 stable isotopes of which ^{16}O (relative atomic mass 15.994 915) is by far the most abundant (99.762 atom%). Of the others, ^{17}O (16.999 134) has an abundance of only 0.038% and ^{18}O (17.999 160) is 0.200% abundant. These values vary slightly in differing natural sources (the ranges being

0.0350–0.0407% for ^{17}O and 0.188–0.215% for ^{18}O) and this variability prevents the atomic weight of oxygen being quoted more precisely than 15.9994 ± 0.0003 (see p. 17). Artificial enrichment of ^{17}O and ^{18}O can be achieved by several physical or chemical processes such as the fractional distillation of water, the electrolysis of water, and the thermal diffusion of oxygen gas. Heavy water enriched to 20 atom% ^{17}O or 98% ^{18}O is available commercially, as is oxygen gas enriched to 95% in ^{17}O or 99% in ^{18}O. The ^{18}O isotope has been much used in kinetic and

[11] W. J. GRANT and S. L. REDFEARN, Industrial Gases, in R. Thompson (ed.), *The Modern Inorganic Chemicals Industry*, pp. 273–301. Chem. Soc. Special Publ. No. 31, 1978.

mechanistic studies.[12] Ten radioactive isotopes are also known but their very short half-lives make them unsuitable for tracer work. The longest lived, ^{15}O, decays by positron emission with $t_{\frac{1}{2}}$ 122.2 s; it can be made by bombarding ^{16}O with ^{3}He particles: $^{16}O(^{3}He,\alpha)^{15}O$.

The isotope ^{17}O is important in having a nuclear spin ($I = \frac{5}{2}$) and this enables it to be used in nmr studies.[13] The nuclear magnetic moment is -1.8930 nuclear magnetons (very similar to the value for the free neutron, -1.9132 NM) and the relative sensitivity for equal numbers of nuclei is 0.0291, compared with ^{1}H 1.00, ^{11}B 0.17, ^{13}C 0.016, ^{31}P 0.066, etc. In addition to this low sensitivity, measurements are made more difficult because the quadrupolar nucleus leads to very broad resonances, typically $10^{2}–10^{3}$ times those for ^{1}H. The observing frequency is ~ 0.136 times that for proton nmr. The resonance was first observed in 1951[14] and the range of chemical shifts extended in 1955.[15] The technique has proved particularly valuable for studying aqueous solutions and the solvation equilibria of electrolytes. Thus the hydration numbers for the diamagnetic cations Be^{II}, Al^{III}, and Ga^{III} have been directly measured as 4, 6 and 6 respectively, and several exchange reactions between "bound" and "free" water have been investigated. Chemical shifts for ^{17}O in a wide range of oxoanions $[XO_n]^{m-}$ have been studied and it has been found that the shifts for terminal and bridging O atoms in $[Cr_2O_7]^{2-}$ differ by as much as 760 ppm. The technique is proving increasingly valuable in the structure determination of complex polyanions in solution; for example all seven different types of O atoms

in $[V_{10}O_{28}]^{6-}$ (p. 986) have been detected.[16] The exchange of ^{17}O between $H_2{}^{17}O$ and various oxoanions has also been studied. Less work has been done so far on transition metal complexes of CO and NO though advances in techniques are now beginning to yield valuable structural and kinetic data.[17]

The electronic configuration of the free O atom is $1s^{2}2s^{2}2p^{4}$, leading to a $^{3}P_2$ ground state. The ionization energy of O is $1313.5\,kJ\,mol^{-1}$ (cf. S on p. 662 and the other Group 16 elements on p. 754). The electronegativity of O is 3.5; this is exceeded only by F and the high value is reflected in much of the chemistry of oxygen and the oxides. The single-bond atomic radius of O is usually quoted as 73–74 pm, i.e. slightly smaller than for C and N, and slightly larger than for F, as expected. The ionic radius of O^{2-} is assigned the standard value of 140 pm and all other ionic radii are derived from this.[18]

Molecular oxygen, O_2, is unique among gaseous diatomic species with an even number of electrons in being paramagnetic. This property, first observed by M. Faraday in 1848, receives a satisfying explanation in terms of molecular orbital theory. The schematic energy-level diagram is shown in Fig. 14.1; this indicates that the 2 least-strongly bound electrons in O_2 occupy degenerate orbitals of π symmetry and have parallel spins. This leads to a triplet ground state, $^{3}\Sigma_g^-$. As there are 4 more electrons in bonding MOs than in antibonding MOs, O_2 can be formally said to contain a double bond. If the 2 electrons, whilst remaining unpaired in separate orbitals, have opposite spin, then a singlet excited state of zero resultant spin results, $^{1}\Delta_g$. A singlet state also results if the 2 electrons occupy a single π^* orbital with opposed spins, $^{1}\Sigma_g^+$. These 2 singlet states lie 94.72 and $157.85\,kJ\,mol^{-1}$ above the ground state and are extremely important in gas-phase oxidation reactions (p. 614). The excitation is

[12] I. D. DOSTROVSKY and D. SAMUEL, in R. H. HERBER (ed.), *Inorganic Isotopic Syntheses*, Chap. 5, pp. 119–42, Benjamin, New York, 1962.

[13] C. ROGER, N. SHEPPARD, C. MCFARLANE and W. MCFARLANE, Chap. 12A in R. H. HARRIS and B. E. MANN (eds.). *NMR and the Periodic Table*, pp. 383–400, Academic Press, London, 1978. H. C. E. MCFARLANE and W. MCFARLANE, in J. MASON (ed.), *Multinuclear NMR*, Plenum Press, New York, 1987, pp. 403–16.

[14] F. ALDER and F. C. YU, *Phys. Rev.* **81**, 1067–8 (1951).

[15] H. E. WEAVER, B. M. TOLBERT and R. C. LAFORCE, *J. Chem. Phys.* **23**, 1956–7 (1955).

[16] W. G. KLEMPERER and W. SHUM, *J. Am. Chem. Soc.* **99**, 3544–5 (1977).

[17] R. L. KUMP and L. J. TODD, *J. Chem. Soc., Chem. Commun.*, 292–3 (1980).

