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The Chemistry of
OXYGEN

E. A. V. Ebsworth, J. A. Connor and J. J. Turner

Chapter 22 of
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PREFACE

The excellent reception that has been accorded to *Comprehensive Inorganic Chemistry* since the simultaneous publication of the five volumes of the complete work has been accompanied by the plea that sections should be made available in a form that would enable specialists to purchase copies for their own use. To meet this demand the publishers have decided to issue selected chapters and groups of chapters as separate editions. These chapters will, apart from the corrections of misprints and the addition of prefatory material and individual indices, appear just as they did in the main work. Extensive revision would delay publication and greatly raise the cost, so limiting the circulation of these definitive reviews.

A. F. TROTMAN-DICKENSON
Executive Editor

22. OXYGEN

E. A. V. EBSWORTH

University of Edinburgh

J. A. CONNOR

The University of Manchester

and

J. J. TURNER

The University, Newcastle-upon-Tyne

1. OXYGEN

1.1. DISCOVERY OF OXYGEN¹

By the middle of the seventeenth century it was appreciated that air contained a component associated with breathing and burning. In the first theory of burning to become widely accepted, this component was called phlogiston. When something burned, it was believed to release phlogiston to the air around it. If the burning took place in a sealed system, it stopped after a time because the air in the system became saturated with phlogiston. There were serious difficulties about this interpretation. For instance, metals such as tin gain in weight when they burn. However, the theory was widely accepted until the end of the eighteenth century.

Both the experimentalists generally credited with the discovery of oxygen, Joseph Priestly and Carl Wilhelm Scheele, were believers in the phlogiston theory. Indeed, Scheele called his experiments "... proofs that Heat or Warmth consists of Phlogiston and Fire Air". Scheele obtained oxygen, which he called fire air, by heating nitrates, mercuric oxide, or manganese dioxide in retorts to the ends of which bladders had been fixed; Priestly heated mercuric oxide with a magnifying glass and collected the gas over water. Both found that the gas they had obtained would support combustion better than does common air; and after some experiments with mice Priestly ventured to breath some of it himself, with very pleasant results. Priestly isolated what he called "dephlogisticated air" on 1 August 1774; after further experiments he wrote about his results to Sir John Pringle, the President of the Royal Society, in March 1775, and his letter was read before the Society on 23 March, while a detailed account of his experiments was published in the same year in the second volume of his book *Experiments and Observations on Different Kinds of Air*. Scheele worked at about the same time, but he had difficulties with his publishers (as others have

¹ M. E. Weeks, *The Discovery of the Elements*, 6th edn., published by the *Journal of Chemical Education*, New York (1956); D. McKie, *Antoine Lavoisier*, Gollancz, London (1935); J. G. Gillam, *The Crucible*, Robert Hale, London (1954); *The Collected Papers of C. W. Scheele* (translated by L. Dobbin), Bell, Edinburgh (1931).

had since then), and his book, *Chemische Abhandlung von der Luft und dem Feuer*, did not appear until 1777.

Neither Priestly nor Scheele, however, seems fully to have understood the significance of their discoveries. When Priestly was in Paris in October 1774, he mentioned some of his results to the distinguished French Academician, Antoine Lavoisier, who was interested in combustion. Lavoisier was also in touch with Scheele. He repeated and extended Priestly's experiments, and began to consider his results in the light of the deficiencies of the phlogiston theory. He burned tin in a sealed vessel, and showed that after combustion the weight of the vessel was effectively unchanged as long as the seal was not broken; thus the increase in weight of the tin on combustion could not be derived from outside the vessel. If the tin had lost phlogiston, then the phlogiston must have negative mass. From these and other experiments he concluded that when the metal burned what really happened was that it combined with something in the air; that "something" was the gas discovered by Priestly and Scheele, which Lavoisier called "principe oxygine". His view was not absolutely correct. He thought he was talking of a principle of acidity, for "oxygine" comes from the Greek word *oxus*, meaning sharp, and hence acid. But it was Lavoisier's penetration of mind, coupled with the experiments of himself, of Priestly, and of Scheele, that led to the collapse of the phlogiston theory and to the development of modern chemistry.

1.2. GENERAL

Oxygen is the eighth element in the Periodic Table. The electronic structure can be represented in terms of one-electron wave functions as $1s^2 2s^2 2p^4$; the ground state and some of the lower excited state terms are given in Table 1, with their energies above the ground state, and some other important properties of oxygen are given in Table 2. Detailed calculations of the wave function for the oxygen atom have been made using SCF and other methods².

Oxygen forms compounds with all the elements of the Periodic Table except for the lightest rare gases. These compounds could in principle be formed if oxygen were to lose electrons (forming cations), to gain electrons (forming anions) or to share electrons (forming bonds). The first four ionization potentials and the first two electron affinities are given in Table 2. These values show that the loss of electrons from oxygen is a process requiring much energy. Compounds are known in which oxygen is formally cationic, such as $O_2^+PtF_6^-$, but in all known cases the cations are polyatomic, and in general the chemistry of oxygen is not cationic. The doubly charged anion O^{-2} is a common species, even though its formation from the gaseous atom involves substantial absorption of energy; in ionic oxides the lattice energies are very high and more than compensate for the energy of formation of O^{-2} . This must also explain why the singly charged O^- is only known as an unstable species in irradiated solids and in the gas phase; in oxides it is unstable with respect to disproportionation to O_2 and O^{-2} . The coordination numbers of O^{-2} ions in oxides are set out in Table 2, and are considered in more detail in section 3.3.

Oxygen can form two additional bonds either by forming two σ -bonds with other atoms or groups, as in $(CH_3)_2O$, or by forming a σ -bond and a π -bond with the same other atom

² A. L. Merts and M. D. Torrey, *J. Chem. Phys.* **39** (1963) 694; C. C. J. Roothaan and P. S. Kelly, *Phys. Rev.* **131** (1963) 1177; E. Clementi, *J. Chem. Phys.* **40** (1964) 1944.

TABLE 1. ATOMIC ENERGY LEVELS OF OXYGEN

Electron configuration	State	<i>J</i>	Energy above ground state (cm ⁻¹)
$2s^22p^4$	$2p^4 \quad {}^3P$	2	0.0
		1	158.5
		0	226.5
$2s^22p^3(4S^0)3s$	$2p^4 \quad {}^1D$	2	15 867.7
		0	33 792.4
		2	73 767.81
$2s^22p^3(4S^0)3s$	$3s \quad {}^5S^0$	2	76 794.69
$2s^22p^3(4S^0)3s$	$3s \quad {}^3S^0$	1	
$2s^22p^3(4S^0)3p$	$3p \quad {}^5P$	1	86 625.35
		2	86 627.37
		3	86 631.04
$2s^22p^3(4S^0)3p$	$3p \quad {}^3P$	2	88 630.84
		1	88 630.30
		0	88 631.00
$2s^22p^3(4S^0)4s$	$4s \quad {}^5S^0$	2	95 476.43
$2s^22p^3(4S^0)4s$	$4s \quad {}^3S^0$	1	96 225.5
$2s^22p^3(4S^0)3d$	$3d \quad {}^5D^0$	4	97 420.24
		3, 2	97 420.37
		2, 1, 0	97 420.50
Ionization: $2s^22p^3$	$2p^3 \quad 4S^0$	3/2	109 836.7

Data from C. E. Moore, *Atomic Energy Levels*, NBS Circular 467 (1949).

TABLE 2. SOME PHYSICAL PROPERTIES OF THE OXYGEN ATOM

Ionization potentials ^a (eV)	1st, 13.614; 2nd, 35.146; 3rd, 54.934; 4th, 77.394
Electron affinities (eV)	1st, 1.478 ± 0.002 ^b ; 2nd, ($O_2 \rightarrow O_2^-$), -7.8 ± 0.3
Atomic weight (C ¹² scale) ^d	15.9994
Atomic radius ^c	0.73 Å
Ionic radius ^d	1.39 ± 0.004 Å
Van der Waals radius ^f	~ 1.50 Å
Electronegativity ^g	3.46
Coordination numbers at oxygen: ^h	
(i) In ionic or near-ionic compounds	2 (e.g. SiO ₂), 3 (e.g. rutile), 4 (e.g. ZnO), 6 (e.g. MgO), 8 (e.g. Na ₂ O)
(ii) In molecular compounds	1 (e.g. CO), 2 (e.g. H ₂ O), 3 (e.g. Me ₂ OBFB ₃), 4 (e.g. Be ₄ OAc)

^a C. E. Moore, *Atomic Energy Levels*, NBS Circular 467, 1949.^b R. S. Berry, J. C. Mackie, R. L. Taylor and R. Lynch, *J. Chem. Phys.* **43** (1965) 3067.^c From thermochemical cycles: M. F. C. Ladd and W. H. Lee, *Acta Cryst.* **13** (1960) 959.^d A. E. Cameron and E. Wickers, *J. Am. Chem. Soc.* **84** (1962) 4175.^e R. T. Sanderson, *Chemical Periodicity*, Reinhold (1960).^f A. Bondi, *J. Phys. Chem.* **68** (1964) 441. The value is about the same for $-O-$ and for $=O$.^g See section 3.

or group, as in >C=O . Species in which oxygen forms just one σ -bond with another group (e.g. OH) have been detected spectroscopically, but they are free radicals and are not normally stable under chemical conditions. For once, all scales of electronegativity agree that oxygen is a very electronegative element. The electronegativity depends on the orbitals and the electron configuration; calculations have been made of the parameters associated with the valence state of oxygen, based on spectroscopic measurements³. As expected, the double bonds are shorter than the single bonds, and they have higher energies and stretching frequencies. Bonds of intermediate order are found in many compounds, including oxyanions such as RCO_2^- , CO_3^{2-} , NO_3^- , or SO_4^{2-} ; relationships between bond length, bond order and stretching force constants have been described for BO⁴, CO⁵, NO⁶, SiO⁷, PO⁷, SO⁸ and ClO⁷ bonds. Like fluorine, oxygen is a ligand which tends to promote oxidation of other elements to which it is bound (cf. $\text{Os}^{\text{VIII}}\text{O}_4$).

Bonds from 2-coordinated oxygen are usually considered as formed from (roughly) sp^3 hybrid orbitals, leading to bond angles at oxygen near the tetrahedral value. This leaves two lone pairs, which are also regarded as being in roughly sp^3 -orbitals. Thus in each of the compounds H_2O , Me_2O and F_2O , the angles are near 109° (Table 3). However, oxygen can also use its lone pairs to form either intermolecular σ -bonds or intramolecular π -bonds additional to the normal σ -bonds.

Additional σ -bonds. Despite its high electronegativity, oxygen is a lone pair donor. Compounds like Me_2O form complexes with acceptors such as BF_3 , and values for the energies of some donor-acceptor bonds involving oxygen are given in Table 4, with some values for other elements for comparison. Water is a well-known donor ligand in transition metal chemistry; oxygen is also a hydrogen bond acceptor, as in carboxylic acid dimers and in ice. All these interactions involve the lone pairs. In ice and in basic beryllium acetate, the angles at the 4-coordinated oxygen atoms are roughly tetrahedral, which also implies that the lone pairs are in approximately sp^3 -orbitals; similarly, in H_3O^+ , which is isoelectronic with NH_3 , the angle is near 109° . In compounds, where it forms two σ -bonds (e.g. Me_2O), oxygen is a hard (class A) base, though in compounds like $\text{Me}_2\text{C=O}$ it has some "soft" character. Water comes near the "small Δ " end of the spectrochemical series; water and OH^- have small *trans*-effects, and in the nephelauxitic series water and OH^- come close to F^- as ligands with the smallest effect.

Internal π -bonding. If an attached atom or group Q has empty orbitals of π -symmetry relative to the Q-O σ -bond, these will overlap the lone pair orbitals at oxygen, and the overlap may lead to the formation of a donor π -bond. Thus in carbon monoxide the CO bond is of higher order than 2, and the strength of the bond can be attributed at least partly to an interaction of the form ($\text{O}^+ \equiv \text{C}^-$). In compounds in which oxygen is forming two or more σ -bonds, donor π -bonding like this will affect bond angles at oxygen. The donor π -overlap will be greatest when the lone pairs are in pure p -orbitals. If one lone pair is in a pure p -orbital, the two σ -bonds and the other lone pair must be built from one s - and two p -orbitals. This would lead (if all three σ -orbitals are equivalent) to an angle of 120° . If both lone pairs are in pure p -orbitals, the σ -bonds must be built from sp -orbitals,

³ G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.* **24** (1962) 937.

⁴ J. Krogh-Moe, *Acta Chem. Scand.* **17** (1963) 843.

⁵ J. P. Fackler and D. Coucouvanis, *Inorg. Chem.* **7** (1968) 181.

⁶ Yu. Ya. Kharitonov, *Izv. Akad. Nauk SSSR, Otdel Khim. Nauk* 1962, 1953.

⁷ E. A. Robinson, *Can. J. Chem.* **41** (1963) 3021.

⁸ P. Haake, W. B. Miller and D. A. Tyssee, *J. Am. Chem. Soc.* **86** (1964) 3577.

TABLE 3. ANGLES AT OXYGEN

	Angle	How measured	Phase	Reference
In species QOZ				
1. Neither Z nor Q π -acceptors:				
H ₂ O	104.52°	vib.	vap.	a
F ₂ O	103.1 ± 0.05°	μ wave	vap.	b
(CH ₃) ₂ O	111.5 ± 1.5°	ED	vap.	c
CH ₃ OH	109° ± 3°	ED	vap.	c
RbOH	180°	μ wave	vap.	d
2. Q, π -acceptor; Z, not:				
SiH ₃ OCH ₃	120.6 ± 0.9°	ED	vap.	e
3. Q and Z both π -acceptors:				
Cl ₂ O	110.8 ± 1°	ED	vap.	f
Cl ₂ O ₇	118.6 ± 0.7°	ED	vap.	g
SiH ₃ OC ₆ H ₅	121 ± 1°	ED	vap.	h
(SiH ₃) ₂ O	144.1 ± 0.9°	ED	vap.	i
SiOSi in silicates	140–180°	X-ray	solid	j
(GeH ₃) ₂ O	126.5 ± 0.3°	ED	vap.	k
[O ₃ POPO ₃] ⁻⁴	133.5°	X-ray	solid	l
[O ₃ SOSO ₃] ⁻²	124°	X-ray	solid	m
[O ₃ CrOCrO ₃] ⁻²	115°	X-ray	solid	n
[Cl ₅ MOMCl ₅] ⁻⁴	180°	X-ray	solid	o
(M = Ru, Re)				
4. Q ₃ O ⁺ :				
H ₃ O ⁺	112°	X-ray	solid	p
(ClHg) ₃ O ⁺	120°	X-ray	solid	q

^a W. S. Benedict, N. Gailar and E. K. Plyler, *J. Chem. Phys.* **24** (1956) 1139.

^b Y. Morino and S. Saito, *J. Mol. Spectrosc.* **19** (1966) 435.

^c K. Kimura and M. Kubo, *J. Chem. Phys.* **30** (1959) 151.

^d C. Matsuma and D. R. Lide, *J. Chem. Phys.* **50** (1969) 71.

^e C. Glidewell, D. W. H. Rankin, A. G. Robiette and G. M. Sheldrick (to be published).

^f J. D. Dunitz and K. Hedberg, *J. Am. Chem. Soc.* **72** (1950) 3108.

^g B. Beagley, *Trans. Faraday Soc.* **61** (1965) 1821.

^h C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley and J. M. Freeman, *Trans. Faraday Soc.* **65** (1969) 2621.

ⁱ A. Almenningsen, O. Bastiansen, V. Ewing, K. Hedberg and M. Traetteberg, *Acta Chem. Scand.* **17** (1963) 2455.

^j D. W. J. Cruickshank, *J. Chem. Soc.* 1961, 5486; D. W. J. Cruickshank, H. Lynton and G. A. Barclay, *Acta Cryst.* **15** (1962) 493.

^k C. A. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley and S. Craddock, *J. Chem. Soc. (A)*, 1970, 315.

^l D. M. Macarthur and C. A. Beevers, *Acta Cryst.* **10** (1957) 428.

^m H. Lynton and M. R. Truter, *J. Chem. Soc.* 1960, 5112.

ⁿ C. A. Brystrom and K. A. Wilhelmi, *Acta Chem. Scand.* **5** (1951) 1003.

^o A. M. Mathieson, D. P. Mellor and N. C. Stephenson, *Acta Cryst.* **5** (1952) 185; J. C. Morrow, *Acta Cryst.* **15** (1962) 851.

^p C. E. Nordman, *Acta Cryst.* **15** (1962) 18.

^q S. Šćavničar and D. Grdenić, *Acta Cryst.* **8** (1955) 275.

TABLE 4. GAS-PHASE DISSOCIATION ENTHALPIES FOR SOME MOLECULAR COMPLEXES (kcal mol⁻¹)

Complex	ΔH	Complex	ΔH
Me ₂ OBf ₃	13.3	Me ₂ SGaMe ₃	~ 8
Et ₂ OBf ₃	10.9	Me ₂ SBH ₃	5.2
THF · Bf ₃	13.4	Me ₃ NBF ₃	b
Me ₂ OBMe ₃	a	Me ₃ NAlMe ₃	b
Me ₂ OAlMe ₃	b	Me ₃ NGaMe ₃	21
Me ₂ OGaMe ₃	9.5	Me ₃ PBF ₃	18.9
Me ₂ OBH ₃	a		

Data from F. G. A. Stone, *Chem. Rev.* **58** (1958) 101.^a Too unstable to study.^b Too stable to determine.^c For dissociation into Me₂S and B₂H₆.

and the angle at oxygen will be 180°. These possibilities, which are represented below in valence-bond terms, are extremes: intermediate angles might be expected, deriving from a balance between π -bonding (widening the angle, and removing electrons from oxygen) and charge distribution (which will tend to keep electrons on the oxygen atom):

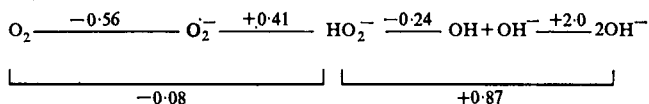
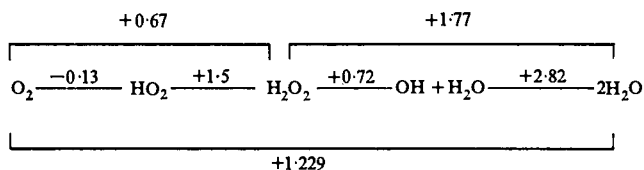


Internal π -bonding will lead to shorter and stronger bonds, and should weaken the donor properties of the oxygen atom; the shortness and strength of bonds between oxygen and boron⁹, silicon¹⁰ or transition elements¹¹ have been accounted for in terms of this type of interaction. Several compounds are known in which oxygen is bound to one or two π -acceptors and in which the angle at oxygen is unusually wide (see Table 3). A similar argument could be used to explain why angles in Q₃O⁺ might be nearer 120° than 109°; π -interactions between silicon and Q would be greatest if the lone pair at Q were in a pure *p*-orbital. However, this argument should be used with some caution; the angle at oxygen in RbOH is 180°, yet there is unlikely to be significant π -bonding between rubidium and oxygen.

Oxygen is known in a variety of formal oxidation states, from +2 to -2. Of these, the positive states are (by definition) only found when oxygen is bound to a more electro-negative element—which must be fluorine—or forms part of a cation such as O₂⁺. In other oxidation states greater than -2 the oxygen atom concerned must either be bound to at least one other oxygen atom or form part of a cation or free radical. A potential diagram for the redox chemistry of oxygen in aqueous solution is given in Table 5.

⁹ C. A. Coulson and T. W. Dingle, *Acta Cryst.* **B24** (1968) 153.¹⁰ D. W. J. Cruickshank, *J. Chem. Soc.* 1961, 5486.¹¹ F. A. Cotton and R. M. Wing, *Inorg. Chem.* **4** (1965) 867.

(a) E°



Data from W. L. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solution*, 2nd edn., Prentice-Hall (1952).

1.3. ISOTOPES OF OXYGEN

Unstable Isotopes

The known radioactive isotopes of oxygen are all artificial; they are listed in Table 6 with representative nuclear reactions by which they have been made. The half-lives are all so short that the isotopes are unsatisfactory for tracer work, though some tracer studies¹² have been made with O^{15} .

TABLE 6. RADIOACTIVE ISOTOPES OF OXYGEN

Isotope	Formation	$t_{\frac{1}{2}}$, sec	Decay	Reference
O ¹³	O ¹⁶ (He ³ , He ⁶)O ¹³			a
O ¹⁴	C ¹² (He ³ , n)O ¹⁴	73	β^+	b
O ¹⁵	O ¹⁶ (He ³ , α)O ¹⁵	122	β^+	b
O ¹⁹	O ¹⁸ (n, γ)O ¹⁹	29.4	β^-	b
O ²⁰	O ¹⁸ (t, p)O ²⁰	14	β^-	b

* G. W. Butler, US Atomic Energy Comm. UCRL-17783, CFSTI, 1967. *CA* **68** (1968) 64756n.

^b R. L. Heath, in *Handbook of Chemistry and Physics*, Chemical Rubber Co., New York (1967).

Stable Isotopes

By far the most abundant isotope of oxygen is O^{16} , but natural oxygen (both element and compounds) contains small amounts of O^{17} and O^{18} (Table 7). The proportions of

¹² C. T. Dollery and J. B. West, *Nature* **187** (1960) 1121.

these isotopes depend to a significant extent upon the source of oxygen. Natural processes such as the evaporation of water lead to some fractionation because of the influence of molecular weight upon physical properties; there are small differences in the proportion of O^{18} in water from different natural sources, and indeed the proportion of O^{18} in ocean water varies with the depth¹³. There is also some isotopic fractionation in chemical cycles in nature that involve oxygen. The variations in apparent atomic weight of natural oxygen may be as great¹⁴ as ± 0.0003 .

TABLE 7. STABLE ISOTOPES OF OXYGEN

Isotope	Mass ^a	Natural abundance ^a
	($C^{12} = 12.000\,000\,0$)	
O^{16}	15.994 915	99.7587
O^{17b}	16.999 134	0.0374
O^{18}	17.999 160	0.2039

^a W. H. Johnson and A. O. Nier, *Handbook of Physics*, McGraw-Hill, 2nd edn., 1967, pp. 9-63.

^b Nuclear spin = $5/2$; nuclear magnetic moment = 1.8930 nuclear magnetons; nuclear quadrupole moment = $-4e \times 10^{-27} \text{ cm}^2$. (From J. A. Pople, W. G. Schneider and H. J. Bernstein, *Nuclear Magnetic Resonance*, McGraw-Hill, 1959.)

Many different processes have been described for producing molecular oxygen or oxygen compounds enriched in O^{17} or O^{18} ; some make use of the slightly different equilibrium constants for compounds of O^{16} and O^{17} or O^{18} , but most depend on some physical property of O_2 or oxygen compounds such as H_2O or N_2O . In practice the most important processes are the fractional distillation of water and (for high enrichments) the thermal diffusion of oxygen gas; the gas fed into the column for separation by thermal diffusion may be obtained by the electrolysis of water that has already been enriched in O^{18} by fractional distillation. Heavy water of enrichment up to 98 atom-% O^{18} and 20 atom-% O^{17} is commercially available, as is oxygen gas 99% in O^{18} or 90-95% in O^{17} . These are the most commonly used starting materials; of course it is possible to produce enriched O_2 by the electrolysis of enriched water. Samples of oxygen and its compounds are usually analysed for isotopic composition by mass spectrometry; if compounds are involatile, their oxygen must be converted into some volatile species first.

O^{18} . Oxygen-18 has been extensively used to study mechanisms of reactions, and in particular of hydrolysis. The exchange rates of many common oxyacids and oxyanions have been studied quantitatively or semi-quantitatively¹⁵; the structures of simple molecules containing oxygen have been determined by microwave spectroscopy¹⁶ with the help of samples enriched in O^{18} , and vibrations involving the movement of oxygen atoms have been identified by the extent to which they shift in samples enriched in O^{18} . In the infrared

¹³ M. Dole, *J. Gen. Physiol.* **49** (1965) 5.

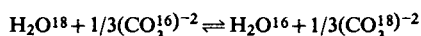
¹⁴ A. E. Cameron and E. Wickers, *J. Am. Chem. Soc.* **84** (1962) 4175.

¹⁵ D. Samuel, in *Oxygenases* (ed. O. Hayashi), Academic Press, New York (1962).

¹⁶ M. C. L. Gerry, J. C. Thompson and T. M. Sugden, *Nature* **211** (1966) 846.

spectra of adducts of molecular oxygen with compounds of transition metals, there is a band near 800–900 cm^{-1} that is assigned to the (O–O) stretching mode. In $(\text{tbnC})_2\text{Ni}(\text{O}_2)$ and $(\text{tbnC})_2\text{Pd}(\text{O}_2)$ this band splits into three when the complex is prepared from O_2 containing 25 atom-% O^{18} : the three components are due to stretching modes in $\text{L}_2\text{M}(\text{O}_2^{16})$, $\text{L}_2\text{M}(\text{O}^{16}\text{O}^{18})$ and $\text{L}_2\text{M}(\text{O}_2^{18})$; the relative intensities and the differences in frequency between the bands confirm this assignment¹⁷. A similar approach has led to the identification in matrices at low temperatures of active species containing more than one oxygen atom.

The preparation of O^{18} in naturally occurring systems has been much studied in connection with climatology and palaeoclimatology. The variation in O^{18} content of arctic snow over the year helps to establish the origin of the water from which the snow was formed¹⁸. In palaeoclimatology it is the oxygen isotopic composition of carbonate in fossils that is measured^{19, 20}. The variation with temperature of the equilibrium constant for the reaction



has been determined accurately. Certain fossil shell-fish contain carbonate rock. The temperature at which this carbonate was precipitated can be determined from the isotopic distribution of the carbonate in the shell, using the equation

$$t = 16.5 - 4.3\delta + 0.14\delta^2$$

where t is the temperature in $^{\circ}\text{C}$ and δ is a measure of the difference between the O^{18} content of the sample and of the standard working gas. This use of the O^{18} content of carbonate is sometimes referred to as the carbonate thermometer.