[18] R. D. SHANNON, *Acta Cryst.* **A32**, 751–67 (1976).
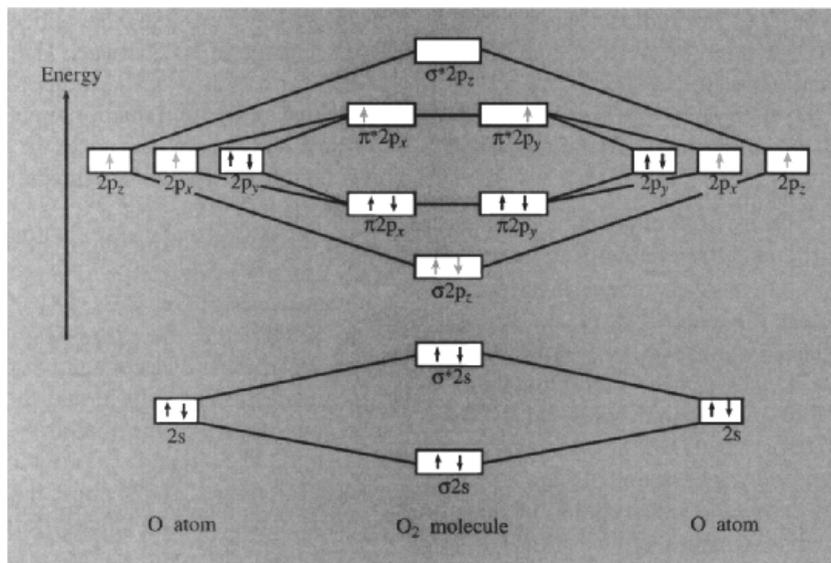
Figure 14.1 Schematic molecular–orbital energy level diagram for the molecule O_2 in its ground state, $^3\Sigma_g^-$. The internuclear vector is along the z-axis.

accompanied by a slight but definite increase in the internuclear distance from 120.74 pm in the ground state to 121.55 and 122.77 pm in the excited states. The bond dissociation energy of O_2 is 493.4(2) kJ mol^{-1}; this is substantially less than for the triply bonded species N_2 (945.4 kJ mol^{-1}) but is much greater than for F_2 (158.8 kJ mol^{-1}). See also the discussion on p. 616.

Oxygen is a colourless, odourless, tasteless highly reactive gas. It dissolves to the extent of 3.08 cm^3 (gas at STP) in 100 cm^3 H_2O at 20° and this drops to 2.08 cm^3 at 50°. Solubility in salt water is slightly less but is still sufficient for the vital support of marine and aquatic life. Solubility in many organic solvents is about 10 times that in water and necessitates careful degassing if these solvents are to be used in the preparation and handling of oxygen-sensitive compounds. Typical solubilities (expressed as gas volumes dissolved in 100 cm^3 of solvent at 25°C and 1 atm pressure) are Et_2O 45.0, CCl_4 30.2, Me_2CO 28.0 and C_6H_6 22.3 cm^3.

Oxygen condenses to a pale blue, mobile paramagnetic liquid (bp $-183.0°C$ at 1 atm).

The viscosity (0.199 centipoise at $-183.5°$ and 10.6 atm) is about one-fifth that of water at room temperature. The critical temperature, above which oxygen cannot be liquefied by application of pressure alone, is $-118.4°C$ and the critical pressure is 50.15 atm. Solid oxygen (pale blue, mp $-218.8°C$) also comprises paramagnetic O_2 molecules but, in the cubic γ-phase just below the mp, these are rotationally disordered and the solid is soft, transparent, and only slightly more dense than the liquid. There is a much greater increase in density when the solid transforms to the rhombohedral β-phase at $-229.4°$ and there is a further phase change to the monoclinic α-form at $-249.3°C$; these various changes and the accompanying changes in molar volume ΔV_M are summarized in Table 14.2.

The blue colour of oxygen in the liquid and solid phases is due to electronic transitions by which molecules in the triplet ground state are excited to the singlet states. These transitions are normally forbidden in pure gaseous oxygen and, in any case, they occur in the infrared region of the spectrum at 7918 cm^{-1} ($^1\Delta_g$) and 13 195 cm^{-1} ($^1\Sigma_g^+$). However, in the condensed phases a

Table 14.2   Densities and molar volumes of liquid and solid O_2

Transition	bp/1 (atm)	mp (triple pt)	$\gamma \longleftrightarrow \beta$	$\beta \longleftrightarrow \alpha$	
T/K	90.18	54.35	43.80	23.89	
$d/\text{g cm}^{-3}$	1.1407(1)	1.3215(1)	1.334(γ)	1.495(β)	1.53(α)
$\Delta V_M/\text{cm}^3\,\text{mol}^{-1}$	3.84	0.23	2.58	0.49	

single photon can elevate 2 colliding molecules simultaneously to excited states, thereby requiring absorption of energy in the visible (red-yellow-green) regions of the spectrum.[19] For example:

$$2O_2(^3\Sigma_g^-) + h\nu \longrightarrow 2O_2(^1\Delta_g);$$
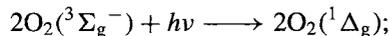
$$\bar{\nu} = 15\,800\,\text{cm}^{-1}, \text{ i.e. } \lambda = 631.2\,\text{nm}$$

$$2O_2(^3\Sigma_g^-) + h\nu \longrightarrow O_2(^1\Delta_g) + O_2(^1\Sigma_g^+);$$
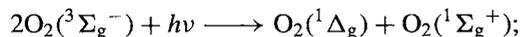
$$\bar{\nu} \sim 21\,100\,\text{cm}^{-1}, \text{ i.e. } \lambda = 473.7\,\text{nm}$$

The blue colour of the sky is, of course, due to Rayleigh scattering and not to electronic absorption by O_2 molecules.

14.1.5 Other forms of oxygen

Ozone [20]

Ozone, O_3, is the triatomic allotrope of oxygen. It is an unstable, blue diamagnetic gas with a characteristic pungent odour: indeed, it was first detected by means of its smell, as reflected by its name (Greek ὄζειν, *ozein*, to smell) coined by C. F. Schönbein in 1840. Ozone can be detected by its smell in concentrations as low as 0.01 ppm; the maximum permissible concentration for continuous exposure is 0.1 ppm but levels as high as 1 ppm are considered non-toxic if breathed for less than 10 min.

The molecule O_3 is bent, as are the iso-electronic species ONCl and ONO$^-$. Microwave measurements lead to a bond angle of $116.8 \pm 0.5°$ and an interatomic distance of 127.8 (± 0.3) pm between the central O and each of the 2 terminal O atoms as shown in Fig. 14.2a. This implies an O$\cdots$O distance of only 218 pm between the 2 terminal O atoms, compared with the normal van der Waals O$\cdots$O distance of 280 pm. A valence-bond description of the molecule is given by the resonance hybrids in Fig. 14.2b and a MO description of the bonding is indicated in Fig. 14.2c: in this, each O atom forms a σ bond to its neighbour using an sp^2-type orbital, and the 3 atomic p$_\pi$ orbitals can combine to give the 3 MOs shown. There are just sufficient electrons to fill the bonding and nonbonding MOs so that the π system can be termed a 4electron 3-centre bond. The total bond order for each O$-$O bond is therefore approximately 1.5 (1 σ bond and half of 1 π-bonding MO). It is instructive to note that SO_2 has a similar structure (angle O$-$S$-$O 120°): the much greater stability of this molecule when compared with O_3 has been ascribed, in part, to the possible involvement of d$_\pi$ orbitals on the S atom which would allow the filled nonbonding orbital in O_3 to become bonding in SO_2 (see also p. 700). Other comparisons of O$-$O bond orders, interatomic distances and bond energies are in Table 14.4 (p. 616).

Ozone condenses to a deep blue liquid (bp $-111.9°$C) and to a violet-black solid (mp $-192.5°$C). The colour is due to an intense absorption band in the red region of the spectrum between 500$-$700 nm (λ_{max} 557.4 and 601.9 nm). Both the liquid and the solid are explosive

[19] E. A. OGRYZLO, Why liquid oxygen is blue, *J. Chem. Educ.* **42**, 647–8 (1965).

[20] M. HORVATH, L. BILITZKY and J. HÜTTNER (eds.), *Ozone*, Elsevier, Amsterdam, 1985, 350 pp.
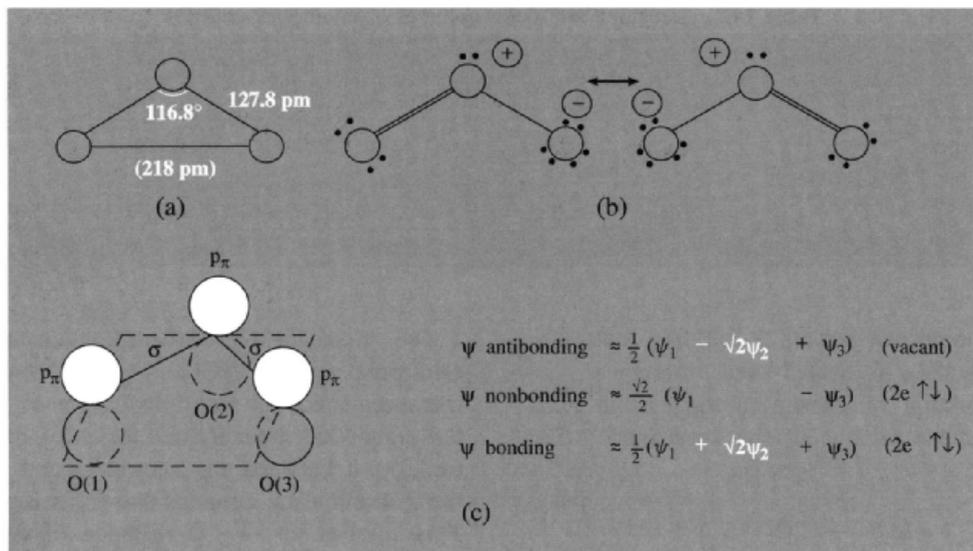
Figure 14.2 (a) Geometry of the O_3 molecule, (b) valence-bond resonance description of the bonding in O_3, and (c) orbitals used in the MO description of the bonding in O_3, where ψ_1 is the $2p_\pi$ orbital of O(1), etc.

due to decomposition into gaseous O_2. Gaseous ozone is also thermodynamically unstable with respect to decomposition into dioxygen though it decomposes only slowly, even at 200°, in the absence of catalysts or ultraviolet light:

$$\tfrac{3}{2}O_2(g) \longrightarrow O_3(g); \quad \Delta H_f^\circ + 142.7\,\text{kJ mol}^{-1};$$

$$\Delta G_f^\circ + 163.2\,\text{kJ mol}^{-1}$$
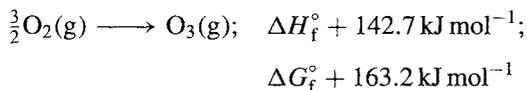
Other properties of ozone (which can be compared with those of dioxygen on p. 606) are: density at $-119.4°C$ $1.354\,\text{g cm}^{-3}$ (liquid), density at $-195.8°C$ $1.728\,\text{g cm}^{-3}$ (solid), viscosity at $-183°C$ 1.57 centipoise, dipole moment 0.54 D. Liquid ozone is miscible in all proportions with CH_4, CCl_2F_2, $CClF_3$, CO, NF_3, OF_2 and F_2 but forms two layers with liquid Ar, N_2, O_2 and CF_4.

A particularly important property of ozone is its strong absorption in the ultraviolet region of the spectrum between 220–290 nm (λ_{max}255.3 nm); this protects the surface of the earth and its inhabitants from the intense ultraviolet radiation of the sun. Indeed, it is this absorption of energy, and the consequent rise in temperature, which is the main cause for the existence of the stratosphere in the first place.

Thus, the mean temperature of the atmosphere, which is about 20°C at sea level, falls steadily to about $-55°$ at an altitude of 10 km and then rises to almost 0°C at 50 km before dropping steadily again to about $-90°$ at 90 km. Concern was expressed in 1974[21] that interaction of ozone with man-made chlorofluorocarbons would deplete the equilibrium concentration of ozone with potentially disastrous consequences, and this was dramatically confirmed by the discovery of a seasonally recurring "ozone hole" above Antarctica in 1985.[22] A less prominent ozone hole was subsequently detected above the Arctic Ocean. The detailed physical and chemical conditions required to generate these large seasonal depletions of ozone are extremely complex but the main features have now been elucidated (see p. 848). Several accounts of various aspects of the emerging story, and of the consequent international governmental actions to

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[21] M. J. MOLINA and F. S. ROWLAND, *Nature* **249**, 810–12 (1974). (Shared 1995 Nobel Prize for Chemistry with P. Crutzen.)