In practice, matters are not so simple¹⁹. For the information obtained to have any meaning, certain conditions must be fulfilled. The carbonate must have been precipitated in isotopic equilibrium with the surrounding water; the isotopic composition of that water must be known; and there must have been no subsequent exchange. Though some shell-fish (e.g. coral) precipitate carbonate that is not in equilibrium with the surrounding water, in molluscs the equilibrium is maintained. For shells from open oceans it is usually assumed that the O^{18} content of the surrounding water was not very different from that of ocean water nowadays; for isolated oceans this may well not be so because of such things as evaporation, and allowance must be made for this (perhaps by using the O^{18} content of the phosphate of the shell). But it is with the third condition that the most serious difficulties arise. It is hard enough to make sure that the oxygen from the carbonate in the shell is extracted and analysed without exchange; it is even harder to make sure that nothing untoward has happened to the sample between fossilization and analysis. Fortunately there are some internal tests that can be applied. For example, in most, but not all, fossil shells studied the ratio of $(\text{O}^{18}:\text{O}^{16})$ to Sr^{+2} is the same as it is in oceans at present; therefore shells in which this ratio is very different may be supposed to have undergone "diagenetic" changes (in other words they are useless for isotopic analysis). However, there is always the nagging possibility that a particular sample may be atypical—some molluscs, for instance, do not deposit carbonate uniformly throughout the year—and it is rare that

¹⁷ K. Hirota, M. Yamamoto, S. Otsuka, A. Nakamura and Y. Tatsuno, *Chem. Commun.* 1968, 533.

¹⁸ L. Aldaz and S. Deutsch, *Earth Planet Sci. Letters* 3 (1967) 267.

¹⁹ H. A. Lowenstam, in *Problems in Palaeoclimatology* (ed. A. E. M. Nairn), Wiley (1964), p. 227.

²⁰ R. Bowen, *Palaeotemperature Analysis*, Elsevier, Amsterdam (1966).

enough good samples from a particular area are available for a proper statistical analysis. Some claims about palaeotemperature may have been based on very slender evidence derived from the carbonate thermometer; but when all is said and done the remarkable thing is that such an extrapolation to the temperatures of past ages is even possible.

O¹⁷. The isotope O¹⁷ is important despite its small natural abundance because it is the only stable isotope of oxygen with nuclear spin, and so is the only one that can be used to study oxygen n.m.r. or oxygen hyperfine interactions in electron resonance spectroscopy²¹. Unfortunately, however, the spin of 5/2 is associated with a large quadrupole moment, leading to broad n.m.r. lines because of the relatively rapid relaxation of the oxygen nuclei. Chemical shifts are difficult to determine, and coupling is often not observed at all. However, broadening due to quadrupolar relaxation has itself been used to give information about the field gradient at the oxygen nucleus; lines are sharper when oxygen is bound to an electropositive element, even in a high oxidation state, because then the oxygen atom approximates to the ion O⁻² in which the field gradient at the nucleus is zero.

Some values for O¹⁷ chemical shifts are given in Table 8; they were measured relative to H₂O¹⁷ (usually as external standard), and some of the uncertainties are substantial. It is clear from these and other values that oxygen forming two σ -bonds gives resonance in the range -250 to 0 ppm from H₂O¹⁷ (+ve to high field), but that oxygen forming a double bond gives resonance in the range -1400 to -250 ppm. The dichromate ion²², for instance, gives two resonances, the one (stronger and sharper) at -1129 ppm due to the terminal, and the other (weaker and broader) at -345 ppm due to the bridging oxygen atoms. Similarly²³, aqueous acetone gives a single O¹⁷ resonance in the >C=O region, at -523 ppm, indicating that the molecule dissolves unchanged; formaldehyde gives a resonance at -51 ppm, in the "single-bond" region, so it is concluded that the species present is the hydrated form H₂C(OH)₂. Acetaldehyde gives two peaks, the one at -550 ppm associated with the unchanged molecule CH₃CHO, and the other at -67 ppm associated with the hydrated form CH₃CH(OH)₂. Exchange between these two species and the solvent is slow on the n.m.r. timescale.

For doubly-bound oxygen there is a correlation between the chemical shift and the frequency of the first ultraviolet/visible absorption band²⁴. Furthermore, a correlation has been reported between bond length, bond order and O¹⁷ chemical shifts in some Cr(VI)-O species²⁵. The full range of validity of the latter correlation has still to be established.

Ion hydration has been extensively studied by O¹⁷ n.m.r. spectroscopy. For certain paramagnetic ions there are "contact shifts" which with Co⁺² and Ni⁺² lead to the observation of separate resonances due to water in the hydration shell of the cation and to the solvent itself. For certain diamagnetic ions which exchange their hydration water slowly with the solvent, separate O¹⁷ resonances for solvent and for solvating water have been observed (Table 9). There are other cases where exchange on other grounds is known to be slow, but where, none the less, the only O¹⁷ resonance observed is that due to the solvent. The addition of Co⁺² or Dy⁺³ ions to the solution causes the solvent resonance to shift to low field through the "contact shift" mechanism, and so can expose the resonance due to the hydrated diamagnetic cation; this device has also been used to separate the

²¹ B. L. Silver and Z. Luz, *Quart. Rev.* **21** (1967) 458.

²² B. N. Figgis, R. G. Kidd and R. S. Nyholm, *Can. J. Chem.* **43** (1965) 145.

²³ P. Greenzaid, Z. Luz and D. Samuel, *J. Am. Chem. Soc.* **89** (1967) 749.

²⁴ B. N. Figgis, R. G. Kidd and R. S. Nyholm, *Proc. Roy. Soc. A*, **269** (1962) 469.

²⁵ R. G. Kidd, *Can. J. Chem.* **45** (1967) 605.

TABLE 8. CHEMICAL SHIFTS FOR O¹⁷, RELATIVE TO H₂O¹⁷ (ppm)

Transition element systems	Main group systems	Carbon-oxygen systems ^c
Na ₃ VO ₄ ^a -571 ± 4 Na ₂ CrO ₄ ^a -835 ± 5 K ₂ MoO ₄ ^a -540 ± 2 Na ₂ WO ₄ ^a -420 ± 2 NaMnO ₄ ^a -1219 ± 8 NaTeO ₄ ^a -749 ± 7 NaReO ₄ ^a -569 ± 4 RuO ₄ ^a -1119 ± 10 OsO ₄ ^a -796 ± 3	H ₂ O ₂ (30% aq.) a K ₂ CO ₃ (7 M ^b) a HNO ₃ (100%) a POCl ₃ (l) a H ₃ PO ₄ (l) c SOCl ₂ (l) a SO ₂ Cl ₂ (l) a H ₂ SO ₄ (conc.) c Na ₂ SeO ₄ (3 M ^b) a H ₆ TeO ₆ (aq.) g NaClO ₃ (2.4 M ^b) a HClO ₄ (60% aq.) c NaClO ₄ (2.4 M ^b) a NaBrO ₃ (2.4 M ^b) a XeOF ₄ h Xe(OH) ₂ ^h (aq.) i	MeOH +37 EtOH -6 tBuOH -70 Furan -241 CH ₃ CHO -595 Acetic acid -254 CH ₃ COOCH ₃ { -355 (C=O) -137 (OMe) -393 (C=O) (CH ₃ CO) ₂ O { -259 (C=O) -269 di-tBu ₂ O ₂ -35 MeONH ₂ -838 (N=O) tBuONO -513 (C=O)
CrO ₂ Cl ₂ (l) ^d -1460 ± 8 Na ₂ Cr ₂ O ₇ ^d -1129 (term.) -345 (br.) UO ₂ ⁺ aq. ^f -1115 ± 2 Fe(CO) ₅ ^e (l) -388 ± 8 Ni(CO) ₄ ^e (l) -362 ± 8		

^a Data for aqueous solutions, unless otherwise stated, from B. N. Figgis, R. G. Kidd and R. S. Nyholm, *Proc. Roy. Soc. A*, **269** (1962) 469.

^b 0.1 N aqueous alkali.

^c Data for pure liquids from H. A. Christ, P. Diehl, H. R. Schneider and H. Dahn, *Helv. Chim. Acta* **44** (1961) 865.

^d B. N. Figgis, R. G. Kidd and R. S. Nyholm, *Canad. J. Chem.* **43** (1965) 145.

^e R. Bramley, B. N. Figgis and R. S. Nyholm, *Trans. Faraday Soc.* **58** (1962) 1893; R. G. Kidd, *Canad. J. Chem.* **45** (1967), 605.

^f S. W. Rabideau, *J. Phys. Chem.* **71** (1967) 2747.

^g Z. Luz and I. Pecht, *J. Am. Chem. Soc.*, **88** (1966), 1152.

^h J. Shamir, H. Selig, D. Samuel and J. Reubin, *J. Am. Chem. Soc.* **87** (1965) 2359.

ⁱ J. Reuben, D. Samuel, H. Selig and J. Shamir, *Proc. Chem. Soc.* 1963, 270.

resonances of water and of phosphoric acid²⁶. The hydration of ions or complexes of Be^{+2} , Al^{+3} , Ga^{+3} , VO^{+2} , Ti^{+3} , Co^{+2} , Ni^{+2} and Cu^{+2} has been studied using these and similar techniques. Finally, O^{17} n.m.r. affords information about H bonding and the structure of aqueous solutions; O^{17} resonances, like proton resonances, are shifted to low field by hydrogen bonding²⁷.

The e.s.r. spectra of organic compounds containing O^{17} have been important in relation to calculations of the electronic structures of these compounds, and particularly of heterocyclic compounds. The hyperfine interaction constants in O^{17} -labelled $\text{Mn}(\text{acac})_3$ has been used²⁸ as the basis for an estimate of the covalent character of the metal-oxygen bonds. The e.s.r. spectrum of a sample of CF_3OOCF_3 that had been photolysed in the

TABLE 9. COUPLING CONSTANTS INVOLVING O^{17} (Hz)

Species	Coupling nuclei	Coupling constants	Reference
ClO_4^-	$\text{Cl}^{35}-\text{O}^{17}$	85.5 ± 0.5	a
XeOF_4	$\text{Xe}^{129}-\text{O}^{17}$	692 ± 10	b
H_2O	H^1-O^{17}	79 ± 2	c
$(\text{MeO})_3\text{P}$	$\text{P}^{31}-\text{O}^{17}$	160	d
Cl_3PO	$\text{P}^{31}-\text{O}^{17}$	225	d
MnO_4^-	$\text{Mn}^{55}-\text{O}^{17}$	30	e
Me_2CO	$\text{C}^{13}-\text{O}^{17}$	22	e

^a M. Alei, *J. Chem. Phys.* **43** (1965) 2904.

^b J. Shamir, H. Selig, D. Samuel and J. Reuben, *J. Am. Chem. Soc.* **87** (1967) 2359.

^c A. E. Florin and M. Alei, *J. Chem. Phys.* **47** (1967) 4268.

^d H. A. Christ, P. Diehl, H. R. Schneider and H. Dahn, *Helv. Chim. Acta* **44** (1961) 865.

^e M. Broze and Z. Luz, *J. Phys. Chem.* **73** (1969) 1600.

presence of small amounts of O_2 enriched ($\sim 30\%$) in O^{17} showed that a free radical had been formed with three different sets of O^{17} hyperfine splitting constants, and it was concluded²⁹ that the radical was the trioxide species CF_3COOO . Hyperfine structure in the e.s.r. spectrum of $[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5]^{+5}$ due to O^{17} in the peroxy-bridge provided the first direct evidence that the unpaired electron is associated with the bridge as well as with the cobalt nuclei³⁰.

1.4. OCCURRENCE AND EXTRACTION

Oxygen is the most abundant element³¹. In combined form it makes up 46.60% by weight of the rocks of the earth's crust, and (as the element) $20.946 \pm 0.002\%$ by volume of

²⁶ J. A. Jackson and H. Taube, *J. Phys. Chem.* **69** (1965) 1844.

²⁷ Z. Luz and G. Yagil, *J. Phys. Chem.* **70** (1966) 554.

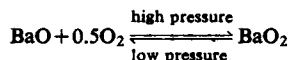
²⁸ Z. Luz, B. L. Silver and D. Fiat, *J. Chem. Phys.* **46** (1967) 469.

²⁹ R. W. Fessenden, *J. Chem. Phys.* **48** (1968) 3725.

³⁰ J. A. Weil and J. K. Kinnaird, *J. Phys. Chem.*, **71** (1967) 3341.

³¹ *The Production of Oxygen, Nitrogen and the Inert Gases*, British Oxygen Co. (1967).

dry air at sea level. Nowadays the atmosphere is the primary source of oxygen for large-scale commercial production of the gas or liquid, but chemical processes have been devised and extensively used in the past. Most are based on substances which combine with oxygen at one temperature and release it on heating. The old Brin process made use of the reaction between barium oxide and oxygen at 600°:



The barium oxide is heated with air that has been freed of CO₂, water vapour, organic matter and dust; the pressure is lowered, and pure oxygen is evolved. A modification of the process has recently been devised³² in which use is made of the fact that the melting point of BaO₂ (450°) is much lower than that of BaO (1923°). Several similar processes have been proposed for making pure oxygen, which has also been made electrolytically, but almost all oxygen is now produced by the liquefaction and fractional distillation of air. Methods for doing this differ in detail. The Linde double column consists of one fractionating column operating at about atmospheric pressure, and another operating at 5–6 atm. At the higher pressure nitrogen boils at –170°, and so may be condensed using liquid oxygen from the column at lower pressure as refrigerant. After initial compression and cooling by water, the air is further cooled by heat exchange with gases leaving the columns; the cooling by expansion that follows may take place under Joule–Thompson conditions, by doing external work, or by a combination of the two. In the production of oxygen gas, the use of heat exchangers called regenerators is of considerable importance³³.

Alternative sources of oxygen for enclosed systems have become of increasing importance in the past few years with the development of space craft and nuclear submarines. Schemes have been devised for producing oxygen from CO₂ by means of algae, or by catalytic hydrogenation followed by electrolysis of the water formed³⁴. Oxygen “candles” have been proposed for carrying oxygen; these consist of salts of oxy-anions which are both thermally unstable and rich in oxygen, such as LiClO₄, NaClO₃ or KO₂. A lithium perchlorate candle has been described consisting of 84.82% by weight of LiClO₄, 10.94% Mn and 4.24% of Li₂O₂; the solid is compressed to a density of 2.32 g/cc, and the oxygen available on heating is equivalent, volume for volume, to that from liquid oxygen³⁵.

In the laboratory³⁶, oxygen may be made by heating potassium permanganate or other salts thermally unstable and rich in oxygen, but commercial oxygen can be purified by successive treatment with KMnO₄, with KOH, and with concentrated H₂SO₄. The best method of making pure oxygen in the laboratory is to catalyse the decomposition of 30% H₂O₂ with thin nickel sheet suspended by a platinum wire; electrolysis may also be used.

³² S. A. Guerrieri, US pat. 3,310,381, 1966 (*Chem. Abstr.* 66 (1967) 106659z).

³³ R. L. Shower and L. C. Matsch, *Adv. Petrol Chem. Refining* 9 (1964) 1.

³⁴ P. J. Hannan, R. L. Shuler and C. Patouillet, NASA Acc. No. N63-14930, 1962 (*Chem. Abstr.* 62 (1965) 2006a); NASA Acc. No. N64-10551, 1963 (Report No. AD 420927) (*Chem. Abstr.* 61 (1964) 16488d).

³⁵ C. S. Coe, *Chem. Engng. Progress, Symp. Ser.* 60 (1964) 161.

³⁶ G. Brauer (ed.), *Handbook of Preparative Inorganic Chemistry*, 2nd edn., Academic Press, New York (1963), p. 334.

1.5. STRUCTURAL PROPERTIES

Electronic Structure

The electronic structure of the oxygen molecule can be represented very simply as $O=O$. This representation indicates that the O—O bond should be short and strong (as it is—see Table 10) but offers no explanation for the paramagnetism of the molecule. To account for this property in terms of simple valence-bond theory, it is necessary to invoke

TABLE 10. SOME MOLECULAR PROPERTIES OF O_2 IN ITS GROUND STATE

		Reference
Bond dissociation energy	$D = 5.114 \pm 0.002$ eV	a
Bond length	$= 1.207\,398$ Å (from u.v. spectrum)	b
	$= 1.207\,41 \pm 0.000\,02$ Å	c
	(from the e.s.r. spectrum)	
Bond stretching-force constant	$k = 11.409 \times 10^{-5}$ dyne cm^{-1}	b
Ionization potential (adiabatic)	$= 12.075 \pm 0.01$ eV	d
Electron affinities: 1st	$= 0.43 \pm 0.01$ eV	e
'Double'	$= -6.7 \pm 0.6$ eV	f
	(for $O_2(g) \rightarrow O_2^{-2}(g)$)	
Polarizability: $\alpha_{xx} = \alpha_{yy}$	$= 1.2 \times 10^{-24}$	g
α_{zz}	$= 2.4 \times 10^{-24}$	
α_0	$= 1.6 \times 10^{-24}$	
Spin-orbit coupling constant λ	$= 1.985$ cm^{-1}	h

^a P. Brix and G. Herzberg, *Can. J. Phys.* **32** (1954) 110.

^b G. Herzberg, *Spectra of Diatomic Molecules*, 2nd edn., van Nostrand (1950).

^c M. Tinkham and M. W. P. Strandberg, *Phys. Rev.* **97** (1955) 951.

^d K. Watanabe, *J. Chem. Phys.* **26** (1957) 542.

^e J. L. Pack and A. V. Phelps, *J. Chem. Phys.* **44** (1966) 1870.

^f L. A. D'Orazio and R. H. Wood, *J. Chem. Phys.* **69** (1965) 2558.

^g Landolt-Börnstein, *Zahlenwerte und Funktionen aus Physik-Chemie-Astronomie-Geophysik und Technik*, Sechste Auflage, 1 Band, 3 Teil, p. 510.

^h K. Kayama and J. L. Baird, *J. Chem. Phys.* **46** (1967) 2604.

three-electron bonds³⁷ or to use the "double quartet" approach³⁸. In simple molecular orbital terms, the paramagnetism is explained by the two unpaired electrons in the anti-bonding π_g -orbital³⁹. The configuration is

$$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2.$$

Although in B_2 , C_2 and N_2 the $(\sigma_g 2p)$ level is above the $(\pi_u 2p)$ level because of interaction with $(\sigma_g 2s)$, in O_2 the order is as shown. More detailed calculations using the LCAO SCF method with configurational interaction⁴⁰ gives good agreement with the observed value for the total energy, but the agreement between the observed and the calculated values for the dissociation energy is less satisfactory.

The photo-electron spectrum of molecular oxygen excited using HeI radiation (21.23 eV) gives at least four and possibly five bands, all with vibrational progressions. The adiabatic ionization potentials and observed vibration frequencies are given in Table 11A.

³⁷ L. Pauling, *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, NY.

³⁸ J. W. Linnett, *The Electronic Structure of Molecules*, Methuen, London (1964).

³⁹ J. N. Murrell, S. F. A. Kettle and J. M. Tedder, *Valence Theory*, Wiley, New York (1965).

⁴⁰ K. Ohno, in *Middle U.V.: Its Science and Technology* (ed. A. E. S. Green), Wiley, New York (1966).

The band at lowest I.P. corresponds to removal of an anti-bonding π_g electron producing O_2^+ in its electronic ground-state $2\Pi_g$; as would have been expected, the vibration frequency is greater than in O_2 . The next band, with a long vibrational progression, corresponds to removal of a π -bonding electron giving $O_2^+(4\Pi_u)$; peaks associated with the production of $O_2^+(2\Pi_u)$ may also occur in this region. The next band corresponds to removal of a σ -bonding electron giving $O_2^+(4\Sigma_g)$, and the fifth band may correspond to the formation of $O_2^+(4\Sigma_u)$ or $O_2^+(2\Sigma_g^-)$. In each case the electron removed is bonding, as shown by the drop in vibration frequency on ionization^{40a}.

TABLE 11A. PARAMETERS FROM THE PHOTO-ELECTRON SPECTRUM OF O_2

Adiabatic I.P., eV	Vibration frequency excited (0-1), cm^{-1}	State of O_2 formed
12.07	1780	$2\Pi_g$
16.12	1010	$4\Pi_u$
a	2887	$2\Pi_u$
18.7	1090	$4\Sigma_g$
20.29	1130	$4\Sigma_u$ or $2\Sigma_g^-$

^a The (0-0) transition of this series was not identified.

Data from D. W. Turner *et al.*, *Molecular Spectroscopy*, Wiley, New York, 1970.

Molecular and Crystal Structure

The O-O distance in gaseous O_2 has been determined very accurately by analysis of the Schumann-Runge bands in the u.v. and also by microwave spectroscopy (see Table 10). The O-O distances in liquid and solid oxygen have not been accurately determined, but the diffraction measurements for the three solid forms are consistent with (O-O) bonded distances close to those for free O_2 , as is the small change in (O-O) stretching frequency with change in phase.

TABLE 11B. SOLID O_2 -STRUCTURES

Form	Class	Space group	Unit cell dimensions	Molecules in unit cell	Reference
α	Monoclinic	$C2/m(C_{2h}^3)$	$a = 5.403 \pm 0.005$ $b = 3.429 \pm 0.003$ $c = 5.086 \pm 0.005$	2	a
β	Rhombohedral	$R3m(D_{3h}^5)$	$a = 4.210 \pm 0.07$ $\alpha = 46^\circ 16' \pm 9'$	3	b
γ	Cubic	$Pm3n(O_h^3)$	$a = 6.83 \pm 0.05$	8	c

^a C. S. Barrett, L. Meyer and J. Wassermann, *J. Chem. Phys.* **47** (1967) 592.

^b R. A. Alikhanov, *Soviet Physics JETP* **18** (1964) 556; E. M. Hörnl, *Acta Cryst.* **15** (1962) 845.

^c T. A. Jordan, W. E. Streib, H. W. Smith and W. N. Lipscomb, *Acta Cryst.* **17** (1964) 777.

^{40a} D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, *Molecular Spectroscopy*, Wiley, New York, 1970.

The structure of crystalline γ -oxygen (the highest temperature form)⁴¹ is very like that of α -F₂. There are eight molecules in the unit cell: two are roughly spherically disordered, on $m\bar{3}(T_h)$ sites, and six are cylindrically disordered on $\bar{4}2m(D_{2d})$ sites, with the $\bar{4}(S_4)$ axis perpendicular to the molecular axis. This phase is soft and transparent, and less dense than the others; its structure is regarded as more like that of liquid oxygen than like that of the

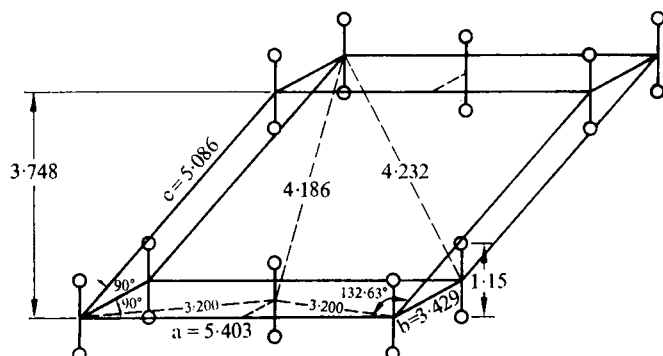


FIG. 1. The structure of α -oxygen; monoclinic $C2/m$. Atom centres and intermolecular distances are indicated; molecules are centred at 000 and $\frac{1}{2}\frac{1}{2}0$, with O-O bonds approximately normal to the (O-O) plane. (Reproduced with permission from C. S. Barrett, L. Meyer and J. Wasserman, *J. Chem. Phys.* **47** (1967) 592.)

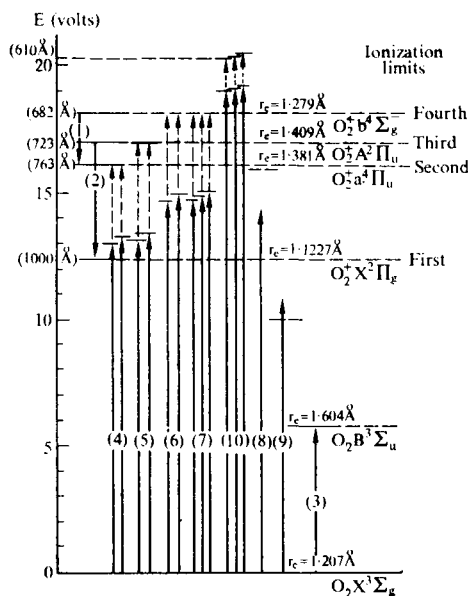


FIG. 2. Energy level diagram of the O₂ molecule. (Reproduced with permission from G. L. Weissler and Po Lee, *J. Opt. Soc. Am.* **42** (1952) 200.)

⁴¹ T. A. Jordan, W. E. Streib, H. W. Smith and W. N. Lipscomb, *Acta Cryst.* **17** (1964) 777.

β -form. This is consistent with the relatively small heat and volume changes on melting (smaller than the corresponding changes associated with the transition of β to α —see Table 15c)^{42, 43}, and with the closely similar vibrational spectra of γ -O₂ and liquid O₂. The β -form is rhombohedral^{42, 43} and the α -form is monoclinic (Table 11B). The structure of the α -form is given in Fig. 1; the O₂ molecules lie parallel to one another, and with their molecular axes perpendicular to the O–O planes⁴³.

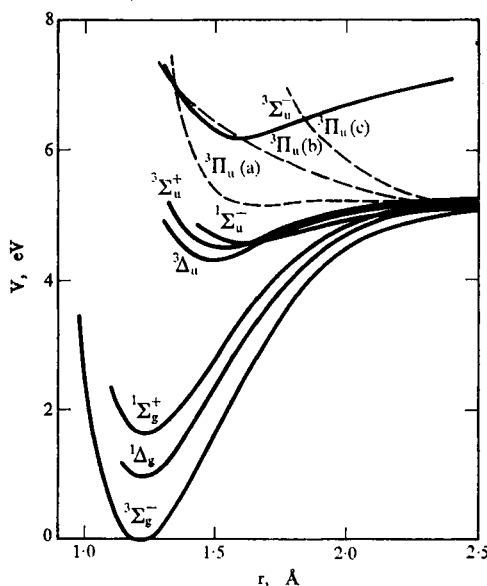


FIG. 3. Potential energy as a function of internuclear distance for states of the O₂ molecule. The dotted lines show results of different calculations for the $3\pi_u$ state. (Reproduced with permission from D. H. Volman, *Advances in Photochemistry* 1 (1963) 46.)

1.6. SPECTROSCOPIC PROPERTIES

Electronic Spectra

The spectrum of isolated O₂. The ground state⁴⁴ of O₂ is $3\Sigma_g^-$. The states $1\Delta_g$ and $1\Sigma_g^+$ are derived from the same electron configuration; transitions to each of these states from the ground state are formally forbidden, but are observed as very weak bands in the absorption of O₂ at $\sim 8000\text{ cm}^{-1}$ ($1\Delta_g \leftarrow 3\Sigma_g^-$) and $\sim 13,200\text{ cm}^{-1}$ ($1\Sigma_g^+ \leftarrow 3\Sigma_g^-$). Transitions to the next states involve excitation of a π_u -electron to a π_g -orbital. Fragments of a very weak band series due to the transition $3\Delta_u \leftarrow 3\Sigma_g^-$ were detected by Herzberg⁴⁵ close to the weak band series for the transition $3\Sigma_u^+ \leftarrow 3\Sigma_u^-$ near $36,000\text{ cm}^{-1}$ (the Herzberg bands) and the even weaker series⁴⁶ associated with the transition $1\Sigma_u^- \leftarrow 3\Sigma_g^-$ near $37,000\text{ cm}^{-1}$. All three of these transitions are forbidden. The strong Schumann–Runge bands near $50,000\text{ cm}^{-1}$ are

⁴² R. A. Alikhanov, *Soviet Physics JETP* 18 (1964) 556.

⁴³ C. S. Barrett, L. Meyer and J. Wassermann, *J. Chem. Phys.* 47 (1967) 592.

⁴⁴ G. Herzberg, *The Spectra of Diatomic Molecules*, 2nd edn., Van Nostrand, New York (1950).

⁴⁵ G. Herzberg, *Can. J. Phys.* 31 (1953) 657.

⁴⁶ P. Brix and G. Herzberg, *Can. J. Phys.* 32 (1954) 110.

TABLE 12. PARAMETERS FROM THE ELECTRONIC SPECTRA OF O₂. STATES ARE FOR O₂ UNLESS OTHERWISE STATED

Electronic state	<i>p</i> -electron configuration	<i>r</i> _e (Å)	<i>T</i> _e (cm ⁻¹)	ω _e (cm ⁻¹)	ω _e <i>x</i> _e (cm ⁻¹)	ω _e <i>y</i> _e (cm ⁻¹)	Reference
² Π _g (O ₂ ⁺)	σ _g ² π _u ⁴ π _g ¹	1.1227		1876.4	16.53		a, b
³ Σ _u ⁻	σ _g ² π _u ³ π _g ²	1.60 ₄	49 357.6	700.36	8.002 ₃	-0.3753 ₅	c
¹ Σ _u ⁻	σ _g ² π _u ³ π _g ²	1.597	36 678.9 ₁	650.4 ₉	17.03 ₆	0.105 ₆	a
³ Σ _u ⁺	σ _g ² π _u ³ π _g ²	[1.42]	36 096	819.0	22.5 ₀		a
¹ Σ _g ⁺	σ _g ² π _u ⁴ π _g ²	1.227 65 ₀	13 195.222 ₁	1432.687 ₄	13.9500 ₈	-0.01075	a
¹ Δ _g	σ _g ² π _u ⁴ π _g ²	1.2155	7918.1	1509.3	12.9		a
³ Σ _g ⁻	σ _g ² π _u ⁴ π _g ²	1.207 39 ₈	0	1580.361 ₃	12.0730	0.0546	a

*r*_e = equilibrium internuclear distance; *T*_e = electronic energy above the ground state; ω_e = harmonic fundamental vibrational frequency; ω_e*x*_e = vibrational constant for second-order anharmonic term; ω_e*y*_e = vibrational constant for third-order anharmonic term.

^a G. Herzberg, *The Spectra of Diatomic Molecules* 2nd edn., van Nostrand, New York (1950).

^b P. Brix and G. Herzberg, *Canad. J. Phys.* 32 (1954) 110.

^c G. Herzberg, *Canad. J. Phys.* 31 (1953) 657.

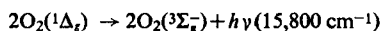
derived from the allowed transition ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$; they converge to a limit at $57,128\text{ cm}^{-1}$ and a continuum to about $70,000\text{ cm}^{-1}$. At higher energies the spectrum becomes complex, and fragments of several Rydberg series have been detected⁴⁷ (Fig. 2).

Band systems associated with all these transitions except ${}^3\Delta_u \leftarrow {}^3\Sigma_g^-$ have been analysed, and the derived molecular constants are given in Table 12; promotion of an electron from π_u to π_g leads to a lengthening of the O–O bond and a decrease in the vibration frequency, as simple theory predicts. On the other hand, ionization strengthens the bond by removing an antibonding electron. In the spectrum of solid α -oxygen at 4°K , the structure of the bands indicate that the molecular constants for the gas and for α -O₂ are very similar but not exactly the same⁴⁸. In γ -O₂ and β -O₂ the bands are broader than in the liquid or in α -O₂⁴⁹. There are further splittings of the vibrational bands in the spectrum of the crystal^{48, 49}.

Potential energy curves have been calculated for all the bound states, and for some of the repulsive ones (Fig. 3).

The lower states dissociate to two 3P oxygen atoms, but the ${}^3\Sigma_u^-$ state gives one 3P and one 1D atom. There is clear evidence for predissociation in the Schumann–Runge system⁵⁰; the relevant repulsive states seems to be ${}^3\Pi_g$, but the details of the process are not clear.

Bands involving intermolecular interactions. In the spectra of condensed or compressed oxygen there are bands that are not due to transitions of isolated O₂ molecules⁵¹; some of these features lie under the banded spectra of the O₂ transitions⁵². They are attributed to transitions in molecular complexes (perhaps short-lived collision complexes), but there must be more than one type of intermolecular process involved, for in compressed oxygen the intensities of different bands vary in different ways as the pressure is changed or as foreign gases are added. The band near $15,800\text{ cm}^{-1}$ is attributed to the (0–0) transition associated with simultaneous excitation of two ${}^3\Sigma_g^-$ oxygen molecules to the ${}^1\Delta_g$ state⁵³. Systems of ${}^1\Delta_g$ molecules show emission at this wavelength due to “energy pooling” of two molecules⁵⁴:



Similar simultaneous excitation of two molecules gives bands near $21,000\text{ cm}^{-1}$ [(0–0) transition of ${}^1\Delta_g + {}^1\Sigma_g^+ \leftarrow 2{}^3\Sigma_g^-$] and $26,500\text{ cm}^{-1}$ [(0–0) transition of $2{}^1\Sigma_g^+ \leftarrow 2{}^3\Sigma_g^-$]. In O₂ gas, the band at 7890 cm^{-1} is induced by the presence of a foreign gas, such as CO₂; the band at 9370 cm^{-1} , however, is only induced by increasing the pressure of O₂, and so is assigned to a transition in a collision complex of O₂ molecules⁵².

The strong bands largely responsible for the blue colour of liquid oxygen are due to (0–0), (0–1) and (0–2) transitions from the $2{}^1\Delta_g \leftarrow 2{}^3\Sigma_g^-$ and the ${}^1\Delta_g + {}^1\Sigma_g^+ \leftarrow 2{}^3\Sigma_g^-$ bands mentioned above⁵³.

Vibrational Spectra

The fundamental of O₂ is forbidden in the infrared, though it has been detected in the infrared spectra of oxygen gas at high pressures, of liquid oxygen, and of all three forms

⁴⁷ G. L. Weissler and Po Lee, *J. Opt. Soc. America* **42** (1952) 200.

⁴⁸ A. F. Prikhotko, T. P. Ptukha and L. I. Shanskii, *Optics Spectrosc.* **22** (1967) 203.

⁴⁹ A. Landau, E. J. Allan and H. L. Welsh, *Spectrochim. Acta* **18** (1962) 1.

⁵⁰ R. D. Hudson and V. L. Carter, *Can. J. Chem.* **47** (1969) 1840.

⁵¹ V. I. Dianov-Klovov, *Optics Spectrosc.* **20** (1966) 530.

⁵² R. M. Badger, A. C. Wright and R. F. Whitlock, *J. Chem. Phys.* **43** (1965) 4345.

⁵³ E. A. Ogryzlo, *J. Chem. Educ.* **42** (1965) 647.

⁵⁴ S. J. Arnold, N. Finlayson and E. A. Ogryzlo, *J. Chem. Phys.* **44** (1966) 2529.

of solid oxygen; the vibration is Raman active, and has been observed in the Raman spectra of all five phases of elementary O₂ (Table 13). The infrared spectra of the different phases of solid oxygen also show broad bands or shoulders to high frequencies of the fundamental band. In α -O₂, the fundamental is very sharp, and there is a broad band centred at 1605 cm⁻¹; the sharp peak is assigned to vibrations of molecules near a lattice imperfection, and the broad band to a combination of ν with lattice modes⁵⁵. Vibrational

TABLE 13. VIBRATIONAL SPECTRA OF O₂

Phase	Infrared (cm ⁻¹)	<i>T</i> (°K)	Raman (cm ⁻¹)	<i>T</i> (°K)
Gas	1556 ^a	? r.t.	1554.7 ± 1 ^d	r.t.
Liquid	1557 (ν) ^b 3102 (2 ν)	55	1552.5 (ν) ^a	77
Solid, γ	1552 (ν) ^b 1610 sh (? $\nu + l$)	44	1552.5 (ν) ^a	48
Solid, β	1552.4 (ν) ^c 1596 br ($\nu + l_1$) 1618 br ($\nu + l_2$)	26–32	46 (l) 1552.5 (ν) ^a	43
Solid, α	1548.4 (ν) ^c 1591 br ($\nu + l_1$) 1671 ($\nu + l_2$)	15–20	44 (l_2) 78 (l_2) 1552.5 (ν) ^a	22

ν = fundamental; l_1, l_2 = librational lattice modes.

^a M. F. Crawford, H. L. Welsh and J. L. Locke, *Phys. Rev.* **75** (1949) 1607.

^b A. L. Smith and H. L. Johnston, *J. Chem. Phys.* **20** (1952) 1972.

^c B. R. Cairns and G. C. Pimentel, *J. Chem. Phys.* **43** (1965) 3432.

^d F. Rasetti, *Phys. Rev.* **34** (1929) 367.

^e J. E. Cahill and G. E. Leroi, *J. Chem. Phys.* **51** (1969) 97.

lattice modes were observed⁵⁶ in the Raman spectra of solid α -O₂ (at 44 cm⁻¹ and 78 cm⁻¹) and β -O₂ (46 cm⁻¹). The strong winging on the Rayleigh line in the Raman spectra of solid γ -O₂ and liquid O₂ is associated with external motion; the torsional motion is highly hindered in each phase, and the r.m.s. torsional amplitude increases⁵⁶ from 9° for α -O₂ to 18° for liquid O₂.

Microwave and e.s.r. Spectra of O₂ ³Σ_g⁻

The O₂ molecule has no permanent dipole moment, but its magnetic moment, associated with electron spin, is coupled to the total rotational angular momentum. This leads to a splitting of the *K*-levels into three non-degenerate rotational states:

$$J = K+1, J = K \text{ and } J = K-1.$$

Transitions between levels where $\Delta J = \pm 1$ are allowed and give rise to weak absorption

⁵⁵ B. R. Cairns and G. C. Pimentel, *J. Chem. Phys.* **43** (1965) 3432.

⁵⁶ J. E. Cahill and G. E. Leroi, *J. Chem. Phys.* **51** (1969) 97.

in the microwave region of the spectrum⁵⁷. At atmospheric pressure the lines are broad, but fine structure has been studied at low pressures^{58, 59}.

The e.s.r. spectrum is very complicated. It arises because of the interaction of the molecular magnetic moment with the magnetic field; the spectrum is influenced by second-order coupling with the orbital motion of the electron and by a rotation-induced magnetic

TABLE 14. MAGNETIC AND RELATED PROPERTIES

<i>Magnetic susceptibility</i>	
Gas ^a	
$\chi_s T = 3115 \pm 7 \times 10^{-5}$ c.g.s. units at 293°K	
Liquid ^b	
$\chi_s(T-\theta') = C'$, where $\theta' = -71^\circ$; $C' = 38,600 \times 10^{-6}$	
Solid ^{c-e}	
γ roughly as for liquid ($\theta' \sim -60$)	
β $\chi = 160 \times 10^{-6}$ c.g.s. units at 43°K	
$\chi = 127 \times 10^{-6}$ c.g.s. units at 24°K	
α $14 < T < 20^\circ\text{K}$, $\chi = 49.3[1 + 0.00276 + (T - 14.50)^2] \times 10^{-6}$	
$1.5 < T < 4.2^\circ\text{K}$, $\chi = 50.7[1 - 0.01719 + (T - 2.906)] \times 10^{-6}$	
<i>Verdet constants</i>	
O ₂ gas (0°, 1 atm; 5460 Å)	5.986×10^{-6} min oe ⁻¹ cm ⁻¹ ^f
O ₂ liquid (5461 Å)	0.776×10^{-2} min oe ⁻¹ cm ⁻¹ at 90.1° ^g
	0.945×10^{-2} min oe ⁻¹ cm ⁻¹ at 63.4°
<i>Kerr constants</i>	
O ₂ gas (0°, 1 atm; $\lambda = 6500$ Å)	$B = 6.94 \times 10^{-12}$ c.g.s. units ^h
O ₂ liquid (5461 Å)	$B = 22.38 \times 10^{-9}$ c.g.s. units ⁱ

^a A. Burris and C. D. Hause, *J. Chem. Phys.* **11** (1943) 442.

^b H. Kamerlingh Onnes and E. Oosterhuis, *Comm. Leiden* 1913, 132e.

^c E. Kanda, T. Hasada and A. Otsubo, *Physica*, **20** (1954) 131.

^d A. S. Borovik-Romanov, *Zh. Exptl. Teoret. Fiz.* **21** (1951) 1303.

For α -oxygen, χ is effectively constant between 4.2 and 14K.

^e A. S. Borovik-Romanov, M. P. Orlova and P. G. Strelkov, *Doklady Akad. Nauk SSSR* **99** (1954) 699.

^f L. R. Ingersoll and D. H. Lieberberg, *J. Opt. Soc. America* **44** (1954) 566.

^g F. Gaume, *Comptes rendus* **232** (1951) 2304.

^h W. M. Breazeale, *Phys. Rev.* **48** (1935) 237.

ⁱ R. Guillien, *Comptes rendus* **200** (1935) 1840.

moment⁶⁰. Analysis of the spectrum gives values for the internuclear distance and the spin-orbit coupling constant. There has been disagreement about some features of the spectrum and their interpretation⁶¹.

1.7. MAGNETIC PROPERTIES

Elementary oxygen is paramagnetic in all phases. The susceptibility of the gas at 1 atm and 20°C corresponds closely with that calculated from the "spin-only" formula⁶²; at

⁵⁷ M. W. P. Strandberg, C. Y. Meng and J. G. Ingersoll, *Phys. Rev.* **75** (1949) 1524.

⁵⁸ R. S. Anderson, W. V. Smith and W. Gordy, *Phys. Rev.* **82** (1951) 264.

⁵⁹ M. Tinkham and M. W. P. Strandberg, *Phys. Rev.* **97** (1955) 937.

⁶⁰ M. Tinkham and M. W. P. Strandberg, *Phys. Rev.* **97** (1955) 951.

⁶¹ K. D. Bowers, R. A. Kamper and L. D. Lustig, *Proc. Roy. Soc. A*, **251** (1959) 565; L. K. Keys, *J. Phys. Chem.* **70** (1966) 3760; A. Carrington, D. H. Levy and T. A. Miller, *J. Phys. Chem.* **71** (1967) 2372.

⁶² A. Burris and C. D. Hause, *J. Chem. Phys.* **11** (1943) 442.

TABLE 15A. BULK PHYSICAL PROPERTIES OF O₂

	Reference
<i>Gas</i>	
Density (1 atm, 0°) = 1.429 00 g l ⁻¹	a
Compressibility $\frac{(pv)_{p=0}}{(pv)_{p=1 \text{ atm}}} (0^\circ) = 1.000\ 92_4$	b
Modified van der Waals equation: $p = [RT/(v - b_0 + b_1 p) - a/v - \alpha]^2$ $R = 0.003\ 666$ between 0°, 1 atm, and $b_0 = 0.002\ 05$ 200°, 400 atm $b_1 = 0.000\ 000\ 9$ $a = 0.002\ 72$ $\alpha = 0.000\ 60$	c
Virial coefficients For $PV_m = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2}\right)$, V_m = molar volume	c'
$B = -21.89 \text{ cm}^3 \text{ mol}^{-1}$ $T = 273.16^\circ \text{K}$ $C = 1230 \text{ cm}^6 \text{ mol}^{-2}$ $P < 135 \text{ atm}$	
Critical temperature, T_c $154.78 \pm 0.03^\circ \text{K}$	d
Critical pressure, P_c $50.14 \pm 0.01 \text{ atm}$	d
Critical density, ρ_c 0.408 g cm^{-3}	e
Critical compressibility, Z_c $(RT_c/P_c V_c) \sim 3.3$	d
Pitzer's acentric factor, ω 0.019	f
Boyle temperature, T_B 150°C	g
Specific heats (1 atm, 300°): C_p $0.2199 \text{ cal g}^{-1}$	h
C_v $0.1575 \text{ cal g}^{-1}$	h
Standard enthalpy, $H_{298.15}^\circ - H_0^\circ$ $2.0746 \text{ kcal mole}^{-1}$	i
Standard entropy, $S_{298.15}^\circ$ $49.003 \text{ cal mol}^{-1} \text{ deg}^{-1}$	i
Viscosity (1 atm, 0°) $1.9192 \times 10^{-4} \text{ poise}$	a
Thermal conductivity (1 atm, 0°) $5.867 \times 10^{-5} \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ }^\circ \text{K}^{-1}$	a
Refractive index (1 atm, 0°; 5897.4 Å) 1.000 275 09	j
Dielectric constant (1 atm, 0°C; 24 000 MHz) 1.000 531 0	k
Velocity of sound (1 atm, 0°) $315.12 \text{ m sec}^{-1}$	l

^a J. Hilsenrath *et al.*, NBS circular 564 (1955).

^b Gmelin, *Handbuch der Anorganische Chemie, Sauerstoff*, Lieferung 3, System-nummer 3' (1958), p. 395.

^c J. B. Goebal, *Z. phys. Chem.* **47** (1904) 471.

^{c'} J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases*, Oxford University Press, Oxford (1969).

^d H. J. Hoge, *J. Nat. Bureau Standards*, **44** (1950) 321.

^e The critical density is variously given as 0.38 g cm^{-3} and 0.4299 g cm^{-3} . This value is from A. V. Voronel, A. V. Chashkin, V. A. Popov and V. G. Sinikin, *Zh. Eksp. Teor. Fiz.* **45** (1963) 828.

^f H. W. Cooper and J. C. Goldfrank, *Hydrocarbon Processing* **46** (12) (1967) 141.

^g L. Holborn and J. Otto, *Z. Physik.* **23** (1924), 77.

^h *Properties of Materials at Low Temperature (Phase 1)* (ed. V. J. Johnson), Pergamon Press, New York (1961).

ⁱ From NBS Technical Note 270-3 (1968). Values over a range of temperature are given in ref. a.

^j R. Ladenburg and G. Wolfsohn, *Z. Physik.* **79** (1932) 42.

^k L. Esson and K. D. Froome, *Proc. Phys. Soc.* **B64** (1951) 862.

^l D. Bancroft, *Am. J. Phys.* **24** (1956) 355.

TABLE 15B. PROPERTIES OF THE LIQUID

	Reference
Boiling point: 90.1777°K	a
Vapour pressure: $\log_{10} p_{\text{mm}} = 28.901\,847 - 10.534\,702 \log_{10} T + 0.019\,329\,48T - \frac{667.855\,76}{T} + \frac{1937.538}{T^2}$	a
Density, ρ (g/cc) = $(1.5656 - 4.896 \times 10^{-3}T + 2.136 \times 10^{-6}T^2) + p(-0.533\,27 + 0.028\,24T) \times 10^{-4}$ (Range: 65–90°K; p up to 150 kg cm ⁻² ; T in °K; p in kg cm ⁻²)	b
$\rho = 1.142$ g cm ⁻² at 90°K	c
Viscosity:	
$\ln(10^5 \eta) = 3.490 + \frac{0.756\rho}{(1.6144 + 0.632 \times 10^{-4}p - \rho)}$	d
at 89.7° 11 kgf cm ⁻² , $\eta = 0.001\,99$ poise	
Specific heats:	
At 56.95°K $C_p = 12.76$ cal mole ⁻¹ °K ⁻¹	e
At 90.33°K $C_p = 12.99$ cal mole ⁻¹ °K ⁻¹	
Surface tension:	
Between 71°K and 90°K, $\gamma_T = 36.479 - 0.259T$	f
At 70°, 18.35; at 90°, 13.23 dyne cm ⁻²	g
Thermal conductivity at 73.16°K, 20 atm, = 1.721 mW cm ⁻¹ °K ⁻¹	c
Dielectric constant:	
At 54.33°K $\epsilon = 1.594$	c
At 90.14°K $\epsilon = 1.4837$	
In this range, $P = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{1}{\rho} = 0.1211 \pm 0.05\%$	
Adiabatic compressibility:	
At 60.5° 0.608 × 10 ⁻¹⁰ cm ² dyn ⁻¹	h
At 90.0° 1.050 × 10 ⁻¹⁰ cm ² dyn ⁻¹	
Refractive index (5461 Å) ¹	
At 65.0°K 1.2483	i
At 90.3°K 1.2243	
Velocity of sound (535 kHz)	
At 60.5° 1128.9 m sec ⁻¹	h
At 90.5° 902.3 m sec ⁻¹	

* R. Muijlwijk, M. R. Moussa and V. Van Dijk, *Physica* **32** (1966) 805. For measurements so precise as these, the thermometry becomes important; this reference discusses the small differences between precise measurements of the same parameter in different laboratories.

^b A. Van Itterbeek and O. Verbeke, *Cryogenics* **1** (1960) 77.

^c *Properties of Materials at Low Temperatures (Phase I)* (ed. V. J. Johnson), Pergamon Press, New York (1961).

^d W. Grevendonk, W. Herreman, W. de Pesseroey and A. de Bock, *Physica* **40** (1968) 207.

^e W. F. Giaque and H. L. Johnston, *J. Am. Chem. Soc.* **51** (1929) 2300.

^f P. Waldon, *Z. phys. Chem.* **65** (1909) 129.

^g E. Kanda, *Bull. Chem. Soc. Japan* **12** (1937) 469.

^h A. Van Itterbeek, A. de Back and L. Verhaegen, *Physica* **15** (1949) 624.

ⁱ H. E. Johns and J. O. Wilhelm, *Canad. J. Res.* **A15** (1937) 101.

higher temperatures the Curie law is obeyed with agreement between observed and calculated values of about 1.5%, and agreement is still good at low temperatures⁶³. Similarly, the susceptibility at high pressures is given by $\chi(T + \theta') = \text{const.}$, where θ' depends on the pressure⁶⁴; at low temperatures and high pressures Curie's law is not obeyed⁶⁵. The susceptibilities of liquid oxygen and of γ -O₂ obey the Curie-Weiss law with a negative value for θ' ; both α -O₂ and β -O₂ show antiferromagnetic properties. In α -O₂, neutron diffraction

⁶³ H. Kamerlingh Onnes and E. Oosterhuis, *Communs. Leiden* **134d** (1913) 31.

⁶⁴ M. Kanzler, *Ann. Phys.* **36** (1939) 38.

⁶⁵ H. R. Woltjer, C. W. Coppoolse and E. C. Wiersma, *Communs. Leiden* **201** (1929) 35.

TABLE 15C. SOLID OXYGEN

Phase changes

Change	Temperature (°C)	ΔH (cal mole ⁻¹)	ΔV (cm ³ mole ⁻¹)
Melting point (triple point)	54.3496 ^a	106.3 ± 0.3 ^b	0.918 ± 0.02 ^c
γ - β	43.800 ^c	177.6 ± 0.5 ^b	1.08 ± 0.05 ^c
β - α	23.886 ± 0.005 ^c	22.4 ± 0.1 ^b	

Vapour pressure equation ^d

$$\gamma\text{-O}_2: \log_{10} p_{\text{mm}} = \frac{-478.4}{T} + 12.40 - 2.055 \log_{10} T$$

$$\beta\text{-O}_2: \log_{10} p_{\text{mm}} = \frac{-452.2}{T} + 2.061 - 4.78 \log_{10} T$$

$$\alpha\text{-O}_2: \log_{10} p_{\text{mm}} = \frac{-454.7}{T} + 1.794 + 5.085 \log_{10} T$$

	$\gamma\text{-O}_2$	$\beta\text{-O}_2$	$\alpha\text{-O}_2$
Density: measured (g cm ⁻³)	1.30 ^e	1.395 ^e	1.426 ^f
from crystallography	1.334 ^g	1.495 ^h	1.53 ⁱ

Specific heat (cal mol⁻¹ °K⁻¹)^b 11.03 at 45.90°K; 5.42 at 25.02°K; 9.34×10^{-4} at 4°
 11.06 at 52.12°K; 10.73 at 42.21°K; 4.40 at 22.24°
 (cal gm⁻¹)^j $C/T = 1.46 \times 10^{-5} T^2$ below 4°K

^a R. Muiklwijk, N. R. Moussa and H. Van Dijk, *Physica* **32** (1966) 805.