[22] J. C. FARMAN, B. G. GARDINER and J. D. SHANKLIN, *Nature* **315**, 207–10 (1985).

ameliorate or reverse the depletion have been published.[7,23−27]

Ozone is best prepared by flowing O_2 at 1 atm and 25° through concentric metallized glass tubes to which low-frequency power at 50–500 Hz and 10–20 kV is applied to maintain a silent electric discharge (see also p. 611). The ozonizer tube, which becomes heated by dielectric loss, should be kept cooled to room temperature and the effluent gas, which contains up to 10% O_3 at moderate flow rates, can be used directly or fractionated if higher concentrations are required. Reaction proceeds via O atoms at the surface M, via excited $O_2{}^*$ molecules, and by dissociative ion recombination:

$$O_2 + O + M \longrightarrow O_3 + M^*; \quad \Delta H^\circ_{298} - 109\,\text{kJ mol}^{-1}$$

$$O_2 + O_2{}^* \longrightarrow O_3 + O$$

$$O_2{}^+ + O_2{}^- \longrightarrow O_3 + O$$
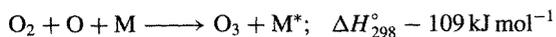
However, the reverse reaction of ozone with atomic oxygen is highly exothermic and must be suppressed by trapping out the ozone if good yields are to be obtained:

$$O_3 + O \longrightarrow 2O_2; \quad \Delta H^\circ_{298} - 394\,\text{kJ mol}^{-1}$$

An alternative route to O_3 is by ultraviolet irradiation of O_2: this is useful for producing low concentrations of O_3 for sterilization of foodstuffs and disinfection, and also occurs during the generation of photochemical smog. The electrolysis of cold aqueous H_2SO_4 (or $HClO_4$) at very high anode current densities also affords modest concentrations of O_3, together with O_2 and $H_2S_2O_8$

(p. 712) as byproducts. Other reactions in which O_3 is formed are the reaction of elementary F_2 with H_2O (p. 804) and the thermal decomposition of periodic acid at 130° (p. 872).

The concentration of ozone in O_2/O_3 mixtures can be determined by catalytic decomposition to O_2 in the gas phase and measurement of the expansion in volume. More conveniently it can be determined iodometrically by passing the gas mixture into an alkaline boric-acid-buffered aqueous solution of KI and determining the I_2 so formed by titration with sodium thiosulfate in acidified solution:

$$O_3 + 2I^- + H_2O \longrightarrow O_2 + I_2 + 2OH^-$$

The reaction illustrates the two most characteristic chemical properties of ozone: its strongly oxidizing nature and its tendency to transfer an O atom with coproduction of O_2. Standard reduction potentials in acid and in alkaline solution are:

$$O_3 + 2H^+ + 2e^- \rightleftharpoons O_2 + H_2O; \quad E^\circ + 2.075\,\text{V}$$

$$O_3 + H_2O + 2e^- \rightleftharpoons O_2 + 2OH^-; \quad E^\circ + 1.246\,\text{V}$$
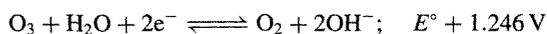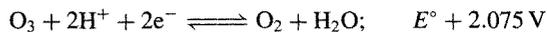
The acid potential is exceeded only by fluorine (p. 804), perxenate (p. 901), atomic O, the OH radical, and a few other such potent oxidants. Decomposition is rapid in acid solutions but the allotrope is much more stable in alkaline solution. At 25° the half-life of O_3 in 1 M NaOH is ~2 min; corresponding times for 5 M and 20 M NaOH are 40 min and 83 h respectively.

The highly reactive nature of O_3 is further typified by the following reactions:

$$CN^- + O_3 \longrightarrow OCN^- + O_2$$

$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

$$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$$

$$3I^- + O_3 + 2H^+ \longrightarrow I_3{}^- + O_2 + H_2O$$

$$2Co^{2+} + O_3 + 2H^+ \longrightarrow 2Co^{3+} + O_2 + H_2O$$
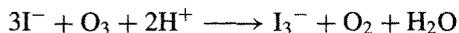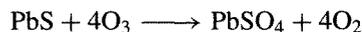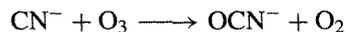
An important reaction of ozone is the formation of ozonides MO_3. The formation of a red coloration when O_3 is passed into concentrated aqueous alkali was first noted by C. F. Schönbein in 1866, but the presence

[23] D. G. COGAN, *Stones in a Glass House: CFCs and Ozone Depletion*, Investor Responsibility Research Center Inc., Washington, DC, 1988, 147 pp.

[24] ARJUN MAKHIJANI, ANNIE MAKHIJANI and A. BICKEL, *Saving our Skins: Technical Potential and Policies for the Elimination of Ozone-Depleting Compounds*, Environmental Policy Institute and Institute for Energy and Environmental Research, Washington, DC, 1988, 167 pp.

[25] R. P. WAYNE, *Proc. Royal Institution* **61**, 13–49 (1989).

[26] M. J. MOLINA and L. T. MOLINA, Chap. 2 in D. A. DUNNETTE and R. J. O'BRIEN (eds.), *The Science of Global Change: The Impact of Human, Activities on the Environment*, ACS Symposium Series, Am. Chem. Soc., Washington, DC, 1992, pp. 24–35.

[27] P. S. ZURER, *Chem. and Eng. News*, May 24, 1993, pp. 8–18.

of O_3^- was not established until 1949.[28] The compounds are best prepared by action of gaseous O_3 on dry, powdered MOH below $-10°$ (or O_3/O_2 mixtures on CsO_2) followed by extraction with liquid ammonia (which may also catalyse their formation). The compounds are red-brown paramagnetic solids ($\mu = 1.74-1.80$ BM)[29] and they decrease in stability in the sequence $Cs > Rb > K > Na$; unsolvated LiO_3 has not been prepared but the ammine $LiO_3.4NH_3$ is known. Likewise the stability of $M^{II}(O_3)_2$ decreases in the sequence $Ba > Sr > Ca$. Above room temperature MO_3 decomposes to the superoxide MO_2 (p. 616) and the compounds are also hydrolytically unstable:

$$MO_3 \xrightarrow{\text{warm}} MO_2 + \tfrac{1}{2}O_2$$

$$KO_3 + H_2O \longrightarrow KOH + O_2 + \{OH\}$$

$$2\{OH\} \longrightarrow H_2O + \tfrac{1}{2}O_2$$
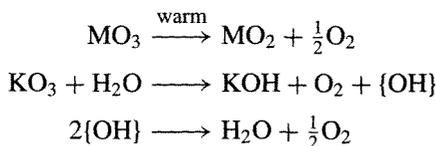
The ozonide ion O_3^- has the expected C_{2v} symmetry like O_3 itself and the isoelectronic, paramagnetic molecule ClO_2 (p. 845). Early attempts at X-ray structural analysis were frustrated by the thermal instability of the compounds, their great reactivity, the difficulty of growing single crystals and the tendency to rotational disorder.[30] However, it is now clear that the O_3^- ion is indeed bent, the most accurate data being obtained on crystals of the surprisingly stable red compound $[NMe_4]O_3$ (decomp. 75°, cf. CsO_3 53°):[31] the angle $O-O-O$ is 119.5(5)°, only slightly larger than for O_3 itself, and the $O-O$ and $O\cdots O$ distances

are 126.4(4) and 222.2(4) pm, respectively (cf. Fig. 14.2).