^b W. F. Giaque and H. L. Johnston, *J. Am. Chem. Soc.* **51** (1929) 2300.

^c J. A. Jahnke, *J. Chem. Phys.* **47** (1967) 336.

^d Landolt-Börnstein, *Zahlenwerte und Funktionen aus Physik-Chemie-Astronomie-Geophysik und Technik*, Sechste Auflage, II Band, 2 Teil, pp. 5, 10, 15.

^e L. Vegard, *Nature* **136** (1935) 720.

^f J. Dewar, *Proc. Roy. Soc.* **73** (1904) 251.

^g T. A. Jordan, W. E. Streib, H. W. Smith and W. N. Lipscomb, *Acta Cryst.* **17** (1964) 777.

^h E. M. Hörl, *Acta Cryst.* **15** (1962), 845.

ⁱ C. S. Barrett, L. Meyer and J. Wassermann, *J. Chem. Phys.* **47** (1967) 592.

^j *Properties of Materials at Low Temperatures (Phase I)* (ed. V. J. Johnson), Pergamon Press, New York (1961).

indicates that at 4°K the magnetic vectors of the individual molecules are aligned so that the vector of each molecule, perpendicular to the molecular axis, is opposed to the vectors of its eight nearest neighbours⁶⁸. There may be a further antiferromagnetic transition⁶⁹ at

⁶⁶ H. Kamerlingh Onnes and A. Perrier, *Communs. Leiden* **116** (1910) 1.

⁶⁷ A. S. Borovik-Romanov, M. P. Orlova and P. G. Strelkov, *Doklady Akad. Nauk SSSR* **99** (1954) 699.

⁶⁸ C. S. Barrett, L. Meyer and J. Wassermann, *J. Chem. Phys.* **47** (1967) 592.

⁶⁹ W. H. Lien and N. E. Phillips, *J. Chem. Phys.* **34** (1961) 1073.

temperatures below 15°K. There is no evidence from neutron diffraction for long-range magnetic order in β -O₂, but some features of the diffraction patterns are consistent with short-range antiferromagnetism⁷⁰. Intermolecular magnetic interaction in the liquid phase is strong, for the susceptibility increases at a given temperature on dilution with liquid nitrogen, and in very dilute solution approaches the "spin-only" value⁷¹. (Tables 14, 15A, 15B, 15C and 16.)

TABLE 16. SOLUBILITY OF O₂ *

1 cm³ water dissolves 0.0308 cm³ O₂ (measured at s.t.p.) at 20°, 0.0208 cm³ at 50° and 0.0177 cm³ at 80°. The concentration in ppm of O₂ in contact with air saturated with water vapour (total pressure one atmosphere) is given by

$$C = 14.161 - 0.3943t + 0.007714t^2 - 0.0000646t^3 \quad (t \text{ in } ^\circ\text{C})$$

The solubility is lower in solution of electrolytes, bases, or acids, but goes through a minimum in sulphuric acid and is nearly as great in 96% H₂SO₄ as in water. At 25° under a pressure of atmosphere O₂, 1 cm³ of each of the following solvents dissolves the stated volume of O₂ (measured at 1 atm and 25°):

CCl ₄	0.302
benzene	0.223
acetone	0.280
diethyl ether	0.455

* W. F. Linke, *Solubilities of Inorganic and Metal-Organic Compounds*, Vol. II, American Chemical Society (1965).

1.8. REACTIONS OF O₂

General

The bond in O₂ is very strong, but oxygen forms strong bonds with many other elements, and most elements and many compounds are thermodynamically unstable to O₂. Living organisms are unstable with respect to oxidation by O₂ to carbon dioxide and water; most metals are unstable with respect to oxidation by O₂ to an oxide. In aqueous solution O₂ is thermodynamically a powerful oxidizing agent. In practice, however, few of these systems react with O₂ under normal conditions; most of the processes are kinetically controlled. Activation energies for the oxidation of organic systems are often high; a metal may become protected by a thin film of oxide. Such metastable systems may of course be activated; under some conditions, the chain reaction between H₂ and O₂, with explosion limits depending on composition and other conditions, can be set off by a catalyst. Indeed, much of the interest in the chemistry of O₂ has been associated with different ways of activating O₂: converting it into atoms, using catalysts or by means of radiation. Oxygen, after all, is by far the most abundant oxidizing agent, and the cheapest. Oxidations based on molecular oxygen are the primary sources of energy in many living organisms; catalysts called oxygenases which can use O₂ in oxidizing cycles are associated with systems (oxygen carriers) that take up oxygen from the atmosphere (or from the lungs of the organism) and release it in the organism, so that the release of energy can be controlled. These aspects are discussed in subsequent sections. Despite the kinetic barriers to the reactions of O₂, liquid oxygen reacts explosively with organic matter and with many metals, which makes the handling of the material hazardous.

⁷⁰ M. F. Collins, *Proc. Phys. Soc.* **89** (1966) 415.

⁷¹ A. Perrier and H. Kamerlingh Onnes, *Communs. Leiden* **139d** (1914) 37.

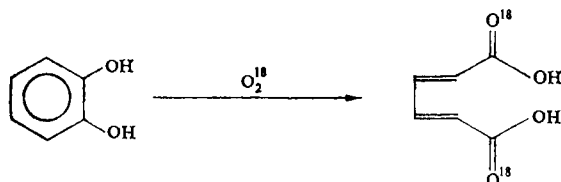
The process of "apparently uncatalysed oxidation of a substance exposed to the oxygen of the air" has been defined as autoxidation⁷²; species that autoxidize include unsaturated organic systems, transition metals in low oxidation states and many free radicals. Oxygen, with its triplet ground state, is in condition to combine with other molecules with paramagnetic ground states or low-lying excited states. Indeed, many autoxidations involve free radicals. Some are sensitized by other species, not themselves oxidized; the wide variety of processes and systems cannot be discussed in detail here.

Oxygenation in Solution

Oxygen carriers and oxygenases. Oxygen carriers⁷³, which combine reversibly with molecular oxygen, maintain the level of molecular oxygen in the blood of animals and reptiles; oxygenases⁷⁴ are the catalysts that enable organisms to obtain energy by oxidation processes involving molecular oxygen. Molecular oxygen is not very soluble in blood, but the presence of oxygen carriers enables the blood of reptiles to contain 5–10%, and that of mammals 15–30%, of its own volume of O₂ in equilibrium with the atmosphere at room temperature⁷⁵. The best-known natural oxygen carrier is haemoglobin, in which the oxygen is associated with Fe(II); the stereochemical arrangement of the combined O₂ is still a matter of controversy (see section 7). A number of systems containing Fe(II) react with O₂; indeed, many oxygenases contain iron. However, in most of these systems the products of the reaction are Fe(III) and H₂O₂ or water, and though the iron may be reduced back to Fe(II), the result of the reaction is the reduction of O₂ and the oxidation of iron or some other substrate. The remarkable thing about haemoglobin is not that it combines with O₂, but that it releases the combined O₂ reversibly. Other oxygen-carrying systems found in nature contain iron or copper; haemocyanin, the oxygen-carrier in snail's blood, contains Cu(I). Complexes of other transition metals, such as cobalt or iridium, have been shown to combine reversibly with molecular oxygen.

There is an enormous variety of oxygenases and related enzymes; like the oxygen carriers, most contain some transition element such as iron, copper or molybdenum. Among the enzymes associated with oxidation by molecular oxygen the following types have been distinguished⁷⁶:

- (1) Oxygenases proper, in whose operations both atoms of the O₂ molecule are transferred to the substrate. Among them is pyrocatecholoxidase, which catalyses the oxidation of catechol:



⁷² N. Uri, in *Autoxidation and Antioxidants* (ed. W. O. Lundberg), Interscience, New York, 1 (1961) 55.

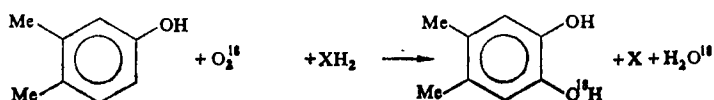
⁷³ L. H. Vogt, H. M. Faigenbaum and C. E. Wiberley, *Chem. Rev.* **63** (1963) 269; C. Manwell, *Ann. Rev. Physiol.* **22** (1960) 191.

⁷⁴ O. Hayaishi (ed.), *Oxygenases*, Academic Press, New York (1964).

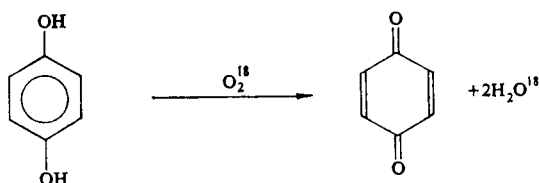
⁷⁵ J. Krog, in *Oxygen in the Animal Organism*, Pergamon Press, New York (1964).

⁷⁶ S. Fallab, *Z. Naturw.-med. Grundlagenforschung* **1** (1963) 333.

- (2) Hydroxylases, such as monophenol oxidase, which transfer only one oxygen atom from O_2 to substrate:

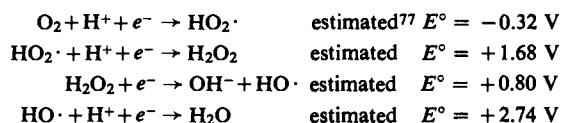


- (3) Electron transferases, such as laccase, in the course of whose action both atoms of O_2 are reduced to water:

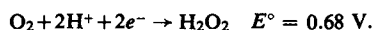


Some of the enzymic systems, such as the cytochrome oxidase system, are extremely complex and imperfectly understood. The formation of Fe(IV) has been proposed as part of the mechanism of operation of some iron-containing oxygenase systems⁷⁷.

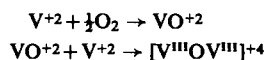
Autoxidation and homogeneous catalysis. In the homogeneous oxidation of metal ions in aqueous solution^{78, 79} at least two types of mechanism have been proposed. In one of these oxygen is reduced to water by a series of one-electron steps:



As is obvious from the E° values, the first of these steps is energetically unfavourable, whereas the rest all proceed with release of energy. Moreover, the direct reduction of O_2 to H_2O_2 is also energy-releasing:



In the alternative mechanism, the first step involves transfer of two electrons, giving H_2O_2 directly and avoiding the energetically awkward formation of $HO_2 \cdot$. In some cases there is evidence to indicate that the second mechanism operates. The autoxidation of V(II), for example, produces polynuclear V(III) species whose formation can be understood in terms of the steps below:



Measurements of rates of autoxidation of transition metals clearly imply that in most cases studied the transfer of electrons from metal to O_2 takes place within some complex in which O_2 is bound to the metal, though some of the evidence is indirect; the transfer of

⁷⁷ P. George, in *Oxidases and Related Systems* (ed. T. E. King, H. S. Mason and M. Morrison), Wiley, New York (1965), p. 3.

⁷⁸ S. Fallab, *Angew. Chem., Int. Edn.* **6** (1967) 496.

⁷⁹ H. Taube, *J. Gen. Physiol.* **49** (1965) 29.

protons to combined O_2 from water or OH groups also bound to the metal may be important too.

The autoxidation of organic compounds in the liquid phase is catalysed by a variety of metal ions. The process that has been most extensively studied is the oxidation of olefins; this is catalysed by ions of such metals as⁸⁰ iron, cobalt, nickel, copper or zinc. The catalysed process occurs through a radical mechanism, the initiation of which is brought about in most cases by the interaction of olefin hydroperoxide with the metal ion. The redox behaviour of the metal has an important influence in the course of the reaction, and, indeed, for some metals the chief function of molecular oxygen may be to reoxidize the metal, which itself acts as the primary oxidizing agent and is reduced in oxidizing the substrate. In other systems, however, there is evidence that the oxidizing species is a complex of O_2 with the metal; some, but not all, of the metal- O_2 complexes that have been isolated are effective oxidants⁸¹.

Chemisorption and Heterogeneous Catalysis

Oxygen is chemisorbed by almost all metals, by many metal oxides and by a variety of other materials; this chemisorption is involved in the heterogeneous catalysis of the reactions of molecular oxygen^{82, 83}. Heats of adsorption of oxygen on metals are high; adsorption is rapid, and it is usually supposed that oxygen is present on the surface as monatomic species. This view is generally supported by results of low-energy electron diffraction⁸⁴. The surface of nickel on which oxygen has been adsorbed shows some of the properties of a surface oxide⁸⁵. A study⁸⁶ by mass spectrometry of the flash desorption of O_2 chemisorbed on tungsten ribbon indicates that only monatomic oxygen species or WO_n ($n = 1-3$) are evolved, so it seems unlikely that significant concentrations of diatomic oxygen species (O_2 or O_2^-) are present on the surface. On many metals (among them tungsten and silver)⁸⁷ at least two modes of chemisorption have been recognized; on silver it has been suggested that one mode involves the adsorption of peroxy-species, and experiments with $^{18}O_2$ were taken as confirming this view, but it now seems that insufficient allowance was made for the retention of unlabelled oxygen in the silver metal catalyst even after degassing at 500° under vacuum⁸⁸. The inability of the oxygenated silver surface to catalyse the *ortho-para*-hydrogen conversion also implies the absence of such paramagnetic species as O_2 . On the other hand, silver does catalyse the oxidation of cumene to cumene hydroperoxide⁸⁹.

Chemisorption on metal oxides⁹⁰ is closely connected with the presence of lattice defects or with metals that can easily be oxidized or reduced. Defects induced by radiation may be associated with chemisorption of O_2 . Furthermore, some e.s.r. signals associated with

⁸⁰ A. Chalk and F. Smith, *Trans. Faraday Soc.* **53** (1957) 1214.

⁸¹ E. A. V. Ebsworth and J. A. Connor, *Advances in Inorganic Chemistry and Radiochemistry* (ed. H. J. Emeléus and A. G. Sharpe), Academic Press, New York, **6** (1964) 279.

⁸² D. O. Hayward and B. N. W. Trapnell, *Chemisorption*, 2nd edn., Butterworths (1964).

⁸³ J. M. Thomas and W. T. Thomas, *Introduction to Principles of Heterogeneous Catalysis*, Academic Press, New York (1967).

⁸⁴ A. J. Pignocco and G. E. Pellissier, *J. Electrochem. Soc.* **112** (1965) 1188.

⁸⁵ M. W. Roberts and B. R. Wells, *Disc. Faraday Soc.* **41** (1966) 162.

⁸⁶ B. McCarroll, *J. Chem. Phys.* **46** (1967) 863.

⁸⁷ J. H. Singleton, *J. Chem. Phys.* **47** (1967) 73.

⁸⁸ Y. L. Sandler and W. M. Hickam, *Proc. 3rd Int. Congr. Cat.* **1** (1964) 227.

⁸⁹ J. H. deBoer, *Discussion, 2nd Int. Conf. Surface Activity*, Butterworths, **II** (1957) 337.

⁹⁰ F. S. Stone, *Adv. Catalysis* **13** (1962) 1.

⁹¹ J. H. Lumford and J. P. Jayne, *J. Chem. Phys.* **44** (1966) 1487.

lattice defects disappear in many systems when oxygen is adsorbed⁹¹. The chemisorbed species may be O_2 , O_2^- , O^\cdot , O^- or O^{-2} , and the formation of such polymers as O_4 or O_4^- has been suggested^{92,93}; the electrons necessary for the formation of the reduced species must come, of course, from the lattice. In all cases, however, oxygen will behave as an electron sink on adsorption; for this reason, adsorption of oxygen on oxides which are *n*-type semiconductors will be limited, whereas on *p*-semiconductors the same limitation will not hold. The e.s.r. spectra of zinc^{91,94} or titanium⁹⁵ oxides on which O_2 has been chemisorbed have been interpreted as showing the presence of O_2^- and perhaps O_2 , but none of the signals assigned to these species was observed⁹⁵ for O_2 chemisorbed on MoO_3 .

TABLE 17. HETEROGENEOUS CATALYSIS OF SOME REACTIONS OF O_2

Other reactant(s)	Important product(s)	Catalyst
H_2	Water	Metals ^a
CO	CO_2	Cu_2O , NiO, etc. ^b
SO_2	SO_3	V_2O_5 or Pt ^{a, b}
NH_3	N oxides	Pt or Rh
C_2H_4	Ethylene oxide	Ag ^{a, b}
Propylene	Acrolein	Cu_2O ^b
Propylene + NH_3	Acrylonitrile	Bi(III)/Mo(VI) oxides ^d
Olefins	Dienes, aldehydes, acids, CO, CO_2	Bi(III)/Mo(VI) oxides ^{b, e}
Benzene	Maleic anhydride	V_2O_5 ^b
$C_2H_4 + HCl$	Ethylene dichloride	$CuCl_2$ ^c
$CH_4 + H_2O$	Formaldehyde	Cu or Ag ^a

^a G. C. Bond, *Catalysis by Metals*, Academic Press (1962).

^b J. M. Thomas and W. T. Thomas, *Introduction to Principles of Heterogeneous Catalysis*, Academic Press (1967).

^c E. F. Edwards and T. Weaver, *Chem. Eng. Prog.* **61** (1965) 21. This is important because the product may be cracked to give vinyl chloride.

^d C. R. Adams and T. J. Jennings, *J. Catalysis* **3** (1964) 549.

^e It has been suggested that dehydrogenation is specifically associated with reaction with lattice oxygen.

or NiO. On MgO that had previously been γ -irradiated, adsorption of O_2 was associated with the appearance of a signal in the e.s.r. spectrum that was assigned to O_2^- , and with O_2 enriched in O^{17} the signal showed hyperfine structure that could be interpreted in terms of a mixture of $O^{18}O^{17}$ and O_2^{17} in the proportions required by the statistical distribution of O^{18} and O^{17} . There appeared to be no oxygen exchange with the lattice over several months at room temperature⁹⁶. When adsorption is associated with rapid exchange between $^{16}O_2$ and $^{18}O_2$ it has been argued that the O–O bonds must be broken on adsorption, but more recently it has been suggested that such exchange could occur through the formation of

⁹² P. Chan and A. Steinmann, *Surface Sci.* **5** (1966) 267.

⁹³ K. Hirota and M. Chono, *Sci. Papers Int. Phys. Chem. Res. Tokyo* **58** (1964) 115.

⁹⁴ R. J. Kokes, *Proc. 3rd Int. Congr. Cat., Amsterdam* **1** (1964), 484.

⁹⁵ P. F. Cornaz, J. H. C. Van Hoof, F. J. Pluijm and G. C. A. Schuit, *Disc. Faraday Soc.* **41** (1966) 290.

⁹⁶ A. J. Tench and P. Holroyd, *Chem. Commun.* 1968, 471.

⁹⁷ G. K. Boreskov, *Disc. Faraday Soc.* **41** (1966) 263.

O_4 or O_4^- species⁹³ on the surface. Formation of O^{-2} should lead to exchange between the metal oxide and the oxygen gas. Many metal oxides which have been preheated in O_2 are effective catalysts for the exchange between $^{16}O_2$ and $^{18}O_2$ only at high temperatures; the exchange has the same rate parameters as the exchange between the O_2 gas and lattice oxide ions, and is presumed to involve lattice oxide. On the other hand, oxides preheated under vacuum are effective catalysts for $^{16}O_2/^{18}O_2$ exchange at low temperatures, under conditions where exchange with lattice oxide does not occur⁹⁷. The rates of isotopic exchange on many metal oxides have been determined, and the kinetic parameters discussed in terms of possible mechanisms of exchange⁹⁸. The unusual ease of exchange of O_2 with Cu_2O has been related to the unusual structure of the oxide⁹⁰.

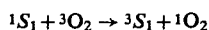
Catalytic oxidation at the surfaces of metal oxides may take place through direct interaction between the adsorbed species and the material to be oxidized; alternatively, the substrate may be oxidized by lattice oxide ions, with reduction of the catalyst, which is then reoxidized by oxygen. The oxidation of SO_2 or of hydrocarbons on a catalyst of V_2O_5 is believed to follow the latter mechanism⁸³; on the other hand, experiments using labelled oxygen⁸³ indicate that lattice oxide is not involved in the oxidation of CO with O_2 on NiO. Some examples of reactions of molecular oxygen catalysed by a variety of solid materials are given in Table 17. The unique oxidation of ethylene to ethylene oxide at a silver catalyst is remarkable, since most olefins on all other catalysts give aldehydes, acids or (ultimately) CO and CO_2 .

Photochemical Oxygenation: Reactions of Singlet O_2

Electronically excited O_2 molecules are not efficiently produced by radiation at frequencies less than $50\,000\text{ cm}^{-1}$. Many reactions of molecular oxygen, however, particularly those with unsaturated or aromatic organic compounds, may be induced photochemically, either with or without a sensitizer; compounds that act as sensitizers are usually dyes or other strong absorbers of light (e.g. rose bengal, eosin or chlorophyll). The system initially absorbs energy from radiation by electronic excitation of either the substrate or the sensitizer; this energy must lead to the production of some active intermediate. Various mechanisms have been proposed⁹⁹:

(a) Free radicals may be produced by dissociation of the electronically excited substrate. The photochemical oxidation of aldehydes, for example, is believed to take place by initial formation of radicals¹⁰⁰. Such processes in which free radicals are involved are called "type-1 photochemical oxygenations".

(b) Reactions involving only excited molecules are called type-2 processes. The species initially excited by radiation may be either the substrate or the sensitizer. In either case, the state formed is usually the first excited singlet state, here labelled 1S_1 . This can transfer energy to O_2 with conservation of spin:



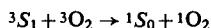
where 3S_1 is the lowest triplet state of S (assumed to have a singlet ground state). Singlet O_2 can only be formed in this way⁹⁹ if the energy gap $^1S_1 \rightarrow ^3S_1$ is greater than the gap $^3O_2 \rightarrow ^1O_2$, which for $O_2(^1\Delta_g)$ is $22.6\text{ kcal mole}^{-1}$; if the energy transferred is greater than

⁹⁸ E. R. S. Winter, *J. Chem. Soc. A*, 1968, 2889.

⁹⁹ K. Gollnick, *Adv. Photochem.* (Wiley) **6** (1968) 1.

¹⁰⁰ M. Niclaude, J. Lemaire and M. Letort, *Adv. Photochem.* (Wiley) **4** (1966) 25.

37 kcal mole⁻¹, some O₂(¹Σ_g⁺) may also be produced, until at a value of 49 kcal mole⁻¹ about ten times as much O₂(¹Σ_g⁺) as O₂(¹Δ_g) may be formed. If the excited sensitizer or substrate is in an excited triplet state, however, singlet O₂ can be produced with the other species (substrate or sensitizer) in its ground state:

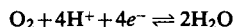


This is because the interaction of molecules with spin vectors of magnitude 1 can give a singlet collision complex, which can then dissociate to form singlet O₂ and the substrate or sensitizer in its singlet ground state¹⁰¹. It is also possible that the active intermediate might be the excited substrate itself, produced by the initial absorption of radiation; alternatively, the excited substrate or sensitizer might form a longer-lived activated complex (or moloxide) with O₂. Recently it has proved possible to study O₂ containing substantial amounts of singlet O₂; this species is formed by the action of an electrodeless discharge on oxygen gas¹⁰², by the reaction between hydrogen peroxide and hypochlorite or chlorine in aqueous solution¹⁰³, or by the decomposition at -78° of the adduct of triphenyl phosphite with ozone¹⁰⁴. The product in the last case has been shown to contain O₂(¹Δ_g) by its e.p.r. spectrum¹⁰⁵. The reactions of singlet O₂ from these different sources are very like the photochemically induced reactions of O₂, not only in products but also (in some cases) in kinetics. It therefore seems very likely that singlet O₂ is the active intermediate in photochemical oxygenations of type 2. Of the two mechanisms described above for the production of singlet O₂, the latter is by far the more important; the triplet sensitizer or substrate may be formed by intersystem crossing.

The products of many photochemical oxygenations depend on the solvent and the conditions, and are not always the same in sensitized and in unsensitized processes; with 1,4-dienes, O₂ may behave as a dienophile to give products of what is effectively a Diels-Alder reaction. Peroxides, hydroperoxides or substituted allyl alcohols may be prepared in this way. Unsaturated sulphur compounds or sulphides are oxidized photochemically by O₂ in the presence of a sensitizer; amines are also oxidized, but it is not clear what the primary products are⁹⁹.

The O₂ Electrode¹⁰⁶

The electrochemistry of oxygen is of great and increasing importance, impinging as it does on batteries and fuel cells, on corrosion and on the analytical chemistry of oxygen. The reversible potential for the reaction



(see Table 5, p. 691) has been calculated from thermodynamic data as +1.229 V, and the reversible rest potential has been observed for platinum that has been anodized and heated in pure O₂ or treated with HNO₃; such an electrode is probably covered with a uniform film of oxide. The electrode behaves reversibly so long as the current drawn is less than

¹⁰¹ J. S. Griffith, *Oxygen in the Animal Organism* (ed. F. Dickens and E. Neil), Pergamon Press, New York (1964).

¹⁰² R. P. Wayne, *Adv. Photochem.* (Wiley) **7** (1969) 311.

¹⁰³ C. S. Foote, S. Wexler, W. Ando and R. Higgins, *J. Am. Chem. Soc.* **90** (1968) 975.

¹⁰⁴ R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.* **90** (1968) 4161.

¹⁰⁵ E. Wassermann, R. W. Murray, M. L. Kaplan and W. A. Yagen, *J. Am. Chem. Soc.* **70** (1968) 4160.

¹⁰⁶ T. P. Hoar, *The Electrochemistry of Oxygen*, Interscience (1968).

$40 \mu\text{A cm}^{-2}$, and it follows that the mechanism for the reduction of O_2 under these conditions must be precisely the reverse of the mechanism for O_2 evolution. It is believed that in the reversible reduction of O_2 the O–O bond is broken before electron transfer. The reversible potential value has also been observed for bright platinum electrodes in acid solutions, but here the process is irreversible and the mechanism is different: the system in this case has been described as a polyelectrode, and in the reduction of O_2 under these conditions peroxide is an intermediate. The rest potential of an oxygen electrode on other noble metals rarely corresponds to the reversible potential, and depends very much on the nature of the metal surface under O_2 (about which little is known); for this reason the electrochemical behaviour of O_2 is closely related to chemisorption.

The overvoltage for evolution of O_2 is substantial. Oxygen electrodes are very easily polarized, and the polarization depends on the nature of the electrode and on the current density. The mechanism for the evolution of O_2 from acid solutions on platinum is believed to involve the formation of adsorbed OH radicals, giving oxygen atoms, which then combine to give O_2 molecules. The mechanism in alkaline solution may be different. Cathodes at which O_2 is reduced are also very easily polarized. On platinum in acid solutions the slow step is the formation of O_2^- on the surface of the electrode from adsorbed O_2 ; this is protonated and followed by further reduction and protonation to give H_2O_2 . The overvoltage for reduction of O_2 in alkali is lower, and under these conditions it has been suggested that the intermediate is HO_2^- .

Particular impetus to the study of the oxygen electrode has come from the development of the H_2/O_2 fuel cell as a source of energy for many systems, including space craft¹⁰⁷. In a fuel cell the reaction between hydrogen and oxygen is used to provide electrical energy; a hydrogen electrode forms the anode and an oxygen electrode the cathode. It is important to prevent diffusion of the electrode gases through the electrolyte, as they may then react chemically without the production of electrical energy; for this reason the gases are usually allowed to diffuse through porous electrode materials (such as nickel or carbon) on which some catalytic material such as platinum is held. The electrolyte solvent may be aqueous, but salt melts (with anions that are not easily oxidized or reduced) have been widely used for high-temperature cells. The electrochemical behaviour of the oxygen electrode in fused salts is complicated. In fused nitrates, for example, reversible systems have been described and E° values determined, but the electrode appears to behave under some conditions as a one-electron and under others as a two-electron system^{108, 109}. It seems that in silica-free and thoroughly dried nitrate melts the concentration of oxide ion at 229° cannot be appreciable¹⁰⁹.

1.9. REMOVAL OF O_2

Oxygen may have to be removed from various systems for a variety of reasons; there are very many ways of doing this. Gases may have to be purified of the last traces of oxygen for the study of systems very sensitive to oxygen; this may be achieved using physical adsorption¹¹¹, by adding hydrogen and treating the gas with a catalyst to remove O_2 as water¹¹⁰, or by treatment with alkali metals (liquid or vapour) or with the amalgams of

¹⁰⁷ K. R. Williams (ed.), *An Introduction to Fuel Cells*, Elsevier (1966).

¹⁰⁸ R. N. Kust, *J. Phys. Chem.* **69** (1964) 3662.

¹⁰⁹ P. G. Zambonin and J. Jordan, *J. Am. Chem. Soc.* **91** (1969) 2225.

¹¹⁰ B. Schaub and J. P. Molin, *Vide* **20** (1965) 281.

¹¹¹ H. C. Kauchmann and E. F. Yeudall, US Pat. 3,169,845 (1965).

aluminium, calcium or magnesium (which are said to reduce the residual oxygen content to 10^{-25} vol. %)¹¹². The level of O_2 in N_2 can be reduced to $\sim 10^{-5}$ vol. % by passing the gas over heated copper¹¹³. The radical anion $C_6N_4^-$, made from $(NC)_2C \equiv C(CN)_2$ and an alkali metal, is a very good oxygen scavenger¹¹⁴. Oxyanions of sulphur in low oxidation states (e.g. SO_3^{2-} , $S_2O_4^{2-}$) are effective in removing oxygen from aqueous systems¹¹⁵; hydrazine has been proposed as a deoxygenator for boiler plant water¹¹⁶, and oxygen can be removed from closed hot water systems by electrolysis with a steel cathode and an aluminium anode¹¹⁷.

1.10. ANALYSIS

For O_2

In a mixture of gases, molecular oxygen may be determined by gas chromatography, or by magnetic methods, which make use of the fact that O_2 is one of the few common gases that is paramagnetic¹¹⁸. Alternatively, the gas mixture may be treated with a solution that absorbs O_2 , such as alkaline pyrogallol or 20% sodium dithionite containing sodium anthraquinone β -sulphonate. In aqueous systems O_2 is determined by cathodic reduction using a polarograph or some other suitable electrode system¹¹⁹, or by oxidation of Mn(II) in alkaline solution (the Winkler method). The Mn(III), which is formed quantitatively, oxidizes iodide quantitatively to iodine when the solution is acidified¹²⁰. There are special problems associated with the determination of oxygen in water in industrial systems¹²¹.

For O in Compounds of Oxygen

Oxygen in organic compounds may be determined by pyrolysis in a stream of nitrogen; the gases evolved are treated with carbon at high temperatures, when all the oxygen is converted into CO. The CO may then be estimated either as a reducing agent, by treatment with I_2O_5 or (after oxidation) as CO_2 . This is usually called the Unterzaucher method; it is not always satisfactory, but recent modifications have made it much more reliable¹²². Oxygen in compounds may also be determined by activation analysis¹²³.

1.11. TOXIC EFFECTS OF AN EXCESS OF O_2

Oxygen is essential to animal life; but too much oxygen can be fatal. Some of the ill effects of hyperoxia were noticed by Lavoisier, but oxygen toxicity has become a far more

¹¹² E. Steinmetz, K. W. Lange and K. K. G. Schmitz, *Chem. Ing. Tech.* **36** (1964) 1103.

¹¹³ G. Brauer, *Handbook of Preparative Inorganic Chemistry*, 2nd edn., Academic Press, New York (1963), p. 458.

¹¹⁴ S. I. Weissman, US Pat. 3,222,385 (1965).

¹¹⁵ V. Kadlec, J. Wuensch and A. Brodsky, Czech Pat. 116,230 (1965).

¹¹⁶ H. Anders, *Zucker* **19** (1966) 552.

¹¹⁷ V. L. Loser, *Energetik* **13** (1965) 5.

¹¹⁸ H. H. Willard, L. L. Merritt and J. A. Dean, *Instrumental Methods of Analysis*, 4th edn., Van Nostrand, New York (1965).

¹¹⁹ I. M. Kolthoff and J. J. Lingane, *Polarography*, 2nd edn., Interscience, New York (1952); J. P. Payne and D. W. Hill, *Oxygen Measurements in Blood and Tissue, and their Significance*, Churchill, London (1966).

¹²⁰ H. A. Laitinen, *Chemical Analysis*, McGraw-Hill, New York (1960).

¹²¹ British Standards, BS 2690, part 2.

¹²² R. Belcher, G. Ingram and J. C. Majer, *Talanta* **16** (1969) 881.

¹²³ J. R. Vogt and W. D. Ehmann, *Radiochimia Acta* **4** (1965) 24.

serious problem in recent years with the increasing use of oxygen gas at high partial pressure to relieve hypoxia, and with the extension of man's activities to regions (such as space or the depths of the sea) where he must rely on artificial atmospheres.

The lungs of guinea-pigs, when subjected to hyperoxia for an extended period, show adverse effects that include oedema, hepatization, pleural effusion, extravasation of red blood corpuscles, haemorrhage, atelectasis and consolidation to a degree where the lung fails to function, oxygen is not supplied to the organism, and the animal dies from what amounts to hyperoxic anoxia¹²⁴. Adult humans are more resistant than are small laboratory animals to these adverse effects of an excess of oxygen, but continued exposure to oxygen at partial pressures greater than 0.75 atm leads to lung damage in a time that depends inversely on the oxygen pressure but is very dependent on the particular subject. Continued exposure to oxygen at partial pressure of 1 atm or more leads to^{124, 125} fever, vomiting, substernal pain and decreased vital capacity, and oxygen at 3–5 atm precipitates convulsions resembling those associated with grand mal epilepsy¹²⁶. Retrolental fibroplasia in infants, induced by O₂ in excess, may result in blindness¹²⁴.

The ways in which an excess of O₂ operates on the organism are extremely complex. Enzyme systems may be poisoned either directly (by reaction with O₂) or by peroxides formed as a result of other reactions of O₂; however, no effects on isolated enzyme systems are fast enough to explain the speed of onset of convulsions associated with O₂ poisoning in intact animals¹²⁷. High pressures of O₂ saturate the blood haemoglobin and increase the amount of oxygen dissolved in blood and other body fluids, and so influence indirectly the amount of CO₂ dissolved and the general balance of buffering and of gas transport in the body¹²⁶. There is evidence that the endocrine system is involved in some aspects of oxygen poisoning¹²⁴, but the processes and mechanisms are extremely complex and do not yet seem to be fully understood.

1.12. PRODUCTION AND USES OF O₂

Oxygen is produced on a very large scale, and the amount produced is continually rising; in the United States, 10⁶ tons were produced in 1966. Of this, over half went into the production of steel. The use of O₂ as a direct oxidant in processes involving organic systems is also growing¹²⁸. On a smaller scale, oxygen is important in high-temperature processes such as welding; as a refrigerant, liquid oxygen is less popular than liquid nitrogen because of the hazards associated with liquid oxygen, but in some cases its higher boiling point gives it some advantages. The development of space flight has given a very strong impulse to the associated development of the technology of liquid oxygen. Finally, it would be impossible to maintain life under extremely abnormal conditions—in space, under water or in some clinical states—if O₂ gas were not freely available.

¹²⁴ J. W. Bean, in *Oxygen in the Animal Organism*, Pergamon Press, New York (1964), p. 455.

¹²⁵ A. P. Morgan, *Anaesthesiology* 29 (1968) 570.

¹²⁶ C. J. Lambertsen, in *Handbook of Physiology*, American Physiological Society, New York (1965), Section III, Vol. 2, p. 1027.

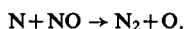
¹²⁷ H. C. Davies and R. E. Davies, *ibid.*, p. 1047.

¹²⁸ M. Sittig, *Combining Hydrocarbons and Oxygen for Profit*, Noyes Development Co., Princeton (1968).

2. OXYGEN ATOMS AND IONS

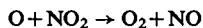
2.1. ATOMIC OXYGEN

Oxygen atoms play an important part in reactions in the earth's atmosphere¹²⁹, and have been extensively studied in the laboratory; but, as with many extremely reactive species, there are serious problems associated with producing and detecting them. In most of the early studies, oxygen atoms were generated by passing a microwave or an electric discharge through oxygen gas¹³⁰. Unfortunately, however, oxygen atoms are not the only active species formed under these conditions; oxygen molecules are excited electronically, and the presence of impurities containing hydrogen leads to the formation of other very reactive radicals¹³¹. In recent studies, some of these difficulties have been avoided by passing the discharge through argon containing a very small proportion of very pure oxygen^{132, 133}; it is hoped that under these circumstances oxygen atoms are the only active species formed. The thermal decomposition of ozone¹³⁴ or nitrous oxide give oxygen atoms, which are also produced when nitrogen atoms (themselves formed by discharging nitrogen) react with nitric oxide¹³⁵:

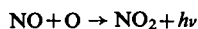


Photolysis of oxygen also gives oxygen atoms, but excited O_2 molecules may also be formed, and the reactions of the two may not be easy to distinguish¹³³; the photolysis of N_2O , however, produces oxygen atoms, together with N_2 , which is inert¹³⁵. The photolysis of NO_2 , giving O and NO , is less satisfactory^{136, 137}. All these methods give $\text{O}(^3P)$ atoms; photolysis of ozone, or photolysis of N_2O , CO_2 or O_2 with radiation of higher energy, gives^{138, 139} $\text{O}(^1D)$ or even $\text{O}(^1S)$, while $\text{O}(^5S)$ may have been detected in the products of a microwave discharge in O_2 by molecular beam magnetic resonance¹⁴⁰.

Oxygen atoms have been detected and estimated using chemical and physical techniques¹³³. Chemically, the best-established technique is the NO_2 titration. Oxygen atoms react very fast indeed with NO_2 , forming NO ¹³⁶:



The NO thus produced reacts much more slowly with any excess of oxygen atoms to reform NO_2 , and this reaction produces a strong glow:



Therefore NO_2 is added to the system until the glow is sharply extinguished; then all the oxygen atoms are consumed in the very fast first process and $[\text{O}] = [\text{NO}_2]$. Absorption and emission spectroscopy have proved useful, but the emission spectra of certain species

¹²⁹ *Disc. Faraday Soc.* **37** (1964); *Can. J. Chem.* **47** (1969) 1703.

¹³⁰ F. Kaufman, *Prog. Reaction Kinetics* **1** (1961) 1.

¹³¹ F. Kaufman and J. R. Kelso, *Disc. Faraday Soc.* **37** (1964) 26.

¹³² M. A. A. Clyne, D. J. McKenny and B. A. Thrush, *Trans. Faraday Soc.* **61** (1965) 2701.

¹³³ H. I. Schiff, *Can. J. Chem.* **47** (1969) 1905.

¹³⁴ F. Kaufman and J. R. Kelso, *J. Chem. Phys.* **40** (1964) 1162.

¹³⁵ D. G. Williamson and K. D. Bayes, *J. Phys. Chem.*, **73** (1969), 1232.

¹³⁶ R. J. Cvetanovic, *J. Chem. Phys.* **23** (1955) 1203.

¹³⁷ A. A. Westerberg and N. deHaas, *J. Chem. Phys.* **50** (1969) 707.

¹³⁸ P. Warneck and J. O. Sullivan, *Ber. Bunsenges. Phys. Chem.* **72** (1968) 159.

¹³⁹ R. A. Young, G. Black and T. S. Slinger, *J. Chem. Phys.* **49** (1968) 4758, 4769.

¹⁴⁰ G. O. Brink, Report AD 643526 (1966) (*Chem. Abstr.* **67** (1967) 59232p).

TABLE 18. METHODS OF PRODUCTION AND SOME REACTIONS OF OXYGEN ATOMS

State	Methods of production	Some reactions studied
3P	Electric or microwave discharge; Hg-sensitized photolysis of N_2O ; photolysis of O_2 , N_2O , NO_2 ; shock tubes; flames	With O^* , O_2^b , NO^c , NO_2^d , H_2^e , Cl_2^f , hydrocarbons, g^h , acetylene (in matrices) ⁱ , P_4^j , PH_3^j , S^k , Se^k , $C_3O_2^l$, CCl_4^m , H_2S^n , $(CN)_2^o$, CN^p , $CICN^{p'}$, ICN^q , $B_5H_9^r$, CO^s , COS^s , CS_2^s , Cl_2O^t
1D	Photolysis of O_3 , CO_2 , N_2O (in absence of Hg); microwave discharge	With O_2^u , N_2^v , CO_2^w , N_2O^x , H_2O^y
1S	Photolysis of O_2^z , CO_2^{**} , N_2O^{bb}	Quenched by H_2 , O_2 , CO , CO_2 , H_2O , N_2O , not by rare gases or N_2

^a F. Kaufman, *Prog. Reaction Kinetics* **1** (1961) 1.^b M. F. R. Mulcahy and D. J. Williams, *Trans. Faraday Soc.* **64** (1968) 59.^c A. McKenzie and B. A. Thrush, *Chem. Phys. Letters* **1** (1968) 681.^d F. S. Klein and J. T. Herron, *J. Chem. Phys.* **41** (1964), 1285.^e A. A. Westenbergh and N. DeHaas, *J. Chem. Phys.* **50** (1969) 2512.^f H. Niki and B. Weinstock, *J. Chem. Phys.* **47** (1967) 3249.^g R. Cvetanović, *Adv. Photochem.* (Wiley) **1** (1963) 115.^h C. Mitchell and J. P. Simons, *J. Chem. Soc. (B)* 1968, 1005.ⁱ G. C. Pimentel, *Proc. Am. Petrol. Inst.* **41** (1961) 189.^j P. B. Davies and B. A. Thrush, *Proc. Roy. Soc. A*, **302** (1967) 243.^k F. Cramarossa, E. Molinari and B. Roio, *J. Phys. Chem.* **72** (1968) 84.^l H. Van Weyssenhoff, S. Dondes and P. Harteck, *J. Am. Chem. Soc.* **84** (1962) 1526.^m A. Y.-M. Ung and H. I. Schiff, *Canad. J. Chem.* **40** (1962) 486.ⁿ E. L. Merryman and A. Levy, *J. Air Poll. Contr. Ass.* **17** (1967) 800.^o D. W. Setser and B. A. Thrush, *Proc. Roy. Soc. A*, **288** (1965) 275.^p J. C. Boden and B. A. Thrush, *Proc. Roy. Soc. A*, **305** (1968) 107.^{p'} P. B. Davies and B. A. Thrush, *Trans. Faraday Soc.* **64** (1968) 1836.^q J. F. Grady, C. G. Freeman and L. F. Phillips, *J. Phys. Chem.* **72** (1968) 743.^r J. P. Rosenkrans, *Diss. Abstr.* **25** (1964) 1608.^s A. A. Westerberg and N. deHaas, *J. Chem. Phys.* **50** (1969) 707.^t C. G. Freeman and L. F. Phillips, *J. Phys. Chem.* **72** (1968) 3025.^u R. A. Young, G. Black and T. G. Slinger, *J. Chem. Phys.* **49** (1968) 4758.^v R. G. W. Norrish and R. P. Wayne, *Proc. Roy. Soc. A*, **288** (1965) 200.^w N. G. Moll, D. R. Clutter and W. E. Thompson, *J. Chem. Phys.* **45** (1966) 4469.^x P. Warnek and J. O. Sullivan, *Ber. Bunsenges. Phys. Chem.* **72** (1968) 159.^y W. D. McGrath and R. G. W. Norrish, *Proc. Roy. Soc. A*, **234** (1958) 317.^z S. V. Filseth and K. H. Welge, *J. Chem. Phys.* **51** (1969) 839.^{**} F. Stuhl and K. H. Welge, *Canad. J. Chem.* **47** (1969) 1870.^{bb} G. Black, T. G. Slinger, G. A. St. John and R. A. Young, *Canad. J. Chem.* **47** (1969) 1873.

are not observed in some systems. Catalytic probes, heated by the recombination of atoms on their surfaces, and special pressure gauges inside which atoms recombine, were extensively employed at one time, but at present the physical techniques most widely used in the measurement of concentrations of oxygen atoms are mass spectrometry and e.s.r.¹³³; gas chromatography is very extensively used to analyse reaction products. Mass spectrometry, particularly when used to give appearance potentials, is a most powerful technique. Of the atomic species of oxygen that are usually studied, only the ground state $O(^3P)$

gives an e.s.r. signal (six lines at room temperature, due to transitions between different M_J states of the 3P_2 and 3P_1 levels)¹⁴¹. These signals may be calibrated using the e.s.r. spectrum of O_2 . The excited states $O(^1D)$ and $O(^1S)$ have so far only been identified by their emission spectra and possibly [for $O(^1D)$ and $O(^5S)$] by molecular beam magnetic resonance; but indirect evidence comes from the processes in which they are formed and by which they react, for their reactions are different from those of $O(^3P)$. Some of the reactions of oxygen atoms that have been studied are set out in Table 18. A particularly interesting example is the reaction between $O(^1D)$ and CO_2 , which has been shown by vibrational spectroscopy and by matrix techniques¹⁴² to give the unstable radical CO_3 . Many of the reactions are associated with strong after-glows, and some of the atmospheric glows are also associated with the reactions of oxygen atoms¹⁴³.

TABLE 19. SOME REACTIONS OF IONIZED SPECIES
DERIVED FROM OXYGEN OR O_2

Reactions of O^- ^a	
$O^- + N_2 + He$	$\rightarrow N_2O^- + He$
$O^- + 2CO_2$	$\rightarrow CO_3^- + CO_2$
$O^- + NO_2$	$\rightarrow O_2^- + NO$
$O^- + NO_2$	$\rightarrow NO_2^- + O$
$O^- + O_3$	$\rightarrow O_3^- + O$
Reactions of O_2^- ^a	
$O_2^- + 2CO_2$	$\rightarrow CO_4^- + CO_2$
$O_2^- + SO_2$	$\rightarrow SO_2^- + O_2$
Reactions of O^+ ^b	
$O^+ + N_2$	$\rightarrow NO^+ + N$
$O^+ + O_2$	$\rightarrow O + O_2^+$
$O^+ + CO_2$	$\rightarrow CO + O_2^+$
Reactions of O_2^+ ^b	
$O_2^+ + NO$	$\rightarrow NO^+ + O_2$
$O_2^+ + Na$	$\rightarrow O_2 + Na^+$
$O_2^+ + Na$	$\rightarrow NaO^+ + O$

^a E. E. Ferguson, *Canad. J. Chem.* **47** (1969) 1815.

^b W. L. Fite, *Canad. J. Chem.* **47** (1969) 1797.

2.2. ION-MOLECULE REACTIONS

The reactions of ionized species derived from oxygen atoms and molecules have been extensively studied in recent years¹⁴⁴. The ions are produced in flames, in mass spectrometers or in molecular beams; some representative reactions are set out in Table 19.

¹⁴¹ A. A. Westenberg and N. deHaas, *J. Chem. Phys.* **40** (1964) 3087.

¹⁴² E. Weissberger, W. H. Breckenridge and H. Taube, *J. Chem. Phys.* **47** (1967) 1764.

¹⁴³ R. A. Young, *Can. J. Chem.* **47** (1969) 1927.

¹⁴⁴ C. F. Giese, *Adv. Chem. Ser.* **58** (1966) 20; J. F. Paulson, *ibid.*, p. 28; A. V. Phelps, *Can. J. Chem.* **47** (1969) 1784; W. L. Fite, *ibid.*, p. 1797; E. E. Ferguson, *ibid.*, p. 1815.

3. OXIDES AS A CLASS

3.1. INTRODUCTION

The formation of an element oxide M_xO , from the reaction between the element M and molecular oxygen is a commonly observed process. Many metallic elements in a high state of purity react spontaneously with oxygen. This is in some respects a remarkable phenomenon when it is realized that the production of oxide ions from molecular oxygen is a strongly endothermic process [$\Delta H_f^\circ(O^{2-}, g) = 220 \text{ kcal mole}^{-1}$]. The same is true of the energetics of oxidation of the element M [e.g. $\Delta H_f^\circ(Fe^{3+}, g) = 1365 \text{ kcal mole}^{-1}$]. The driving force in the process is the high lattice energy of the element oxide.

It is possible to classify oxides under two general headings: acid-base character and structure.

In order to achieve satisfactory order within this section, the term oxide will be considered in its most rigorous sense. Thus only non-charged compounds of the type M_xO , and $X_aY_b \dots O_n$ will be considered and, specifically, oxy-anions such as carbonate, silicate, molybdate and tungstate, for example, will be ignored, as also will be oxy-halides, hydroxides and oxy-chalcogenides.

3.2. ACID-BASE CHARACTER OF SIMPLE OXIDES

The description of an oxide in terms of its acid-base character allows for a subdivision into four classes: acidic, basic, amphoteric and neutral.

An *acidic* oxide is one which, when dissolved in water, affords an acidic solution. For example phosphorus(V) oxide, P_4O_{10} , is completely hydrolysed in water to orthophosphoric acid,



A *basic* oxide is one which, when dissolved in water, affords an alkaline solution. For example, calcium oxide, CaO , affords calcium hydroxide in aqueous solution,

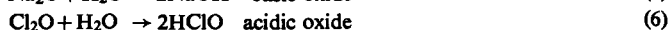


An *amphoteric* oxide is one which, under different conditions, exhibits the properties of both an acidic and a basic oxide. For example, antimony(III) oxide, Sb_4O_6 , will react with both acids and bases,



A *neutral* oxide is essentially inert and unreactive towards water. For example, carbon monoxide and nitrous oxide, which are almost insoluble in water, are classed as neutral oxides. This class is the smallest of the four.

Among the non-transition metal, or main group elements, the oxides of the most electro-positive elements are basic while those of the more electronegative elements are acidic. A comparison between Na_2O and Cl_2O exemplifies this well:



Between these two extremes there is a gradation in behaviour leading to an amphoteric oxide, although it is not usually possible to place a clear boundary between the three classes.

Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀	SO ₃	Cl ₂ O
B	B	AB	A	A	A	A

A = acidic B = basic AB = amphoteric

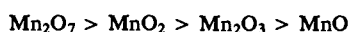
Within any one group, the acid character of any particular oxide M_xO_y, tends to decrease as the atomic number of the element increases.

N ₂ O ₃	P ₄ O ₆	As ₄ O ₆	Sb ₄ O ₆	Bi ₂ O ₃
A	A	A	AB	B

In the case of an element, M, which forms more than one (stoichiometric) oxide and, particularly, where an element can exist in a number of different formal oxidation states, then the oxide of the highest oxidation state is more acidic than that of the lowest oxidation state. This may be expressed in an alternative form by stating that for the oxide M_xO_y, the acidic character of the oxide decreases as the ratio y/x decreases. For example, among the oxides of chlorine, acidity decreases in the order



and among the oxides of manganese,



Although this qualitative classification is apparently quite straightforward, problems immediately arise when we inquire more closely into the reasons for the particular behaviour of any particular oxide. To a certain extent the acidic or basic character of an oxide may be explained in terms of the ionization behaviour of the element concerned. No satisfactory answer can be obtained by asking why Na₂O does not dissolve in water according to the hypothetical equation



or why, conversely, Cl₂O does not behave according to



The appropriate physical data are shown in Table 20.

TABLE 20

	First ionization potential	Electron affinity
Na	118	17
Cl	300	83

Values in kcal mole⁻¹ to nearest whole number.

These figures merely reflect that it is easier to ionize sodium than chlorine and, conversely, that the electron affinity of chlorine is greater than that of sodium. Consequently, the oxides will be expected to react according to eqns. (5) and (6) rather than as indicated by eqns. (7)

and (8). If the question is presented in terms of the contrast between the known behaviour of P_4O_{10} [eqn. (1)] and the hypothetical equation



then the differences become much more apparent. The ionization energy of the P^{5+} ion (4075 kcal mole⁻¹) would appear to make reaction (9) very unfavourable unless there is a correspondingly greater solvation energy.