Ozone adds readily to unsaturated organic compounds[32] and can cause unwanted cross-linking in rubbers and other polymers with residual unsaturation, thereby leading to brittleness and fracture. Addition to alkenes yields "ozonides" which can be reductively cleaved by Zn/H_2O (or $I^-/MeOH$, etc.) to yield aldehydes or ketones. This smooth reaction, discovered by C. D. Harries in 1903, has long been used to determine the position of double bonds in organic molecules, e.g.:
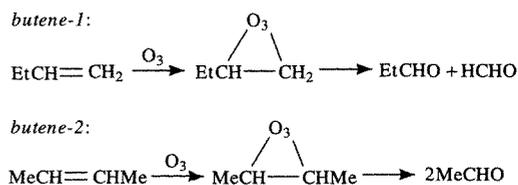
Ozonide formation occurs by a three-step mechanism along the lines first proposed in 1951 by R. Criegee:[33,34]

[28] I. A. KAZARNOVSKII, G. P. NIKOL'SKII and T. A. ABLETSOVA, *Dokl. Akad. Nauk SSSR* **64**, 69–72 (1949).

[29] H. LUEKEN, M. DEUSSEN, M. JANSEN, W. HESSE and W. SCHNICK, *Z. anorg. allg. Chem.* **553**, 179–86 (1981).

[30] L. V. AZÁROV and I. CORVIN, *Proc. Natl. Acad. Sci. (US)* **49**, 1–5 (1963). M. JANSEN and W. HESSE, *Z. anorg. allg. Chem.* **560**, 47–54 (1988).

[31] W. HESSE and M. JANSEN, *Angew. Chem. Int. Edn. Engl.* **27**, 1341–2 (1988). See also W. ASSENMACHER and M. JANSEN, *Z. anorg. allg. Chem.* **621**, 431–4 (1995) for information on the newest ionic ozonides, $[PMe_4]O_3$ and $[AsMe_4]O_3$.

[32] P. S. BAILEY, *Ozonation in Organic Chemistry*, Vol. 1, Olefinic Compounds, Academic Press, New York, 1978, 272 pp.; Vol. 2, Nonolefinic Compounds, 1982, 496 pp. S. D. RAZUMOVSKI and G. E. ZAIKOV, *Ozone and Its Reactions with Organic Compounds*, Elsevier, Amsterdam, 1984, 404 pp.

[33] R. CRIEGEE, *Rec. Chem. Prog.* **18**, 111–20 (1957). *Angew. Chem. Int. Edn. Engl.* **14**, 745–52 (1975).

[34] R. L. KUCZKOWSKI, *Chem. Soc. Revs.* **21**, 79–83 (1992).

The primary ozonides (1), which are 1,2,3-trioxolanes, are formed by a concerted 1,3-dipolar cycloaddition between ozone and the alkene and are detectable only at very low temperatures. For example, at $-175°C$ ethene gives $\overline{CH_2CH_2OOO}$ which was shown by microwave spectroscopy to be non-planar with O–O 145 pm, angle O–O–O 100° and a dihedral angle between the C_2O_2 and O_3 planes of 51°.[35] At higher temperatures the primary ozonides spontaneously rearrange to secondary ozonides: these have a 1,2,4-trioxolane structure (2) and can be studied by a variety of techniques including ^{17}O nmr spectroscopy.[36] Normally, however, the ozonide is not isolated but is reductively cleaved to aldehydes and ketones in solution. Oxidative cleavage (air or O_2) yields carboxylic acids and, indeed, the first large-scale application of the reaction was the commercial production of pelargonic and azelaic acids from oleic acid:

$$Me(CH_2)_7CH=CH(CH_2)_7CO_2H$$
Oleic acid

↓ O_3

O_3
$Me(CH_2)_7CH{-}{-}{-}{-}CH(CH_2)_7CO_2H$
Ozonide

↓ O_2/H_2O

$Me(CH_2)_7CO_2H$ $HO_2C(CH_2)_7CO_2H$
Pelargonic acid + Azelaic acid
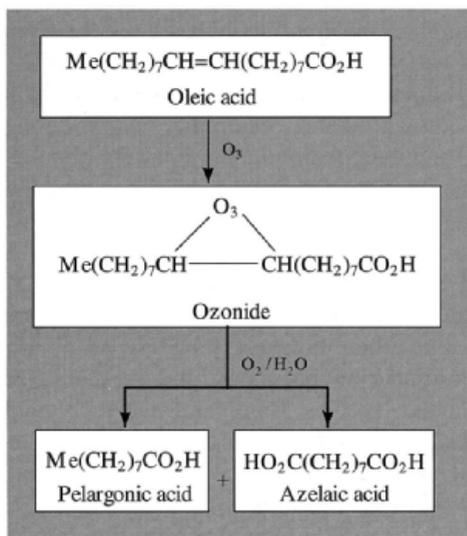
Esters of these acids are used as plasticizers for PVC (polyvinylchloride) and other plastics.

Because of the reactivity, instability and hazardous nature of O_3 it is always generated on site. Typical industrial ozone generators operate at 1 or 2 atm, 15–20 kV, and 50 or 500 Hz. The concentration of O_3 in the effluent gas depends on the industrial use envisaged but yields of up to 10 kg per hour or 150 kg per day from a single apparatus are not uncommon and some plants yield over 1 tonne per day. In addition to pelargonic and azelaic acid production, O_3 is used to make peroxoacetic acid from acetaldehyde and for various inorganic oxidations. At low concentrations it is used (particularly in Europe) to purify drinking water, since this avoids the undesirable taste and smell of chlorinated water, and residual ozone decomposes to O_2 soon after treatment.[37] Of the 1039 plants operating in 1977 all but 40 were in Europe, with the greatest numbers in France (593), Switzerland (150), Germany (136), and Austria (42). Other industrial uses include the preservation of goods in cold storage, the treatment of industrial waste and the deodorizing of air and sewage gases.[38]

Atomic oxygen

Atomic oxygen is an extremely reactive, fugitive species which cannot be isolated free from other substances. Many methods of preparing oxygen atoms also yield other reactive or electronically excited species, and this somewhat complicates the study of their properties. Passage of a microwave or electric discharge through purified O_2 gas diluted with argon produces O atoms in the ^3P ground state (2 unpaired electrons). Mercury-sensitized photolysis of N_2O is perhaps a more convenient route to ground state O atoms (plus inert N_2 molecules) though they can also be made by photolysis of O_2 or NO_2. Photolysis of N_2O in the absence of Hg gives O atoms in the spin-paired ^1D excited state, and this species can also be obtained by photolysis of O_3 or CO_2.

[35] J. Z. GILLIES, C. W. GILLIES, R. D. SUENRAM and F. J. LOVAS, *J. Am. Chem. Soc.* **110**, 1991–9 (1988).