There remains the problem of amphoteric oxides. On the basis of the preceding argument we would expect the energy balance as expressed by electron affinity and ionization potential to be closer. It is difficult to know how much validity can be given to such a procedure, and so the appropriate figures are presented in Table 21.

TABLE 21. IONIZATION POTENTIALS AND ELECTRON AFFINITY OF THE ELEMENTS Na-Cl

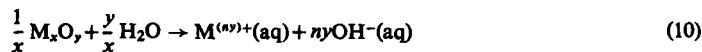
Element	I_1 (eV)	E (eV)	Ion	$\sum_0^n I_n$ (eV)	Oxide
Na	5.14	0.54	Na ⁺	5.14	Na ₂ O
Mg	7.64	-0.22	Mg ²⁺	22.6	MgO
Al	5.98	0.20	Al ³⁺	53.2	Al ₂ O ₃
Si	8.15	1.36	Si ⁴⁺	103.1	SiO ₂
P	10.48	0.71	P ⁵⁺	176.8	P ₄ O ₁₀
S	10.36	2.04	S ⁴⁺	116.1	SO ₂
Cl	13.01	3.62	Cl ⁺	13.01	Cl ₂ O

I_1 , first ionization potential.

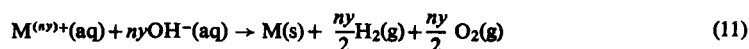
E , electron affinity (R. J. Zollweg, *J. Chem. Phys.* **50** (1969) 4251).

Table 21 shows that there is an increase in E from magnesium to aluminium which might be expected from the amphoteric behaviour of Al₂O₃, but otherwise the data are not particularly helpful. We must, therefore, seek another explanation.

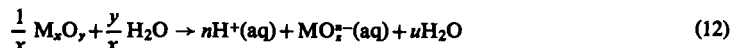
We consider two possible alternative paths for the dissolution in water of an oxide M_xO_y , and define a number n , such that $n = 1$ when $x = 2$, and $n = 2$ when $x = 1$. One path could be



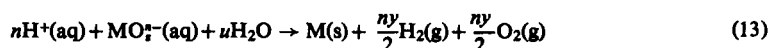
The species on the right-hand side of eqn. (10) can be referred to the standard states of their constituents,



The other path could be



in which we have written $z = n(y+1)/2$ and $u = n(y-1)/2$. As before, the species on the right-hand side of eqn. (12) can be referred to the standard states of their constituents,



By combining the two processes [e.g. eqns. (10) and (12)] through their common origin and common terminus [eqns. (11) and (13)] we obtain the scheme shown in Fig. 4.

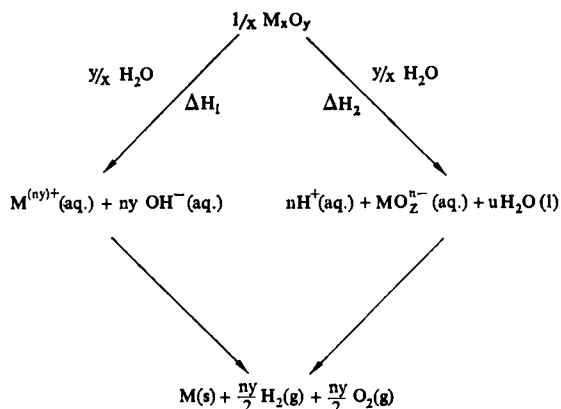
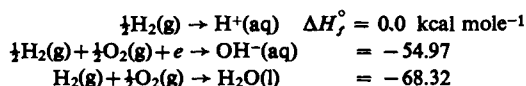


FIG. 4.

The following standard enthalpies (ΔH_f°) are known:



For the purposes of the following argument we shall take values of enthalpy to the nearest whole kilocalorie. From Fig. 4 we obtain the equation

$$\Delta H_1 + A + 55ny = \Delta H_2 + B + 34n(y-1)$$

whence

$$\delta = \Delta H_2 - \Delta H_1 = A + 21ny + 34n - B \quad (14)$$

where $A = -\Delta H_f^\circ [\text{M}^{(ny)+}, \text{aq}]$ and $B = -\Delta H_f^\circ [\text{MO}_z^{n-}, \text{aq}]$.

Values of the part expression, $Q = 21ny + 34n$ are:

n	y	ny	Q (kcal mole ⁻¹)
1	1	1	55
2	1	2	110
1	3	3	97
2	2	4	152
1	5	5	139

For the typical example of an oxide M_2O_3 :

$$x = 2 \therefore n = 1$$

$$y = 3 \therefore Q = 97 \text{ kcal mole}^{-1}$$

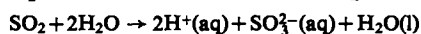
Thus

$$\delta = A + 97 - B$$

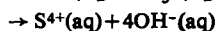
Q is always positive, so that if $A + Q > B$, δ is positive, with the result that dissolution of M_xO_y will lead to an alkaline solution.

Conversely, if $B > A + Q$, δ is negative, with the result that dissolution of M_xO_y will lead to an acidic solution.

Let us consider as an example, the behaviour of SO_2 . Following our treatment, we may describe two equations to represent the dissolution of SO_2 in water:



or



Whereas the value $\Delta H_f^\circ (\text{SO}_3^{2-}, \text{aq}) = -152 \text{ kcal mole}^{-1}$ is known exactly, the value of $\Delta H_f^\circ (\text{S}^{4+}, \text{aq})$ is not known. It is possible to make an approximate estimate of this unknown quantity by using the following equations¹⁴⁵:

$$\Delta G_{\text{soln}}^\circ = -\frac{164Z^2}{r+0.72} \quad (15)$$

$$S^\circ = 1.5R \ln M - \frac{270Z}{(r+x)^2} + 37 \quad (16)$$

For S^{4+} , $r = 0.37\text{\AA}$; $Z = 4$; $x = 2$; $M = 32$.

On substitution of these values in eqns. (15) and (16) we obtain

$$\begin{aligned} \Delta G_{\text{soln}}^\circ &= -2406 \text{ kcal mole}^{-1} \\ S^\circ &= -112 \text{ cal deg}^{-1} \text{ mole}^{-1} \end{aligned}$$

Now

$$\Delta G = \Delta H - T\Delta S$$

so that at 300°K , $\Delta H_{\text{soln}}^\circ = -2443 \text{ kcal mole}^{-1}$ and $\Delta H_f^\circ (\text{S}^{4+}, \text{g}) = 2750 \text{ kcal mole}^{-1}$, so that we obtain

$$\Delta H_f^\circ (\text{S}^{4+}, \text{aq}) = 307 \text{ kcal mole}^{-1}$$

We may now evaluate eqn. (14):

$$\begin{aligned} \delta &= -307 + 152 - 152 \\ &= -307 \text{ kcal mole}^{-1} \end{aligned}$$

which indicates that on thermodynamic grounds alone, SO_2 should dissolve in water to give an acidic solution.

The approximations and inaccuracies inherent in the calculation of $\Delta H_f^\circ [\text{M}^{(n)+}, \text{aq}]$ from eqns. (15) and (16) are well documented, but it is generally conceded that they may provide values of $\Delta H_{\text{soln}}^\circ$ which are correct to better than $\pm 50 \text{ kcal mole}^{-1}$. It is clear that the dominant contributor to $\Delta H_{\text{soln}}^\circ$ is the free energy of solvation, $\Delta G_{\text{soln}}^\circ$. In Table 22, we present representative values of $-\Delta G_{\text{soln}}^\circ$ calculated from eqn. (15).

TABLE 22. VALUES OF $-\Delta G_{\text{soln}}^\circ$ (kcal mole⁻¹)

$Z =$	1	2	3	4	5	6
$r = 0.2$	178	712	1602	2850	4450	6608
0.3	161	644	1449	2756	4025	5796
0.4	146	584	1317	2336	3650	5256
0.5	134	537	1206	2150	3350	4824
0.6	124	496	1118	1984	3105	4664
0.7	115	461	1035	1846	2875	4140

The major factor in $\Delta H_f^\circ [\text{M}^{(n)+}, \text{g}]$ is the total (overall) ionization potential, ΣI_n , for the process $\text{M}(\text{g}) \rightarrow \text{M}^{(n)+}(\text{g})$. This is clearly demonstrated by data for the iso-electronic ions of the second short period (Table 23). The table also includes the value of the effective ionic radius ($r^{\text{VI}}\text{\AA}$), of the 6-coordinate cation¹⁴⁶.

¹⁴⁵ D. A. Johnson, *Some Thermodynamic Aspects of Inorganic Chemistry*, Cambridge University Press (1968).

¹⁴⁶ R. D. Shannon and C. T. Prewitt, *Acta Cryst.* **B25** (1969) 925.

TABLE 23. HEATS OF FORMATION ΔH_f° (g), OVERALL IONIZATION POTENTIAL $\Sigma_0^* I_n$ AND EFFECTIVE IONIC RADIUS r_+^{VI} OF SOME SECOND-ROW ELEMENTS

	Na ⁺	Mg ²⁺	Al ³⁺	Si ⁴⁺	P ⁵⁺	S ⁶⁺	Cl ⁷⁺
ΔH_f° (g) (kcal mole ⁻¹)	146	561	1310	2492	4168	6654	9472
$\Sigma_0^* I_n$ (kcal)	118	523	1228	2378	4075	6379	9431
r_+^{VI} (Å)	1.02	0.72	0.52	0.40	0.35	0.30	0.26

From the data in Tables 22 and 23 it is clear that as the positive charge on an ion increases and the size of the ion decreases, it will become more unlikely that the enthalpy of hydration of the gaseous cation, ΔH_f° (M^{n+} , g) can cancel out the ionization energy. In other words, we expect that the value of A in eqn. (14) will become negative as the charge, $(ny)^+$, on M increases. Consequently we can define three situations as follows:

- | | | |
|----------------|-------------------|--------------------------------|
| (1) ny small | δ positive | $\Delta H_1 < \Delta H_2$ |
| (2) | $\delta \sim 0$ | $\Delta H_1 \simeq \Delta H_2$ |
| (3) ny large | δ negative | $\Delta H_1 > \Delta H_2$ |

These three situations correspond exactly to what are termed respectively as basic, amphoteric and acidic oxides in the preceding discussion.

An oxide M_xO_y will have basic character when the value of y is small, or, alternatively, when the radius of $M^{(ny)+}$ is large; however, the radius of an ion decreases as the value of (ny) increases.

Table 24 contains values of the effective ionic radii of the 6-coordinate ions M^{3+} and M^{5+} of the elements of Group V. In the light of what has just been established, it is clear that Bi_2O_3 must be a more basic oxide than P_2O_5 .

TABLE 24. EFFECTIVE IONIC RADII OF 6-COORDINATE IONS OF THE GROUP V ELEMENTS (Å)

	$r^{VI}(M^{3+})$	$r^{VI}(M^{5+})$
P	0.44	0.35
As	0.58	0.50
Sb	0.76	0.61
Bi	1.02	0.74

In this way we succeed in providing a fairly firm foundation for exploring the empirical facts of our previous discussion. To show the validity of the distinction we have made on thermodynamic grounds, let us consider the case of Al_2O_3 . This system is exceptional in that all the relevant chemical thermodynamic data are known from experiment, and are as follows:

$$\Delta H_f^\circ(Al^{3+}, aq) = -127 \text{ kcal mole}^{-1}$$

$$\Delta H_f^\circ(AlO_2^-, aq) = -220 \text{ kcal mole}^{-1}$$

From eqn. (14) and using $Q = 97 \text{ kcal mole}^{-1}$, $\delta = +4 \text{ kcal mole}^{-1}$.

This fine difference between the enthalpies of the two possible processes suggests that although $\Delta H_1 < \Delta H_2$ and that therefore Al_2O_3 will behave as a basic oxide, a small change in the pH of the medium will cause the appearance of acidic character in Al_2O_3 . This is in good agreement with the known amphoteric character of alumina. In the case of BeO , the value of δ is $+15 \text{ kcal mole}^{-1}$.

We might, therefore, expect that amphoteric oxides will occur for intermediate values of (ny) where the ionic radius of M is within certain defined limits. Table 25 contains information which is relevant to the dissolution of Group III element sesquioxides M_2O_3 , in water.

TABLE 25

M	$r^{\text{VI}} (\text{M}^{3+})$ (Å)	$\Delta H_f^\circ (\text{M}^{3+}, \text{aq})$ (kcal mole $^{-1}$)	$\Delta H_f^\circ (\text{MO}_2^-, \text{aq})$ (kcal mole $^{-1}$)	δ (kcal mole $^{-1}$)
B	0.23	$\sim +200$	-185	-288
Al	0.53	-127	-220	+4
Ga	0.62	-51	?	
In	0.79	-25	?	
Tl	0.88	-47	?	

$r^{\text{VI}} (\text{M}^{3+})$ is the radius of the 6-coordinate M^{3+} ion.

From Table 25 we can estimate that Ga_2O_3 will be amphoteric if $\Delta H_f^\circ (\text{GaO}_2^-, \text{aq})$ is approximately $-146 \text{ kcal mole}^{-1}$. The corresponding figures for In_2O_3 and Tl_2O_3 are -122 and $-50 \text{ kcal mole}^{-1}$ respectively. In practice, the oxides of indium and thallium are purely basic, so that it is reasonable to conclude that the values of $\Delta H_f^\circ (\text{MO}_2^-, \text{aq})$ are much more positive than shown.

There remains the question of what factors contribute most decisively to $\Delta H_f^\circ (\text{MO}_z^{n-}, \text{aq})$. Unfortunately, the use of a thermochemical cycle such as that shown in Fig. 5, contains two unknown quantities $\Delta H_f^\circ (\text{MO}_z^{n-}, \text{g})$ and $\Delta H_{\text{soln}}^\circ (\text{MO}_z^{n-}, \text{g})$. One is therefore confined to an inspection of known values of $\Delta H_f^\circ (\text{MO}_z^{n-}, \text{aq})$ for a clarification of the problem. Table 26 contains a selection of such data for some simple oxyanions.

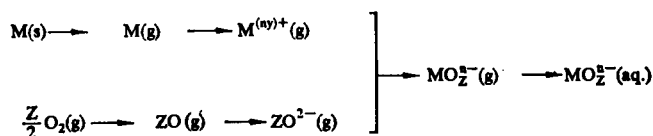


FIG. 5.

With the exception of the halogen oxyanions, for which the values of $\Delta H_f^\circ (\text{MO}_z^{n-}, \text{aq})$ are uniformly small, it is clear that the enthalpy of formation increases as the value of z

increases. A similar change is noted with increasing values of n . Within any one periodic group, the value of ΔH_f° does not appear to change very markedly, thus:

M	$\Delta H_f^\circ (\text{MO}_3^{2-}, \text{aq})$	M	$\Delta H_f^\circ (\text{MO}_3^-, \text{aq})$
S	-152 kcal mole ⁻¹	Cl	-24 kcal mole ⁻¹
Se	-122	Br	-20
Te	-142	I	-53

In general, therefore, $-\Delta H_f^\circ (\text{MO}_z^{n-}, \text{aq})$ increases as the values of n and y increase. This is in complete agreement with our earlier conclusions. There appears to be no correlation between $\Delta H_f^\circ (\text{MO}_z^{n-}, \text{aq})$ and the value of $r[\text{M}^{(n)+}]$, although this is not true for the correlation with the thermochemical "radii" derived by Kapustinski which show that $-\Delta H_f^\circ (\text{MO}_z^{n-}, \text{aq})$ increases with increasing thermochemical radius.

TABLE 26. ENTHALPIES OF FORMATION, $\Delta H_f^\circ (\text{MO}_z^{n-}, \text{aq})$ FOR SOME SIMPLE OXYANIONS OF NON-METALS (kcal mole⁻¹)

BO_2^-	-185			NO_2^-	-25	O_3^-	-11		
BO_3^{3-}	-251*	CO_3^{2-}	-162	NO_3^-	-50				
								ClO^-	-26
AlO_2^-	-220			PO_2^{3-}	-144*			ClO_2^-	-15
				PO_3^{3-}	-233	SO_3^{2-}	-152	ClO_3^-	-24
				PO_4^{3-}	-305	SO_4^{2-}	-217	ClO_4^-	-31
								BrO^-	-22
		GeO_3^{2-}	-198*	AsO_3^{3-}	-175*	SeO_3^{2-}	-122	BrO_3^-	-20
				AsO_4^{3-}	-212	SeO_4^{2-}	-143		
								IO^-	-26
								IO_3^-	-53
				SbO_3^{3-}	-215*	TeO_3^{2-}	-142	IO_4^-	-35
						TeO_4^{2-}	-165*		

The values marked (*) are approximations based on $\Delta H_f^\circ (\text{H}_n\text{MO}_z, \text{aq})$.

It may therefore be concluded that the chemical behaviour of simple oxides in aqueous solution is satisfactorily explained in terms of the chemical thermodynamic properties of the system.

3.3. OXIDES AS A CLASS: STRUCTURES

We may distinguish four broad classes of structure among oxides; there are (a) infinite three-dimensional lattices, (b) layer lattices, (c) chain lattices and (d) molecular units.

We shall deal briefly with each of these in turn. However, it should be pointed out that this topic is treated in much greater detail than is warranted here by Wells¹⁴⁷ (especially chapters 11 and 12) and by Wyckoff¹⁴⁸.

¹⁴⁷ A. F. Wells, *Structural Inorganic Chemistry*, 3rd edn., Clarendon Press, Oxford (1962).

¹⁴⁸ R. W. G. Wyckoff, *Crystal Structures*, 2nd edn., Interscience, Wiley, New York (1963), Vols. 1, 2 and 3.

Infinite Three-dimensional Lattices**(a) Simple Oxides, M_xO_y**

This class includes the majority of known oxide structures in which it is not possible to distinguish the presence of finite structural units. Following Wells, it is possible to subdivide this class according to the formula type M_xO_y , to which a particular oxide belongs and then further to account for differences in the coordination numbers of M and O within the lattice. The generic name of the lattice type and a single example of each is given in Table 27.

TABLE 27

Formula type	Coordination number		Generic name	Example
	M	O		
MO_3	6	2	Rhenium trioxide	ReO_3
MO_2	8	4	Fluorite	UO_2
	6	3	Rutile	TiO_2
	4	2	Silica	GeO_2
	6	4	Corundum	V_2O_3
M_2O_3	*		Lanthanide-A (trigonal)	La_2O_3
	*		Lanthanide-B (monoclinic)	Gd_2O_3
	6	4	Lanthanide-C (cubic)	In_2O_3
	6	6	Sodium chloride	SrO
	4	4	Zinc blende	ZnO
MO	4	4	Wurtzite	BeO
	4	4	Platinum sulphide	CuO
	4	8	Anti-fluorite	Na_2O
	2	4	Cuprite	Cu_2O

* The metal ion in these systems is 7-coordinate.

Among the oxides of the transition metals three factors may, individually or in concert, cause departures from a regularly ordered structure. These are¹⁴⁹:

- (1) The formation of metal-metal bonds which, for example, lead to distorted rutile structures for a number of transition dioxides such as VO_2 , MoO_2 and ReO_2 .
- (2) The presence of a covalent contribution to the metal-oxygen interaction which results in a contraction of one or more metal-oxygen bonds in a lattice.
- (3) The effect of the ligand field of the (close-packed) oxide ion environment of the metal ion.

Even if the coordination number (CN) of the metal atom remains constant, the structure of the oxide will change considerably as the oxidation state of the metal changes; thus, to choose a simple well-known example, in the V-O system we have the situation summarized in Table 28.

¹⁴⁹ J. D. Dunitz and L. E. Orgel, *Adv. Inorg. Radiochem.* 2 (1960) 1.

This relatively simple picture of transition metal oxide systems belies their true complexity. More detailed studies show that in many metal-oxygen phase diagrams there are definite phases corresponding to intermediate oxides¹⁵⁰, many of which are non-stoichiometric. Thus in the case of the Mo-O₂ system the following phases lie between MoO₂ (distorted rutile) and MoO₃ (layer structure: see below); Mo₄O₁₁ (MoO_{2.75}), Mo₈O₂₃ (MoO_{2.875}) and Mo₉O₂₆ (MoO_{2.88}). These are all of the general formula Mo_nO_{3n-1} and have structures which are related to that of ReO₃. Again, in the V-O system there is a series of six oxides intermediate between V₂O₃ and VO₂ which are of the type V_nO_{2n-1} ($n = 3-7$) and have structures related to that of TiO₂.

TABLE 28

Oxide	VO	V ₂ O ₃	VO ₂
Structure	NaCl	Al ₂ O ₃	Distorted rutile
CN of V	6	6	6
CN of O	6	4	2

Among oxides of the type MO and MO₂, where a number of different structures are possible in which the metal is either 4-, 6- or 8-coordinate, the concept of the minimum radius ratio can be useful in determining the type of structure present (Table 29).

TABLE 29

Coordination polyhedron	Coordination number	(r_M/r_O) _{min}
Tetrahedron	4	0.225
Octahedron	6	0.414
Cube	8	0.732

This suggests that, for example, a dioxide MO₂, will adopt the 8-coordinated fluorite structure only if the ratio r_M/r_O ($r[\text{O}^{2-}] = 1.40 \text{ \AA}$) is greater than 0.732; should the radius ratio lie between 0.414 and 0.732, the compound MO₂ will have the 6-coordinated rutile structure¹⁵¹, and if $0.225 < r_M/r_O < 0.414$, then the metal ion will be in a tetrahedral environment as in quartz. This criterion works fairly well in practice as a guide to the type of stereochemistry to be expected, but its use in a strictly quantitative manner is circumscribed both by the crudeness of the simple model adopted and by the uncertainties in the values of the ionic radii employed.

¹⁵⁰ A. D. Wadsley, *Helv. Chim. Acta Fascic. Extraord. A. Werner* 207 (1966).

¹⁵¹ D. B. Rogers, R. D. Shannon, A. W. Sleight and J. L. Gillson, *Inorg. Chem.* 8 (1969) 841.

(b) *Complex Oxides, $X_aY_b \dots O_n$*

In this class it is implied that within the lattice it is not possible to distinguish the presence of discrete complex ions such as SiO_4^{4-} or WO_6^{6-} . It is possible to rationalize the structures of complex oxides by considering them as being derived from simple oxides as shown in Table 30.

TABLE 30

Simple oxide	Ratio M/O	Degree of polymerization	Total cation charge	Complex oxide	Example
MO [M ₃ O ₄]	1	(MO) ₂	4	XYO ₂	NaFeO ₂
	0.75		8	XY ₂ O ₄	MgAl ₂ O ₄
			8	X ₂ YO ₄	Mg ₂ SiO ₄
M ₂ O ₃	0.67	(M ₂ O ₃) ₂	6	XYO ₃	FeTiO ₃
MO ₂	0.5		12	X ₃ YO ₆	Ba ₃ WO ₆
		8	XYO ₄	MgWO ₄	
		12	XY ₂ O ₆	MgNb ₂ O ₆	

It should not be implied from this that the complex oxide necessarily has the same structure as the simple oxide. This is clearly shown by considering next the coordination or packing of the cations and anions in these lattices.

In an array of close-packed oxygen atoms there are two types of hole, which are known as tetrahedral (4-coordinate) and octahedral (6-coordinate) holes, from the number of nearest-neighbour contacts which can be made by a particle of suitable size placed in such a hole. Clearly, the type of structure adopted by a particular complex oxide will depend markedly upon the size of the ions to be incorporated in the lattice. Consequently we expect considerable differences between lattices containing Be^{2+} (0.31 Å) and Ba^{2+} (1.35 Å), especially since in the latter case the barium ion is comparable in size with O^{2-} (1.40 Å).

We shall deal briefly in turn with the structures of complex oxides following the order given in Table 30, column 5.

XYO_2 . In many oxides of this type one of the ions is an alkali metal ion and so we may formulate the class more specifically as $\text{M}^{\text{I}}\text{M}^{\text{III}}\text{O}_2$ complex oxides. Examples of XYO_2 oxides which do not contain an alkali metal are CuCrO_2 and CuFeO_2 . Complex oxides of this type have a structure of the NaCl type in which both X and Y occupy octahedral holes in a close-packed oxide lattice. The simple NaCl structure suffers two types of distortion in XYO_2 oxides. In the one, extension parallel to a body diagonal or edge leads to a rhombohedral structure (e.g. NaInO_2), while in the other compression in the same direction leads to a tetragonal structure (e.g. LiInO_2). It is clear, however, that both modifications preserve the NaCl superstructure which is found for simple oxides, MO (see above).

XY_2O_4 and X_2YO_4 . This class includes many important minerals and is of interest because it introduces the spinel structure. The necessity of formulating both types of oxide is shown when we consider the three most commonly quoted examples of complex oxide in this category, as in Table 31.

The fractions shown in Table 31 indicate the proportion of tetrahedral or octahedral holes which are occupied by the ions X and Y in the oxide lattice. The reader should consult Wells¹⁴⁷ (p. 505) for a characteristically critical summary of the distinction between the olivine and phenacite structures: suffice it to say that arguments based on differences in ionic radii are not acceptable.

TABLE 31

Oxide	Generic name	Tetrahedral		Octahedral	
		X	Y	X	Y
Be ₂ SiO ₄	Phenacite	$\frac{1}{2}$	$\frac{1}{2}$		
Mg ₂ SiO ₄	Olivine		$\frac{1}{2}$	$\frac{1}{2}$	
MgAl ₂ O ₄	Spinel—normal	$\frac{1}{2}$			$\frac{1}{2}$
MgFe ₂ O ₄	Spinel—inverse		$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

Turning to the spinel structures, it is possible to distinguish three kinds of spinel compounds on the basis of oxidation state of the ions X and Y, thus:

X ^{II} Y ^{III} O ₄	2:3	CoAl ₂ O ₄	NiFe ₂ O ₄
X ^{IV} Y ^{II} O ₄	4:2	TiZn ₂ O ₄	SnCo ₂ O ₄
X ^{VI} Y ^I O ₄	6:1	MoAg ₂ O ₄	WN ₂ O ₄

As implied in Table 31, there are two types of spinel structure known as normal and inverse spinels. These differ in the disposition of the X and Y ions among the tetrahedral and octahedral holes in the close-packed oxide lattice. In the examples just quoted, CoAl₂O₄ is a normal spinel (X^{II}Y₂^{III}O₄), while NiFe₂O₄ is an inverse spinel [Y^{III}(X^{II}Y^{III})O₄]. Certain elements form binary oxides, M₃O₄, which have the spinel structure; thus Mn₃O₄ and Co₃O₄ have the normal structure, whilst Fe₃O₄ has the inverse structure.