[36] J. LAUTERWEIN, K. GRIESBAUM, P. KRIEGER-BECK, V. BALL and K. SCHLINDWEIN, *J. Chem. Soc., Chem. Commun.*, 816–7 (1991).

[37] J. KATZ (ed.), *Ozone and Chlorine Dioxide Technology for Disinfection of Drinking Water*, Noyes Data Corp., Park Ridge, New Jersey, 1980, 659 pp. R. G. RICE and M. E. BROWNING, *Ozone Treatment of Industrial Wastewater*, Noyes Data Corp., Park Ridge, New Jersey, 1981, 371 pp.

[38] J. A. WOJTOWICZ, Ozone, *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn. **17**, 953–95. Wiley, New York, 1996.

The best method for determining the concentration of O atoms is by their extremely rapid reaction with NO_2 in a flow system:

$$O + NO_2 \longrightarrow O_2 + NO$$

The NO thus formed reacts more slowly with any excess of O atoms to reform NO_2 and this reaction emits a yellow-green glow.

$$NO + O \longrightarrow NO_2^* \longrightarrow NO_2 + h\nu$$
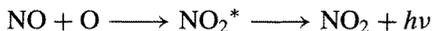
The system is thus titrated with NO_2 until the glow is sharply extinguished.

As expected, atomic O is a strong oxidizing agent and it is an important reactant in the chemistry of the upper atmosphere.[17,18] Typical reactions are:

$$H_2 + O \longrightarrow OH + H$$

$$OH + O \longrightarrow O_2 + H$$

$$O_2 + O \longrightarrow O_3$$

$$Cl_2 + O \longrightarrow Cl_2O, \; ClO_2$$

$$CO + O \longrightarrow CO_2$$

$$CH_4 + O \longrightarrow CO_2, \; H_2O$$

$$HCN + O \longrightarrow CO, \; CO_2, NO, H_2O$$

$$H_2S + O \longrightarrow H_2O, \; SO_2, \; SO_3, \; H_2SO_4$$

$$NaCl + O \xrightarrow{\;aq\;} NaClO_3, Cl_2, NaOH$$
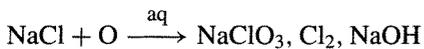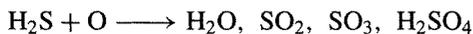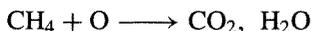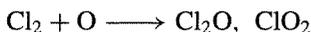
Many of these reactions are explosive and/or chemiluminescent.

14.1.6 Chemical properties of dioxygen, O_2

Oxygen is an extremely reactive gas which vigorously oxidizes many elements directly, either at room temperature or above. Despite the high bond dissociation energy of O_2 ($493.4 \, kJ \, mol^{-1}$) these reactions are frequently highly exothermic and, once initiated, can continue spontaneously (combustion) or even explosively. Familiar examples are its reactions with carbon (charcoal) and hydrogen. Some elements do not combine with oxygen *directly*, e.g. certain refractory or noble metals such as

W, Pt, Au and the noble gases, though oxo compounds of all elements are known except for He, Ne, Ar and possibly Kr. This great range of compounds was one of the reasons why Mendeleev chose oxides to exemplify his periodic law (p. 20) and why oxygen was chosen as the standard element for the atomic weight scale in the early days when atomic weights were determined mainly by chemical stoichiometry (p. 16).

Many inorganic compounds and all organic compounds also react directly with O_2 under appropriate conditions. Reaction may be spontaneous, or may require initiation by heat, light, electric discharge, chemisorption or various catalytic means. Oxygen is normally considered to be divalent, though the oxidation state can vary widely and includes the values of $+\frac{1}{2}$, 0, $-\frac{1}{3}$, $-\frac{1}{2}$, -1 and -2 in isolable compounds of such species as O_2^+, O_3, O_3^-, O_2^-, O_2^{2-} and O^{2-} respectively. The coordination number of oxygen in its compounds also varies widely, as illustrated in Table 14.3 and numerous examples of stable compounds are known which exemplify each coordination number from 1 to 8 (with the possible exception of 7, for which unambiguous examples are more difficult to find). Most of these examples are straightforward and structural details will be found at appropriate points in the text. Linear 2-coordinate O occurs in the silyl ether molecule $[O(SiPh_3)_2]$.[39] Planar 3-coordinate O occurs in the neutral gaseous molecular species OLi_3 and ONa_3[40] and in both cationic and anionic complexes (Fig. 14.3a, b). It also occurs in two-dimensional layer lattices such as tunellite, $[OB_6O_8(OH)_2]^{2n-}$ (cf. Fig. 14.3b) and in the three-dimensional rutile structure (p. 961).

Planar 4-coordinate O occurs uniquely in NbO which can be considered as a defect-NaCl-type structure with O and Nb vacancies at (000) and $\left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$ respectively, thereby having only 3

[39] C. GLIDEWELL and D. C. LILES, *J. Chem. Soc., Chem. Commun.*, 682 (1977).

[40] E.-U. WÜRTHWEIN, P. von R. SCHLEYER and J. A. POPLE, *J. Am. Chem. Soc.*, **106**, 6973–8 (1984).