The fraction of Y atoms in tetrahedral holes λ , may be used to describe spinels which are neither normal ($\lambda = 0$) nor inverse ($\lambda = 0.5$), e.g. MnFe₂O₄ has $\lambda = 0.1$. Calculations indicate that 4:2 spinels will have the inverse structure and all such spinels so far examined confirm this. On the other hand, similar calculations suggest that 2:3 spinels will have the normal structure in the absence of crystal field effects. As we have already seen, a number of 2:3 spinels are inverse, and this suggests that crystal field effects may be important in determining the preference of a metal ion for a particular (tetrahedral or octahedral) environment. Calculations of the difference in stabilization energy acquired by ions in an octahedral environment E_O , compared to that for the same ion in a tetrahedral environment E_T , provides in $(E_O - E_T)$ a measure of the preference of the ion for an octahedral site in a close-packed oxide lattice. This procedure has been used with success to explain the occurrence of inverse 2:3 spinels, especially those containing Fe³⁺ which is shown to have $(E_O - E_T) \sim 0$ and consequently to be capable of incorporation in a tetrahedral hole.

Although most spinels possess cubic symmetry, a small number show tetragonal distortions. These distortions may usually be traced to d^4 and d^9 metal ions in an octahedral

environment or else to d^3 , d^4 , d^8 and d^9 metal ions in a tetrahedral environment. Thus Mn^{3+} (d^4) in Mn^{2+} (Mn^{3+}) $_2O_4$ will be in a distorted octahedral environment with the result that Mn_3O_4 is a tetragonally distorted normal spinel.

XYO₃. When two-thirds of the octahedral holes in a cubic close-packed oxide lattice are occupied, the structure of the oxide M_2O_3 will be that of corundum (α - Al_2O_3). If the cations are of two different types, X and Y, then each will occupy one-third of the octahedral holes. Depending upon the pattern of occupation of the octahedral sites, one may distinguish two types of XYO_3 structure. The most common form, known by the generic name ilmenite ($FeTiO_3$), is commonly exhibited by complex oxides of the $M^{IV}TiO_3$ type in which M^{2+} is small. The other form, exemplified by $LiSbO_3$, has a slightly distorted hexagonal close-packed oxide lattice. For further details see Wells¹⁴⁷ (pp. 127 ff.).

The most common XYO_3 structure is known as the perovskite ($CaTiO_3$) structure. This structure prevails when the cation X is comparable in size with the oxide ion; this results in a lattice of close-packed layers made up of $[XO_3]$ units in an infinite array. The smaller Y cations occupy the octahedral holes in the close-packed $[XO_3]$ lattice. The cation X is 12-coordinate. The ideal perovskite structure is cubic, but the occurrence of distorted variants is common. These distorted perovskites have considerable technological importance because of their dielectric and magnetic properties. There are three classes of perovskite compounds thus:

			$r(X^{n+})$ (Å)	$r(Y^{n+})$ (Å)
$X^IVY^VO_3$	1:5	$KNbO_3$	1.60	0.64
$X^{III}Y^{IV}O_3$	2:4	$BaZrO_3$	1.60	0.72
$X^{III}Y^{III}O_3$	3:3	$LaGaO_3$	1.32	0.62

Typical of the distortions suffered by perovskites are those of $BaTiO_3$:

Distortion	Temperature range (°K)
Rhombohedral	193
Orthorhombic	193–278
Tetragonal	278–393
Cubic	393–1733
Hexagonal	1733–1885 (melting point)

The first three forms are ferroelectric.

There are also a number of complex oxides of the type X_2YO_4 (e.g. Sr_2TiO_4) which have the K_2NiF_4 structure which is in turn closely related to the perovskite structure (e.g. $SrTiO_3$). Whereas in the XYO_3 perovskite structure the X cation has twelve nearest neighbours, in the X_2YO_4 – K_2NiF_4 structure the cation X has only nine nearest neighbours.

X₃YO₆. Complex oxides in this class, which may be more exactly described as having the formula $X_2Y'Y''O_6$ (following Wells¹⁴⁷), have the cubic cryolite $[(NH_4)_3AlF_6]$ structure

or a distorted variant of this structure. As in the XYO_3 class, the close-packed unit is XO_3 and the remaining cations occupy octahedral holes in the lattice. An example of a compound having the $\text{X}_2\text{Y}'\text{Y}''\text{O}_6$ constitution is Ba_2CaWO_6 : the Ca^{2+} and W^{6+} ions occupy octahedral holes in the BaO_3 close-packed lattice.

XYO_4 . While many compounds of this general type are known in which the total formal cation charge is +8, the majority have structures containing discrete YO_4 anions and therefore do not concern us here (iodates, molybdates, tantalates, silicates, phosphates, etc.). Many tungsten-bearing ores are of the type XWO_4 , in which both X^{2+} and the W^{6+} cations occupy one quarter each of the octahedral holes in an hexagonal close-packed oxide lattice. Examples of the cation X^{2+} are Fe (ferberite), Mn (hübnerite), Co and Ni. In many of these, the WO_6 octahedron is more or less severely distorted¹⁵².

XY_2O_6 . Finally, mention must be made of the niobite structure. As in the preceding section, XYO_4 , one-half of the octahedral holes in a close-packed oxide lattice are occupied by the cations. Most of the complex oxides having this structure are of the type $\text{X}^{2+}\text{Y}_2^{3+}\text{O}_6$ and consequently examples are restricted to the larger cations of Groups V^A and V^B. This structural type, together with the trirutile structure (e.g. ZnSb_2O_6) and a hexagonal modification of trirutile (e.g. PbSb_2O_6), are common among complex oxides of antimony of the type $\text{X}^{2+}\text{Sb}_2\text{O}_6$. The trirutile structure is also encountered for certain tantalum compounds such as CoTa_2O_6 .

Bronzes. Brief mention must be made of this type of complex oxide of which, undoubtedly, the tungsten bronzes are the most familiar¹⁵³. When the complex oxide Na_2WO_4 is reduced it is possible to isolate and identify a number of phases, Na_xWO_3 ($x < 1$), which lie between $\text{W}^{\text{VI}}\text{O}_3$ (distorted ReO_3 structure) and the hypothetical $\text{NaW}^{\text{V}}\text{O}_3$ (perovskite). The structure and physical properties of these phases change in a regular manner with the sodium content. These bronzes have a metallic lustre and a wide range of colours; they are electrical conductors. Perhaps the simplest representation of the constitution of the tungsten bronzes is $\text{M}_x^{\text{I}}\text{W}^{\text{V}}\text{W}_{1-x}^{\text{VI}}\text{O}_3$. Complex oxides of this type are discussed in much greater detail elsewhere^{154, 150}.

No attempt has been made in all that has been said to describe in any depth the enormous variety that is to be found among complex oxides, even within the broad general categories we have mentioned. Specifically we have excluded all compounds containing oxy-anions in which there is a high proportion of covalent character in the bonds between a formal cation and a number of oxide ions.

Much of the current interest in mixed metal oxide systems derives from the interest of the electronic industries in exploiting the electrical and magnetic properties of these substances.

Layer Lattices

A small group of simple oxides have layer structures. The compounds concerned are MoO_3 , Re_2O_7 , SnO , PbO and As_2O_3 .

In MoO_3 the molybdenum atom is octahedrally coordinated by six oxygen atoms. Each MoO_6 octahedron shares two adjacent edges with its neighbours and, in addition, the octahedra are linked through corners.

¹⁵² K. S. Vorres, *J. Chem. Educ.* **39** (1962) 566.

¹⁵³ *Bull. soc. chim. France* 1965, 1051–215.

¹⁵⁴ R. Ward, *Prog. Inorg. Chem.* **1** (1959) 465.

In Re_2O_7 , chains of ReO_6 octahedra are linked through corners. These chains are connected through ReO_4 tetrahedra to form double layers, every tetrahedron sharing one oxygen with each of two octahedra. In this way each octahedron is linked to two other octahedra and to two other tetrahedra through corners.

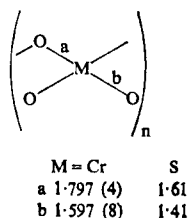
In the low-temperature monoclinic form of As_2O_3 , a hexagonal net of arsenic atoms is joined up through oxygen atoms to give (twelve-membered) hexagonal rings which are puckered.

Both SnO and the tetragonal form of PbO have the same structure in which the metal atom is coordinated by four oxygen atoms all of which lie to one side of the metal. It has been suggested that the fifth coordination position is occupied by a pair of electrons (inert-pair effect). Inter-layer contacts occur through the metal atoms.

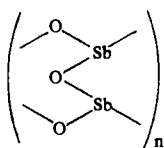
Chain Lattices

A small number of simple oxides have chain structures. The compounds concerned are CrO_3 , Sb_2O_3 , SO_3 , SeO_2 and HgO .

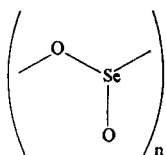
In contrast to its molybdenum and tungsten analogues, CrO_3 has a comparatively low melting point (197°). The structure of the solid consists of infinite chains of tetrahedra in which each chromium atom is coordinated by four oxygen atoms, two of which are shared with two other chromium atoms. The chains are held together by weak (van der Waals) forces. This structure is similar to that of one of the polymorphs of solid SO_3 . In both molecules the $\text{M}-\text{O}$ (in-chain) distance is longer than the out-of-chain (unshared) distance.



The low-temperature orthorhombic form of Sb_2O_3 has an interesting double-chain structure in which there are no unshared oxygen atoms.



The structure of solid SeO_2 consists of infinite chains in which the selenium atom is trigonally coordinated by three oxygen atoms, one of which is unshared ($\text{Se}-\text{O} = 1.73(8) \text{ \AA}$) while the other two (shared) oxygen atoms are included in the chain ($\text{Se}-\text{O} = 1.78(3) \text{ \AA}$).



Both the orthorhombic and hexagonal forms of HgO consist of infinite $[\text{Hg}-\text{O}]_n$ chains. In the former the chains are planar zigzag whilst in the latter they are helical. The coordination around mercury is strongly distorted octahedral.

Molecular Units

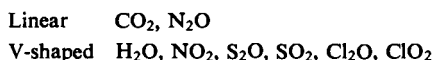
In this group we include all those simple oxides, in whatever phase, which have discrete (finite) molecular structural units. Thus, on the one hand, we have gaseous oxides such as CO_2 and Cl_2O while, on the other hand, there are oxides such as OsO_4 and Tc_2O_7 which have a molecular structure in the solid state.

Once again, this class is large and shows very considerable variation among structures of its members. The majority of molecular oxides are formed by the smaller non-metallic elements. It is possible to classify these oxides according to their formula type (Table 32).

TABLE 32

Formula	O/M	Examples
M_2O	0.5	H_2O , N_2O , S_2O , Cl_2O
MO	1	CO , NO
M_2O_3	1.5	N_2O_3 , P_4O_6 , As_4O_6 , Sb_4O_6
MO_2	2	CO_2 , NO_2 , SO_2 , ClO_2
M_2O_5	2.5	N_2O_5 , P_4O_{10}
M_2O_7	3.5	Cl_2O_7 , Mn_2O_7 (?), Tc_2O_7
MO_4	4	RuO_4 , OsO_4

Within each class as defined by the ratio O/M there may be a variety of structures. The diatomic oxides are, of course, linear. Triatomic oxides M_2O and MO_2 are either linear or bent (V-shaped) thus:



The most straightforward distinction between these two groups is based upon the total number of valence-shell electrons in the compound. Thus the oxides which are linear have a total of sixteen valence-shell electrons [CO_2 : $4+6+6$; N_2O : $5+5+6$]. As the total number of valence electrons increases, the angle about the central atom decreases (see Table 33).

As the number of atoms in the molecule increases, so does the variety of structural types. The tetratomic SO_3 has a planar triangular structure in the gas phase, but in the

solid phase a boat-shaped trimer is found for the orthorhombic modification. The pentatomic molecule N_2O_3 is thought to exist in two forms in the solid state, one of which is believed to be ONONO. The gaseous forms of the lower oxides of phosphorus, arsenic and antimony, $(M_2O_3)_2 \equiv M_4O_6$, have a structure based on a tetrahedron of M atoms. The volatile metal oxides, MO_4 ($M = Ru, Os$), have a tetrahedral structure.

TABLE 33

Compound	Number of valence electrons	Angle ($^\circ$)
CO_2	16	180
NO_2	17	134
O_3	18	117
SO_2	18	119
ClO_2	19	117
Cl_2O	20	111

Dinitrogen tetroxide, the dimer of NO_2 , has the structure of O_2N-NO_2 . The molecule is planar. The "pentoxides" of the Group V elements show similar deviations between nitrogen and the other members of the group as found for the "trioxides". N_2O_5 in the gas phase probably has the structure $O_2N \cdot O \cdot NO_2$, while P_4O_{10} has a structure based on a tetrahedron of phosphorus atoms as found in P_4O_6 and in elementary white phosphorus.

TABLE 34

Oxide	Vapour phase	Solid phase
O_3 SO_2 SeO_2 TeO_2 PoO_2	Molecular: $O\ddot{O}O$ 116.8° Molecular: $O\ddot{S}O$ 119.5° Molecular: $O\ddot{S}eO$ 125°	Molecular Chain lattice: tetragonal Three-dimensional rutile lattice: tetragonal Three-dimensional: tetragonal Three-dimensional: cubic

Summary

It will have become clear that the structures of oxides show a great deal of variety. While all complex oxides, $X_aY_b \dots O_n$ have infinite three-dimensional lattice structure, simple oxides, M_xO_y , may have either a three-dimensional lattice structure, or a layer structure, or a chain structure, or else a molecular structure.

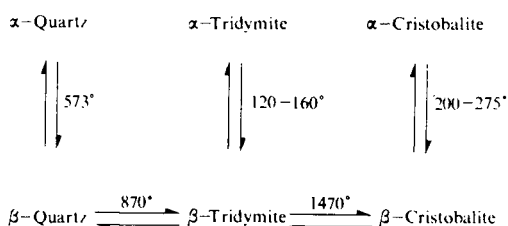
In order to demonstrate the type of variation found among the structures of simple oxides, we present examples from certain homologous series of oxides (Tables 34 and 35).

TABLE 35

Oxide	Solid phase structure
CrO ₃ MoO ₃ WO ₃	Chain lattice Layer lattice Three-dimensional distorted ReO ₃ lattice

3.4. ALLOTROPY OF OXIDES

Many simple oxides, particularly among those of the heavier non-transition metals, crystallize in a number of different allotropic forms. A well-known example of this behaviour is provided by SiO₂ which has three different allotropic forms, each of which occurs as an α - (low temperature) and β - (high temperature) modification.



Only α -quartz is thermodynamically stable at ordinary temperatures, all the other forms being metastable.

Other examples of allotropic oxides are M₂O₃ (M = P, As, Sb, Bi); MO₂ (Ge, Se, Te, Po); SO₃ and P₂O₅. This list is not intended to be exhaustive, and for further information the reader should consult Wyckoff¹⁴⁸.

3.5. THERMODYNAMIC CONSIDERATIONS

Following our earlier explanations, there still remain a number of fundamental questions about metal oxide systems. Many of these, in the absence of sufficient reliable thermo-

TABLE 36. BOND ENERGY TERMS (kcal mole⁻¹)

	M=C	Source	M=Si	Source
$E(\text{M}-\text{O})$	86	Organic	111	SiO ₂ (c)
$E(\text{M}=\text{O})$	192	CO ₂ (g)	153	SiO ₂ (g)
$E(\text{M}\equiv\text{O})$	257	CO (g)	192	SiO (g)

dynamic data, cannot be given an adequate answer. For example, we may ask why is CO₂ a gaseous molecule under normal conditions whereas SiO₂ under the same conditions is a crystalline solid?

To answer this question by referring merely to the availability of *d*-orbitals on silicon is simply to avoid the issue and certainly does not in itself answer the question; thus, as we have just seen, O₃ and SO₂ have very similar structures.

The question is really to be phrased in the following terms: Why does carbon form a double bond to oxygen in CO₂ but silicon forms a formal single bond to oxygen in SiO₂? It is possible in this instance and in a certain restricted number of other cases¹⁴⁵ to provide an adequate answer by considering the relative bond energies in the actual and the hypothetical molecules.

In simple organic molecules, $E(\text{C}-\text{O})$ (e.g. ethers) is roughly $\frac{1}{2}E(\text{C}=\text{O})$ (e.g. in aldehydes or ketones where a typical value for $E(\text{C}=\text{O})$ would be $\sim 177 \text{ kcal mole}^{-1}$). From Table 36 it is seen that $E(\text{C}-\text{O})$ is less than $\frac{1}{2}E(\text{C}=\text{O})$ in CO₂. On the other hand, $E(\text{Si}-\text{O})$ is much more than $\frac{1}{2}E(\text{Si}=\text{O})$. On this simple basis it is easy to show that a silica-like structure for CO₂ is thermodynamically unstable to the gaseous molecule.

Some experimentally determined bond energy values are given in Table 37 (all values in kcal mole⁻¹).

TABLE 37

(a) Single bonds							
B-O	125	C-O	86	N-O	48	O-O	34
		Si-O	111	P-O	88	S-O	65
		Ge-O	86	As-O	79	F-O	51
						Cl-O	49
(b) Double bonds							
		C=O	177	N=O	142	O=O	119
		Si=O	153	P=O	123	S=O	125
(c) Triple bonds							
		C \equiv O	257	N \equiv O	151		
		Si \equiv O	192				

3.6. GEOMETRICAL EFFECTS

In their recent compilation of an empirical set of effective ionic radii in oxide and fluoride structures, Shannon and Prewitt¹⁴⁶ have drawn attention to the small but significant variation of the radius of the oxide ion O²⁻, with its coordination number. The appropriate figures are as shown in Table 38.

TABLE 38

Coordination number	$r(\text{O}^{2-})$ Å	Range Å
2	1.35	1.349 ± 5
3	1.36	1.357 ± 10
4	1.38	1.378 ± 4
6	1.40	1.396 ± 9
8	1.42	

Using these values it is possible to calculate lattice parameters of ionic oxides with considerable accuracy in many cases.

The structures of molecular oxides show considerable variations in the M–O bond length according to the compound studied. In many cases these differences may be correlated with M–O bond order. While extensive compilations of M–O distances are to be found in Wells¹⁴⁷ and elsewhere, we present here (Table 39) a selection of element–oxygen bond lengths in simple oxide systems.

TABLE 39. ELEMENT–OXYGEN DISTANCES IN BINARY COMPOUNDS (Å)

B	C	N	O	F
1.205 BO	1.128 CO 1.162 CO ₂	1.187 N ₂ O 1.150 NO 1.192 NO ₂	1.207 O ₂ 1.278 O ₃	1.418 F ₂ O
	Si 1.509 SiO	P 1.448 PO 1.638 P ₄ O ₆ 1.429 P ₄ O ₁₀	S 1.465 S ₂ O 1.493 SO 1.432 SO ₂ 1.43 SO ₃	Cl 1.700 Cl ₂ O 1.571 ClO 1.473 ClO ₂ 1.405 Cl ₂ O ₇ 1.703
	Ge 1.650 GeO Sn 1.838 SnO 2.05 SnO ₂ Pb 1.922 PbO	As 1.78 As ₄ O ₆	Se 1.61 SeO ₂	Br 1.65 BrO

4. WATER

4.1. PHYSICAL PROPERTIES

Water is one of the most familiar substances on earth. It plays an essential part in the chemical basis of life, and is the commonest solvent for solution studies of inorganic systems. The influence of water on the chemical behaviour of aqueous systems is too large a subject for discussion here; this section will be concerned with the physical properties and structure of water in its various phases^{155, 156}.

¹⁵⁵ N. E. Dorsey, *Properties of Ordinary Water Substance*, Reinhold, New York (1940).

¹⁵⁶ D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press, Oxford (1969).

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	Ge 1.650 GeO Sn 1.838 SnO 2.05 SnO ₂ Pb 1.922 PbO	As 1.78 As ₄ O ₆	Se 1.61 SeO ₂	Br 1.65 BrO

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¹⁵⁶ D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press, Oxford (1969).

TABLE 40. PROPERTIES OF WATER

Dimensions of the free molecule

		Reference
Internuclear distance, \bar{r}_e	$0.9572 \pm 0.0003 \text{ \AA}$	a
Angle	$104.52 \pm 0.05^\circ$	a
Dipole moment (298–484°K)	1.84–1.85 Debyes	b
Mean quadrupole moment, \bar{Q}	$-5.6 \pm 1.0 \times 10^{-26} \text{ e.s.u. cm}^2$	c
Mean polarizability, $\bar{\alpha}$	$1.444 \times 10^{-24} \text{ cm}^3$	c

Crystal parameters of crystalline ice polymorphs^{c, d, e}

Form	Crystal system	Space group	Molecules per unit cell	H atom arrangement
Ice Ih	Hexagonal	$P6_3/mmc$	4	D
Ic	Cubic	$F\bar{4}3m$	8	D
II	Rhombohedral	$R\bar{3}$	12	O
III	Tetragonal	$P4_12_12$	12	D
V	Monoclinic	$A2/a$	28	D
VI	Tetragonal	$P4_2/nmc$	10	D
VII	Cubic	$Im\bar{3}m$	2	D
VIII	Cubic*	$Im\bar{3}m$	2	? O ^d
IX	Rhombohedral	$P4_12_12$	12	O

* Structure incomplete.

Vibrational constants for the water molecule (cm⁻¹)^a

$\omega_1 = 3832.17$	$x_{11} = -42.576$	$x_{12} = -15.933$
$\omega_2 = 1648.4$	$x_{22} = -16.813$	$x_{13} = -165.824$
$\omega_3 = 3942.53$	$x_{33} = -47.566$	$x_{23} = -20.332$

*Vibrational frequencies of water in different phases (cm⁻¹)^{c, *, f}*

Mode	Vapour	Liquid	Ice I	Ice II*	Ice V
ν_T	—	~60, ~190	~60, ~225	~150	169
ν_L	—	685 (vbr)	~840	800	~730
$\delta(\text{HOH}), \nu_2$	1594.59	1650	1650	1690	1680
ν_A	—	2130	2270	2225	2210
$2\nu_2$	3151.4		~3130	3000, 3225	
$\nu_{\text{O,H}} (\nu_1, \nu_3)$	3656.65 (ν_1) 3755.79 (ν_3)	~3250, ~3400, ~3600	3220, ~3350	3230, shs to higher frequency	3250 3440

vbr = very broad; shs = shoulders. * Many submaxima observed in this region 400–800 cm⁻¹ in the infrared.

ν_T are hindered translational lattice modes; ν_L is the librational lattice mode; and ν_A is the "association" band; ν_1 is the a_1 OH stretching mode, ν_2 the bend and ν_3 the b_1 stretch. Bands in the spectra of liquid water and of the disordered forms of ice (I and V in the table) are in general very broad, and the maxima are not always well defined; the spectra of other forms of ice differ in detail, save for ice Ih and ice Ic, where no differences were detected.

Force constants^c

$k_{\bar{r}} = 8.54 \times 10^5 \text{ dynes cm}$	$k_a = 0.761$
$k_{\bar{r}'} = -0.101$	$k_{\bar{r}a} = 0.228$

TABLE 40 (cont.)

Ultraviolet absorption of water

	Vapour ^a	Liquid ^b	Ice ^c
λ_{\max} (Å)	1655	1470	1570
ϵ (mol ⁻¹ cm ⁻¹)	3200	1700	

The value for ice is estimated for the onset of continuous absorption. The measurements above were made in the region > 1300 Å; there is a broad continuum for water vapour between 1150 Å and 1430 Å, on which diffuse bands are superimposed, and diffuse bands have been observed in the region 500–1000 Å ^{a, j}.

N.m.r. spectrum of water

H¹ chemical shift = -0.60 ppm (vapour), -5.18 ppm (liquid) ^k
relative to CH₄ gas; -4.32 ppm in NH₃(l) ^k
relative to Me₄Si external standard

O¹⁷ chemical shift (H₂O¹⁷ vapour–H₂O¹⁷ liquid) = $+36$ ppm ^l
 J (H–O¹⁷) = 79 ± 2 Hz for water vapour ^l

Ionization potentials ^c (eV)

1st 12.62 3rd 16.3 ± 0.3
2nd 14.5 ± 0.3 4th 18.0 ± 0.5
Proton affinity ^m = 164 ± 4 kcal mole⁻¹

Thermodynamic properties ^{c, m, n}

ΔH_f° (0°K) -57.102 kcal mole⁻¹ C_p° (298°K) 8.025 cal mole⁻¹
 ΔH_f° (298°K) -57.796 kcal mole⁻¹ D (H–OH) (0°K) 117.8 kcal mole⁻¹
 ΔG_f° (298°K) -54.634 kcal mole⁻¹ E (H–O) 110.6 kcal mole⁻¹
 S° (298°K) 45.104 cal °K⁻¹ mole⁻¹

Thermodynamics of ice–ice transitions ^c

	t (°C)	p (kbar)	ΔV (cm ³ mol ⁻¹)	ΔS (e.u.)	ΔH (cal mol ⁻¹)
From ice I to ice II	-35	2.13	-3.92	-0.76	-180
I III	-22	2.08	-3.27	0.4	94
II III	-24	3.44	0.26	1.22	304
II V	-24	3.44	-0.72	1.16	288
III V	-17	3.46	-0.98	-0.07	-17
V VI	0.16	6.26	-0.70	-0.01	-4
VI VII	81.6	22	-1.05	~ 0	~ 0
VI VIII	~ 5	~ 21	~ 0.0	~ -1.01	-282

Critical temperature, T_c 647.30°K

Critical pressure, P_c 218.3 atm

Critical volume, V_c 59.1 ± 0.5 cm³ mol⁻¹

Van der Waals constants for water vapour ^b:

a 5.464 , b 0.03049 , when P is in atmospheres and V in litres

Virial coefficients ^p at 573.16°K :

B -112.9 cm³ mol⁻¹, C -3470 cm⁶ mol⁻²

TABLE 40 (cont.)