Table 14.3 Coordination geometry of oxygen

CN	Geometry	Examples
0	—	Atomic O
1	—	O_2, CO, CO_2, NO, NO_2, SO_3(g), OsO_4; terminal O_t in P_4O_{10}, [VO(acac)$_2$], and many oxoanions $[MO_n]^{m-}$ (M = C, N, P, As, S, Se, Cl, Br, Cr, Mn, etc.)
2	Linear	Some silicates, e.g. $[O_3Si-O-SiO_3]^{6-}$ in $Sc_2Si_2O_7$; $[Cl_5Ru-O-RuCl_5]^{4-}$; $ReO_3(WO_3)$-type structures; coesite (SiO_2); $[O(SiPh_3)_2]^{(39)}$
2	Bent	O_3, H_2O, H_2O_2, F_2O; silica structures, GeO_2; P_4O_6 and many heterocyclic compounds with O_μ; complexes of ligands which have O_t as donor atom, e.g. [BF$_3$(OSMe$_2$)], [SnCl$_4$(OSeCl$_2$)$_2$], [{TiCl$_4$(OPCl$_3$)}$_2$], [HgCl$_2$(OAsPh$_3$)$_2$]; complexes of O_2, e.g. [Pt(O_2)(PPh$_3$)$_2$]
3	Planar	OLi$_3$, ONa$_3$;$^{(40)}$ [O(HgCl)$_3$]$^+$Cl$^-$, Mg[OB$_6$O$_6$(OH)$_6$].4$\frac{1}{2}$H$_2$O (macallisterite); Sr[OB$_6$O$_8$(OH)$_2$].3H$_2$O, (tunellite); rutile-type structures, e.g. MO$_2$ (M = Ti; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re; Ru, Os; Rh, Ir; Pt; Ge, Sn, Pb; Te)
3	Pyramidal	[H$_3$O]$^+$; hydrato-complexes, e.g. [M(H$_2$O)$_6$]$^{n+}$; complexes of R$_2$O and crown ethers; organometallic clusters such as [(η-C$_5$H$_5$)$_5$(O)V$_6$(μ_3-O)$_8$]$^{(41)}$
4	Square planar	NbO (see text)
4	Tetrahedral	[OBe$_4$(O$_2$CMe)$_6$]; CuO, AgO, PdO; wurtzite structures, e.g. BeO, ZnO; corundum structures, e.g. M$_2$O$_3$ (M = Al, Ga, Ti, V, Cr, Fe, Rh); fluorite structures, e.g. MO$_2$ (M = Zr, Hf; Ce, Pr, Tb; Th, U, Np, Pu, Am, Cm; Po)
4	See-saw	[Fe$_3$Mn(CO)$_{12}$(μ_4-O)]$^{-(42)}$
5	Square pyram.	[LCu$_4$(OH)]$^{3+(43)}$, [(InOPr^i)$_5$(μ_5-O)(μ_2-OPr^i)$_4$(μ_3-OPr^i)$_4$]$^{(44)}$
6	Octahedral	Central O in [Mo$_6$O$_{19}$]$^{2-}$; many oxides with NaCl-type structure, e.g. MO (M = Mg, Ca, Sr, Ba; Mn, Fe, Co, Ni; Cd; Eu)
7		—
8	Cubic	Anti-fluorite-type structure, e.g. M$_2$O (M = Li, Na, K, Rb)

NbO (rather than 4) per unit cell (see p. 983). Tetrahedral, 4–coordinate O is featured in "basic beryllium acetate" (p. 122) and in many binary oxides as mentioned in Table 14.3. The detailed structure depends both on the stoichiometry and on the coordination geometry of the metal, which is planar in CuO, AgO and PdO, tetrahedral in BeO and ZnO, octahedral in M$_2$O$_3$ and cubic in MO$_2$. Tetrahedral coordination of O also occurs in the unusual species ONa$_4$ and HONa$_3$.$^{(40)}$ The less common see-saw (C_{2v}) coordination mode occurs in the "butterfly" oxo cluster anion [Fe$_3$Mn(CO)$_{12}$(μ_4-O)]$^-$, in which the O atom bridges the [Mn(CO)$_3$] and {Fe(CO)$_3$} wingtips and the two [Fe(CO)$_3$] hinge groups.$^{(42)}$

Five-fold coordination of O has only recently been established, in the μ_4-hydroxo bridged Cu$_4^{II}$ cluster, [Cu$_4$(μ_4-OH)(η^8-L*)], in which the central planar OCu$_4$ group is supported by a circumannular octadentate macrocyclic ligand, L*, with the H atom of the OH group vertically above (or below) this plane.$^{(43)}$ Square pyramidal coordination of O also occurs in the indium *iso*-propoxide cluster [(InOPr^i)$_5$(μ_5-O)(μ_2-OPr^i)$_4$(μ_3-OPr^i)$_4$]$^{(44)}$ and in some complicated [Ba$_5$(μ_5-O)] oxobarium clusters supported by μ_2 and μ_3 phenoxide of *t*-butoxide ligands.$^{(45)}$

^{41} F. BOTTOMLEY, D. F. DRUMMOND, D. E. PAEZ and P. S. WHITE, *J. Chem. Soc., Chem. Commun.*, 1752–3 (1986).
^{42} C. K. SCHAUER and D. F. SHRIVER, *Angew. Chem. Int. Edn. Engl.* **26**, 255–6 (1987).

^{43} V. McKEE and S. S. TANDON, *J. Chem. Soc., Chem. Commun.*, 385–7 (1988). See also K. P. McKILLOP, S. M. NELSON, J. NELSON and V. McKEE, *ibid.*, 387–9 (1988).
^{44} D. C. BRADLEY, H. CHUDZYNSKA, D. M. FRIGO, M. B. HURSTHOUSE and M. A. MAZID, *J. Chem. Soc., Chem. Commun.*, 1258–9 (1988).
^{45} K. G. CAULTON, M. H. CHISHOLM, S. R. DRAKE and K. FOLTING, *J. Chem. Soc., Chem. Commun.*, 1349–51 (1990).
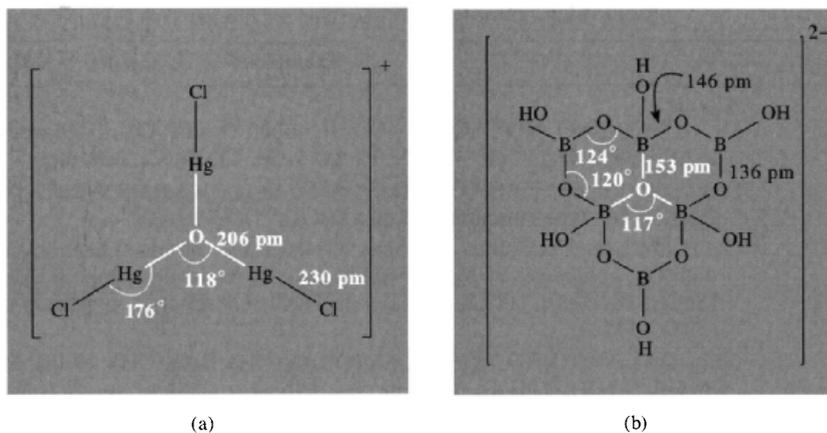
Figure 14.3   Examples of planar 3-coordinate O: (a) the cation in [O(HgCl)$_3$]Cl, (b) the central O atom in the discrete borate anion [OB$_6$O$_6$(OH)$_6$]$^{2-}$ in macallisterite — the three heterocycles are coplanar but the 6 pendant OH groups lie out of the plane.

A recent addition to the many examples of octahedral coordination of O (Table 14.3) is the unusual volatile, hydrocarbon-soluble, crystalline oxo-alkoxide of barium [H$_4$Ba$_6$(μ_6-O)(OCH$_2$-CH$_{2t}$OMe)$_{14}$], which forms rapidly when Ba granules are reacted with MeOCH$_2$CH$_2$OH in toluene suspension.[46]

Much of the chemistry of oxygen can be rationalized in terms of its electronic structure (2s^2 2p^4), high electronegativity (3.5) and small size. Thus, oxygen shows many similarities to nitrogen (p. 412) in its covalent chemistry, and its propensity to form H bonds (p. 52) and p$_\pi$ double bonds (p. 416), though the anionic chemistry of O^{2-} and OH$^-$ is much more extensive than for the isoelectronic ions N^{3-}, NH^{2-} and NH$_2$$^-$. Similarities to fluorine and fluorides are also notable. Comparisons with the chemical properties of sulfur (p. 662) and the heavier chalcogens (p. 754) are deferred to Chapters 15 and 16.

One of the most important reactions of dioxygen is that with the protein haemoglobin which forms the basis of oxygen transport in blood (p. 1099).[47] Other coordination complexes of O$_2$ are discussed in the following section (p. 615).

Another particularly important aspect of the chemical reactivity of O$_2$ concerns the photochemical reaction of singlet O$_2$ (p. 605) with unsaturated or aromatic organic compounds.[48–51] The pioneering work was done in 1931–9 by H. Kautsky who noticed that oxygen could quench the fluorescence of certain irradiated dyes by excitation to the singlet state, and that such excited O$_2$ molecules could oxidize compounds which did not react with oxygen in its triplet ground state. Although Kautsky gave essentially the correct explanation of his observations, his views were not accepted at the time and the work remained unnoticed by organic chemists for 25 years until the reactivity of singlet oxygen was rediscovered independently by two other groups in 1964 (p. 601). With the wisdom of hindsight it seems remarkable that Kautsky's elegant experiments

[46] K. G. CAULTON, M. H. CHISHOLM, S. R. DRAKE and J. C. HUFFMAN, *J. Chem. Soc., Chem. Commun.*, 1498–9 (1990).

[47] T. G. SPIRO (ed.), *Metal Ion Activation of Dioxygen*, Wiley, New York, 1980, 247 pp.

[48] B. RANBY and J. F. RABEK (eds.) *Singlet Oxygen: Reactions with Organic Compounds and Polymers*, Wiley, Chichester, 1978, 331 pp.

[49] A. A. FRIMER, *Chem. Rev.* **79**, 359–87 (1979).

[50] H. H. WASSERMAN and R. W. MURRAY (eds.), *Singlet Oxygen*, Academic Press, New York, 1979, 688 pp.

[51] A. A. FRIMER (ed.), *Singlet O$_2$*, Vol. 1, 236 pp., Vol. 2, 284 pp.; Vol. 3, 269 pp.; Vol. 4, 208 pp.; CRC Press, Boca Raton, Florida, 1985.

and careful reasoning failed to convince his contemporaries.

Singlet oxygen, $^1O_2$, can readily be generated by irradiating normal triplet oxygen, $^3O_2$ in the presence of a sensitizer, S, which is usually a fluorescein-type dye, a polycyclic hydrocarbon or other strong absorber of light. A spin-allowed transition then occurs:

$$^3O_2 + {}^1S \xrightarrow{h\nu} {}^1O_2 + {}^3S$$

Provided that the energy gap in the sensitizer is greater than $94.7 \, \text{kJ mol}^{-1}$, the $^1\Delta_g$ singlet state of O_2 is generated (p. 605). Above $157.8 \, \text{kJ mol}^{-1}$ some $^1\Sigma_g^+ O_2$ is also produced and this species predominates above $200 \, \text{kJ mol}^{-1}$. The $^1\Delta_g$ singlet state can also be conveniently generated chemically in alcoholic solution by the reaction

$$H_2O_2 + ClO^- \longrightarrow Cl + H_2O + O_2({}^1\Delta_g)$$

Another chemical route is by decomposition of solid adducts of ozone with triaryl and other phosphites at subambient temperatures:

$$O_3 + P(OPh)_3 \xrightarrow{-78°} O_3P(OPh)_3 \xrightarrow{-15°} O_2({}^1\Delta_g)$$
$$+ \, OP(OPh)_3$$

Reactions of $^1O_2$ can be classified into three types: 1,2 addition, 1,3 addition and 1,4 addition (see refs. 48–51 for details). In addition to its great importance in synthetic organic chemistry, singlet oxygen plays an important role in autoxidation (i.e. the photodegradation of polymers in air), and methods of improving the stability of commercial polymers and vulcanized rubbers to oxidation are of considerable industrial significance. Reactions of singlet oxygen also feature in the chemistry of the upper atmosphere.

14.2 Compounds of Oxygen

14.2.1 Coordination chemistry: dioxygen as a ligand

Few discoveries in synthetic chemistry during the past three decades have caused more excitement or had more influence on the direction of subsequent work than L. Vaska's observation in 1963 that the planar 16-electron complex *trans*-$[Ir(CO)Cl(PPh_3)_2]$ can act as a reversible oxygen carrier by means of the equilibrium[52]

$$[Ir(CO)Cl(PPh_3)_2] + O_2 \rightleftharpoons$$
$$[Ir(CO)Cl(O_2)(PPh_3)_2]$$
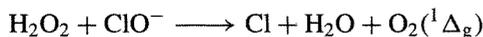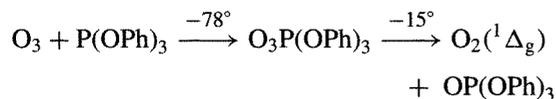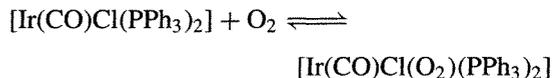
Not only were the structures, stabilities and range of metals that could form such complexes of theoretical interest, but there were manifest implications for an understanding of the biochemistry of the oxygen-carrying metalloproteins haemoglobin, myoglobin, haemerythrin and haemocyanin. Such complexes were also seen as potential keys to an understanding of the interactions occurring during homogeneous catalytic oxidations, heterogeneous catalysis and the action of metalloenzymes. Several excellent reviews are available:[47,53–64]

Dioxygen–metal complexes in which there is a 1:1 stoichiometry of O_2:M are of two main types, usually designated Ia (or superoxo) and IIa (or

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[61] A. B. P. LEVER, G. A. OZIN and H. B. GRAY, *Inorg. Chem.* **19**, 1823–4 (1980).

[62] T. G. SPIRO (ed.), *Metal Ion Activation of Dioxygen*, Wiley-Interscience, New York, 1980, 247 pp.

[63] A. E. MARTELL and D. T. SAWYER (eds.), *Oxygen Complexes and Oxygen Activation by Transition Metals*, Plenum, New York, 1988, 341 pp.

[64] T. VÄNNGÅRD (ed.), *Biophysical Chemistry of Dioxygen Reactions in Respiration and Photosynthesis*, Cambridge Univ. Press, New York, 1988, 131 pp.