Properties for liquid water^a

Density at 0°C	0.999 841 g cm ³
4°C	0.999 973 g cm ³
Density of ice I at 0°C	0.916 71 g cm ³
Absolute refractive index for Na D-line at 20°C	1.333 35
Kerr constant for Na D-line at 17°C	0.0363 cm volt ⁻²
Verdet constant for Na D-line	(131.1 - 0.004 00 <i>t</i> - 0.000 400 <i>t</i> ²) × 10 ⁻⁴ min gauss ⁻¹ cm ⁻¹ (4° < <i>t</i> < 98°C)
Thermal conductivity at 0°C	0.001 348 cal sec ⁻¹ cm ⁻² (°C cm ⁻¹) ⁻¹
Surface tension at 18°C	73.05 dynes cm
Viscosity at 20°C	0.010 019 ± 0.000 003 poise
Ionic dissociation constant ° <i>K</i> at 25°C	[H ⁺][OH ⁻]/[H ₂ O] = 1.821 ₄ × 10 ⁻¹⁶ mol l ⁻¹
Ionic concentrations ° [H ⁺] = [OH ⁻] at 25°C	1.004 × 10 ⁻⁷ mol l ⁻¹
D.c. conductivity ° at 20°C	5.7 × 10 ⁻⁸ ohm ⁻¹ cm ⁻¹
Dielectric constant °, ϵ_0	87.740 - 0.400 08 <i>t</i> + 9.398 × 10 ⁻⁴ <i>t</i> ² - 1.410 × 10 ⁻⁶ <i>t</i> ³ (<i>t</i> = 0-100°C)
Specific magnetic susceptibility χ_g at 20°C	-719.92 ± 0.11 × 10 ⁻⁹ c.g.s.u.

^a W. S. Benedict, N. Gailar and E. K. Plyler, *J. Chem. Phys.* **24** (1956) 1139.^b *Chemical Rubber Handbook*, 48th edn. (1968-9).^c D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press, Oxford (1969).^d E. Whalley, *Ann. Rev. Phys. Chem.* **18** (1966) 205.^e J. E. Bertie and E. H. Whalley, *J. Chem. Phys.* **40** (1964) 1637, 1647.^f J. Schiffer and D. F. Hornig, *J. Chem. Phys.* **49** (1969) 4150.^g K. Watanabe and M. Zelikoff, *J. Opt. Soc. America* **43** (1953) 753.^h R. A. Verrall and W. A. Senior, *J. Chem. Phys.* **50** (1969) 2746.ⁱ K. Dressler and O. Schnepf, *J. Chem. Phys.* **33** (1960) 270.^j S. Bell, *J. Mol. Spectrosc.* **16** (1965) 205.^k W. G. Schneider, H. J. Bernstein and J. A. Pople, *J. Chem. Phys.* **28** (1958) 601; T. Birchall and W. L. Jolly, *J. Am. Chem. Soc.* **87** (1965) 3007.^l A. E. Florin and M. Alei, *J. Chem. Phys.* **47** (1967) 4268.^m NBS Technical Note 270-3 (1968); J. L. Beauchamp and S. E. Buttrill, *J. Chem. Phys.* **48** (1968) 1783.ⁿ T. L. Cottrell, *The Strengths of Chemical Bonds*, 2nd edn., Butterworths (1958).^p J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases*, Oxford University Press, Oxford (1969).^q N. E. Dorsey, *Properties of Ordinary Water Substance*, Reinhold, New York (1940).

The composition of water was established by the early work of Cavendish, Lavoisier, Gay-Lussac and Humbolt. The structure of the free molecule has been determined very accurately (Table 40), but the structures of the various forms of ice and of liquid water are less well understood. The unusual physical properties of liquid water—its high melting point and latent heat of vaporization, the increase in its density from 0° to 4°, the unusual spectroscopic and transport properties—indicate clearly that there is extensive hydrogen bonding in the liquid; this persists in the solid.

There are at least nine different crystalline forms of ice^{156, 157}; each is apparently based on tetrahedrally coordinated oxygen, the oxygen atoms each being bound to two hydrogen atoms by "normal" bonds and to two others by hydrogen bonds. In hexagonal ice I, sometimes called ice Ih, the dimensions of the water molecule are close to those for the free molecule. Pauling showed that if the individual water molecules are preserved, and if each is involved in forming four hydrogen bonds with the hydrogen atoms between pairs of oxygen atoms, ice at 0°K should have residual entropy because of possible disorder in the

¹⁵⁷ E. Whalley, *Ann. Rev. Phys. Chem.* **18** (1967) 205; S. W. Rabideau, E. D. Finch, G. P. Arnold and A. I. Bowman, *J. Chem. Phys.* **49** (1968) 2514.

arrangement of the hydrogen atoms; the residual entropy calculated on this basis¹⁵⁶ is 0.8145 ± 0.0002 e.u., as against an experimental value of 0.82 ± 0.15 e.u. The other forms of ice are stable under different conditions of temperature and pressure (Fig. 6); in at least three the arrangement of the hydrogen atoms appears to be ordered.

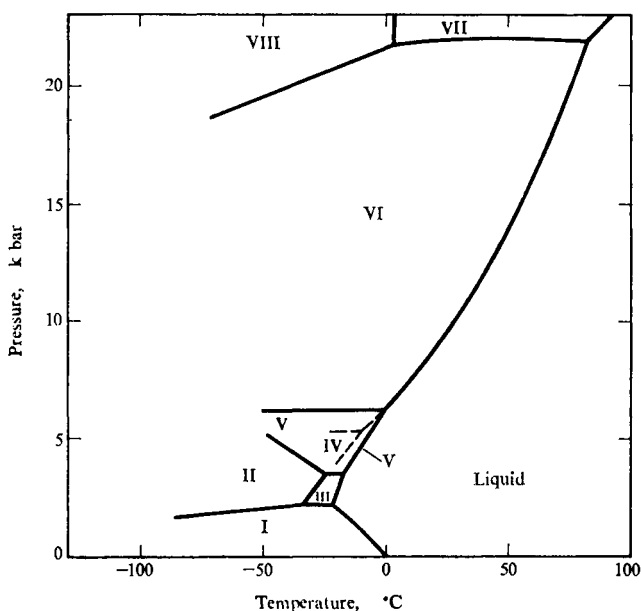


FIG. 6. Phase diagram for H₂O. The field for metastable ice IV, indicated by dashed lines, was mapped only for D₂O. (Reproduced with permission from D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press, 1969, p. 93.)

The structure of liquid water has been investigated by X-ray diffraction, by spectroscopy and by calculation of thermodynamic properties based on different models. Interpretation of diffraction patterns suggests that each water molecule has over a period of time an average of rather more than four nearest neighbours; the average drops a little with increasing temperature. The details of the "instantaneous" structure are controversial. As a consequence of measurements of dielectric relaxation, it now seems unlikely that liquid water consists of a whole range of units from monomer through dimer, trimer and so on up to very highly polymerized species. Models, known as mixture models, have been proposed in which a limited number of distinct species are in equilibrium with one-another; this equilibrium may be maintained by the simultaneous making and breaking of a large number of hydrogen bonds (the "flickering-cluster" picture). The simplest mixture models, "two-state models", postulate monomeric species in equilibrium with high polymers; the

monomeric water molecules have been described as analogous to certain hydrates, with the free molecules as interstitial species in a lattice of water polymers. An alternative approach involves the postulate that the hydrogen bonds are distorted, rather than broken and reformed, as a result of molecular motion in the liquid. Certain features of the infrared spectrum, notably the breadth of the band due to OH stretching and the unexpectedly large intensity of the overtone of the bending mode, have been explained in terms of collisional distortion¹⁵⁸. None of these models is completely satisfactory as yet, but most of the properties of liquid water may be understood at least qualitatively on the base of the two-state model.

The state of water in different solvents depends on the nature of the solvent concerned. In non-polar solvents, it has been shown by classical physical techniques and by spectroscopy that even in solutions approaching saturation the concentrations of dimers or polymers of water are small; in polar solvents, aggregates are formed¹⁵⁹. Association in the vapour is indicated by calculations based on the virial coefficients¹⁵⁶ and by spectroscopic methods¹⁶⁰.

The strength of the hydrogen bonds in water has been variously estimated at between 1 and 12 kcal (mole-bond)⁻¹; at present most estimates lie in the range 2–4 kcal (mole-bond)⁻¹. The ordered structure of liquid water is of the greatest importance in connection with solvation and with life chemistry; it is probably responsible for the enormous mobility of the proton in liquid water, which takes place through a cooperative "proton-switch" mechanism.

In the past few years a material called "anomalous water" or "polywater" has been obtained by condensing water vapour at partial pressures less than the saturated pressure in quartz capillaries in the absence of air¹⁶¹. The liquid obtained in this way is more dense, less volatile and more viscous than ordinary water, and its coefficient of thermal expansion is much higher. The structure and even the composition of anomalous water is uncertain. Structures proposed include tetrameric, tetrahedral units, not unlike P₄O₆ but with only two "terminal" protons, and a polymeric structure with symmetrical hydrogen bonds, giving O–H–O units analogous to the bifluoride ion^{162, 163}. Preliminary studies of the mass, i.r. and n.m.r. spectra, however, revealed no anomalies¹⁶⁴. It now seems almost certain that the anomalous properties are due to the presence of impurities¹⁶⁵ and that pure "anomalous" water does not exist.

Calculations of the properties of the water molecule have been made by the SCF MO method, using both Gaussian and Slater functions; the properties derived from these calculations correlate quite well with experimental values¹⁶⁶.

Some physical and structural properties of water are collected in Table 40.

¹⁵⁸ J. Schiffer and D. F. Hornig, *J. Chem. Phys.* **49** (1969) 4150.

¹⁵⁹ S. D. Christian, A. A. Taha and B. W. Gajh, *Quart. Rev.* **24** (1970) 20.

¹⁶⁰ W. A. P. Luck and W. Ditter, *Ber. Bunsenges. Phys. Chem.* **70** (1966) 1113.

¹⁶¹ B. V. Derjaguin, N. V. Churaev, N. N. Fedyaikin, M. V. Talaev and I. G. Ershova, *Bull. Acad. Sci. USSR* 1967, 2095.

¹⁶² R. W. Bolander, J. L. Kassner and J. T. Zung, *Nature* **221** (1969) 1233.

¹⁶³ E. R. Lippincott, R. R. Strombers, W. H. Grant and G. L. Cessac, *Science* **164** (1969) 1482.

¹⁶⁴ E. Willis, G. R. Rennie, C. Smart and B. Pethica, *Nature* **222** (1969) 159.

¹⁶⁵ P. Barnes, I. Cherry, J. L. Finney and S. Petersen, *Nature* **230** (1971) 31.

¹⁶⁶ S. Aung, R. M. Pitzer and S. I. Chan, *J. Chem. Phys.* **49** (1968) 2071.

4.2. CHEMICAL PROPERTIES

Oxygen in water is in its lowest oxidation state; the oxidation potential is high (see Table 5, p. 691). On many surfaces there is a substantial overvoltage for both oxidation and reduction of water; these overvoltages reflect a kinetic resistance of water to oxidation or reduction, and so the range of redox processes that can be studied in aqueous solution is large. Because of its high dielectric constant and strong solvating properties, water is a good solvent for many ionic and polar species; the hydrogen bond energy of water itself, however, means that substances do not dissolve in water unless they are strongly solvated. As with other "structured" solvents, solutes may be classified as "structure making" or "structure breaking", depending on their effect on the structure of the solvent; the different types may be distinguished by n.m.r. or by study of such physical properties as viscosity.

The importance of the self-ionization of water in the chemistry of aqueous systems is enormous:

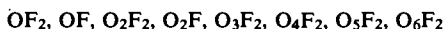


The H_3O^+ ion, which is pyramidal, is, of course, more extensively solvated in aqueous solution; species such as H_5O_2^+ have been identified crystallographically, and aggregates $\text{H}^+(\text{H}_2\text{O})_n$ have been detected in the mass spectrometer. Coordinated water may also behave as an acid, and, indeed, the system $\text{H}_2\text{O} \cdot \text{BF}_3$ is exceptionally acidic. Reactions involving the hydrolysis of halides, or anhydrides, and of cations cannot be described here; suffice it to say that water can be regarded as the parent of the whole series of hydroxy-compounds ROH, and as a base because of the lone pairs of electrons at oxygen.

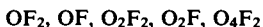
5. OXYGEN FLUORIDES

5.1. INTRODUCTION

The oxygen fluorides have been the object of considerable study and possess unusual chemical and physical properties. At this time of writing (July 1969) the following species have been mentioned in the literature:



By no means has the preparation and characterization of all these species been unequivocally demonstrated. In fact the only ones for which the evidence seems completely reliable are:



For the others, O_3F_2 is almost certainly a mixture of O_2F_2 and O_4F_2 (which is itself in equilibrium with $2\text{O}_2\text{F}$), and the evidence for O_5F_2 and O_6F_2 is based only on the ratio of oxygen to fluorine following decomposition.

The compounds are powerful fluorinating and oxidizing agents and, but for OF_2 , are only stable well below room temperature. In 1963, Streng¹⁶⁷ described the chemistry of the non-radical compounds (OF_2 , O_2F_2 , " O_3F_2 ", O_4F_2) in a comprehensive review article. More recently Turner¹⁶⁸ has considered the physicochemical properties of the compounds and included a description of the preparation and spectroscopic observation of the radicals

¹⁶⁷ A. G. Streng, *Chem. Revs.* **63** (1963) 607.

¹⁶⁸ J. J. Turner, *Endeavour* **27** (1968) 42.

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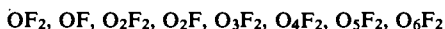


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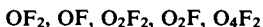
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¹⁶⁸ J. J. Turner, *Endeavour* **27** (1968) 42.

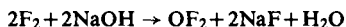
OF and O₂F. A very useful summary of properties of oxygen fluorides is contained in a recent book by Lawless and Smith¹⁶⁹.

In what follows an attempt is made to consider the oxygen fluorides in turn, but there will be considerable overlap; for example, the radical O₂F seems to be present to some extent in all condensed oxygen fluoride systems.

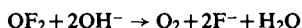
5.2. OXYGEN DIFLUORIDE, OF₂

Preparation

Although the first preparation¹⁷⁰ of an oxygen fluoride involved electrolysis of molten, slightly moist, KF-HF to give OF₂, the most common preparative method¹⁷¹ depends on the reaction of fluorine gas with 2% caustic soda solution:



If the concentration of base is not carefully controlled OF₂ is lost via the secondary reaction:



Full spectroscopic studies on OF₂ demand consideration of isotopic molecules, and Reinhard and Arkell¹⁷² prepared ¹⁷OF₂ and ¹⁸OF₂ by the electrolysis of HF containing up to 0.5% enriched water.

Physical Properties

At room temperature OF₂ is a colourless, very poisonous gas; it decomposes at temperatures above 200°C, and freezes at -223.8°C to give a pale yellow liquid. Table 41 summarizes most of the known physical properties.

The most recent thermochemical determination¹⁷³ of the heat of formation of OF₂ allows an accurate estimate of the *mean* bond energy in OF₂, but to obtain a reliable value for the *dissociation* bond energy (i.e. ΔH for OF₂ → OF + F) is a more difficult problem (see below).

Oxygen difluoride is quite stable at room temperature in *dry* glass vessels.

Some Chemical Properties

Although less reactive than fluorine, OF₂ is a powerful oxidizing agent, sometimes fluorinating and sometimes—particularly in aqueous solution—donating oxygen. Streng¹⁶⁷ and Lawless and Smith¹⁶⁹ have provided a comprehensive catalogue of reactions of OF₂, and here we merely outline some characteristic ones.

Most metals react with OF₂, particularly on warming, to give the corresponding fluoride. Metallic oxides can also produce the fluoride, e.g. CrO₃ forms the fluoride on

¹⁶⁹ E. W. Lawless and I. C. Smith, *Inorganic High-energy Oxidisers*, Arnold, London, and Dekker, New York (1968).

¹⁷⁰ P. Lebeau and A. Damiens, *Compt. rend.* **185** (1927) 652.

¹⁷¹ For example, G. H. Cady, *J. Am. Chem. Soc.* **57** (1935) 246.

¹⁷² R. R. Reinhard and A. Arkell, *Int. J. Appl. Radiation Isotopes* **16** (1965) 498.

¹⁷³ R. C. King and G. T. Armstrong, *J. Res. Natl. Bur. Std. U.S.* **72A** (1968) 113.

gentle warming, whereas CaO only reacts on strong heating. With non-metallic solids, fluorides and oxyfluorides are obtained, e.g. S, Se, Te give among other products SO₂, SF₄, SeF₄ and TeF₄.

TABLE 41. PHYSICAL PROPERTIES OF OXYGEN DIFLUORIDE, OF₂

Melting point	−223.8°C (49.4°K)
Boiling point	−145.3°C (127.9°K)
Decomposition temperature	~200°C
Heat of vaporization	2.650 kcal mole ^{−1} at b.p.
Vapour pressure: vapour	$\log p \text{ (mmHg)} = 7.2242 - \frac{555.42}{T}$ (195°C to −145°C)
liquid	$T \text{ (°K)}$ 60.213 67.535 76.883 89.236 106.317 127.856 $p \text{ (mmHg)}$ 0.01 0.10 1.0 10.0 100.0 760.0 −58.0 ± 0.1°C (215.2 ± 0.1°K)
Critical temperature	48.9 atm
Critical pressure	48.9 atm
Heat of formation (ΔH_f°)	5.86 ± 0.38 kcal mole ^{−1}
Average bond energy	44.72 kcal mole ^{−1}
Bond dissociation energy $D \text{ (F-OF)}^a$	38.0 ± 3.7, 42.7 ± 4.1 kcal mole ^{−1}
Density: vapour	2.41 mg ^{−1} cc at n.t.p.
liquid	$d = 2.190 - 0.00523T \text{ g cc}^{-1}$
Ionization potential	315 ± 4 kcal mole ^{−1} (13.7 ± 0.2 eV)
Ultraviolet spectrum	Gas and liquid very similar—continuum with possible maxima at 4210 Å, 3580 Å and 2940 Å
liquid: $\lambda \text{ (Å)}$	3000 4000 5000 5800
$\epsilon \text{ (l mole}^{-1} \text{ cm}^{-1})^b$	0.48 0.055 0.012 0.0012
$\epsilon \text{ (l mole}^{-1} \text{ cm}^{-1})^c$	0.061 0.021 0.008
Dipole moment	0.2–0.3 D
Infrared maxima (cm ^{−1}) (fundamentals) ^d	461 (s, doublet, $\nu_2[A_1]$); 831 (vs, PQR , $\nu_3[B_1]$); 928 (s, doublet, $\nu_1[A_1]$)
Force constants (mdyn [†] Å ^{−1})	$f_{OF} = 3.95$; $f_{OF-OF} = 0.81$; $f_{FOF} = 0.72$; $f_{OF-FOF} = 0.14$
Structure of gas (microwave) ^e	$r_e \text{ (O-F)} = 1.4053 \pm 0.0004 \text{ Å}$ $\theta_e \text{ (F-O-F)} = 103^\circ 4' \pm 3'$
Chemical shift	¹⁹ F ^g (v. CCl ₃ in ppm): gas, −248 ± 1; liquid, −249 ± 1; in SF ₆ solution −274 ¹⁷ O ^h (v. H ₂ ¹⁷ O in ppm); liquid, −830

Unless stated otherwise, data from A. G. Streng, *Chem. Revs.* **63** (1963) 607 and/or E. W. Lawless and I. C. Smith, *Inorganic High-energy Oxidisers*, Arnold, London, and Dekker, New York (1968).

^a M. A. A. Clyne, R. T. Watson, *Chem. Phys. Letters*, in press; M. C. Lin and S. H. Bauer, *J. Am. Chem. Soc.* **91** (1969) 7737.

^b F. I. Metz, J. W. Nebgen, W. B. Rose and F. E. Welsh, unpublished data.

^c A. G. Streng and L. V. Streng, *J. Phys. Chem.* **69** (1965) 1079.

^d J. W. Nebgen, F. I. Metz and W. B. Rose, *J. Mol. Spectrosc.* **21** (1966) 99; these authors investigated the Fermi resonance between ν_1 and ν_2 first considered in the microwave work of ref. e. See D. J. Gardiner and J. J. Turner, *J. Mol. Spectrosc.* **38** (1971) 428 for liquid Raman data.

^e Y. Morino and S. Saito, *J. Mol. Spectrosc.* **19** (1966) 435.

^f L. Pierce, N. Di Cianni and R. H. Jackson, *J. Chem. Phys.* **38** (1963) 730; the force constants are calculated to be consistent with vibrational spectra and centrifugal distortion constants in microwave.

^g See, for example, J. W. Nebgen, W. B. Rose and F. I. Metz, *J. Mol. Spectrosc.* **20** (1966) 72.

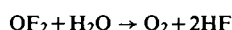
^h I. J. Solomon, J. N. Keith, A. J. Kacmarek and J. K. Raney, *J. Am. Chem. Soc.* **90** (1968) 5408.

Oxygen difluoride and hydrogen sulphide explode on mixing at room temperature: with xenon, XeF₄ and xenon oxyfluorides are produced: with atomic hydrogen, even at 77°K, HF, H₂O and H₂O₂ are formed.

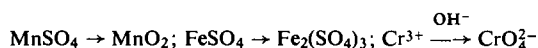
OF₂ and F₂ form cryogenic solutions on mixing in all proportions and do not react up to 300°C. On warming OF₂ with Cl₂, Br₂ and I₂ explosions occur to give largely halogen

fluorides plus perhaps Cl_2O and I_2O_5 . There is *some* evidence for ClOF , which would be the only example of a mixed oxygen halide of general formula XOY ; experiments said to provide evidence for this species include the passage of Cl_2 and OF_2 through a copper tube at 300°C , the action of ultraviolet light on mixtures of Cl_2 and OF_2 and the reaction of ClF and OF_2 at 25°C ¹⁶⁹.

Oxygen difluoride is slightly soluble in water but a slow hydrolysis occurs:

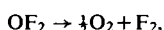


In aqueous solutions of HCl , HBr and HI free halogen is liberated; with H_2S colloidal sulphur is precipitated and reactions which demonstrate oxidation in aqueous solution include:



Properties Relevant to Reaction Mechanism and the OF Radical

Until recently it was widely accepted that the thermal decomposition of OF_2 , which proceeds overall according to



involved the initial simple dissociation¹⁷⁴



and that the reactions



proceed with zero activation energy; thus the overall rate constant k_{ov} should equal k_1 the second-order rate constant for (1). However recent work, particularly using shock-tubes^{175, 176}, has demonstrated the importance of the reverse of (2) and (3). In the most recent work¹⁷⁶:

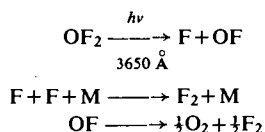
$$k_{ov} = 10^{15.8} e^{-37,800/RT} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \quad (T < 1000^\circ\text{K})$$

$$k_1 = 10^{17.3} e^{-(42,500 \pm 4100)/RT} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

$$k_2 = 10^{12.10 \pm 0.12} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

Thus, applying RRKM theory, $D(\text{FO}-\text{F}) = 42.7 \text{ kcal mole}^{-1}$ and hence combining with $\Delta H_f^\circ(\text{OF}_2)$, $D(\text{OF}) = 48.3 \text{ kcal mole}^{-1}$.

The photochemical behaviour is also best interpreted on the basis of OF and F . For example, Schumaker *et al.*¹⁷⁷ studied the photochemical decomposition between 15° and 45°C to give F_2 and O_2 and deduced the mechanism:



¹⁷⁴ W. Koblitz and H. J. Schumaker, *Z. physik. Chem.* **B25** (1934) 283.

¹⁷⁵ J. A. Blauer and W. C. Solomon, *J. Phys. Chem.* **72** (1968) 2307; W. C. Solomon, J. A. Blauer and F. C. Jaye, *J. Phys. Chem.* **72** (1968) 2311.

¹⁷⁶ M. C. Lin and S. H. Bauer, *J. Am. Chem. Soc.*, **91** (1969) 7737.

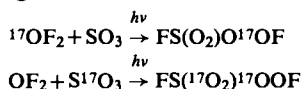
¹⁷⁷ R. Gatti, E. Staricco, J. E. Sicre and H. J. Schumaker, *Z. physik. Chem. (Frankfurt)* **35** (1962) 343.

They also concluded that any reaction



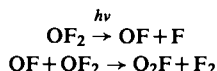
must have an activation energy of at least 15 kcal mole⁻¹, but it has been pointed out¹⁷⁵ that they neglected any contribution from the reverse of (4).

Chemical demonstration that OF₂ reacts photochemically as OF plus F was provided by Franz and Neumayr¹⁷⁸, following Schumaker. The photolysis of OF₂/SO₃, OF₂/S₂F₂O₆, OF₂/SO₂ gas mixtures with light of wavelength 3650 Å (which is absorbed only by OF₂) gave several compounds of F, S and O. For example, with OF₂ and SO₃ the only product was FS(O₂)OOF implying addition of F and OF. More recently Solomon *et al.*¹⁷⁹ have repeated the OF₂/SO₃ photolysis experiments using ¹⁷O labelled compounds. The products were analysed by ¹⁷O nuclear magnetic resonance and the results can be summarized:



thus demonstrating the presence of OF as an intermediate.

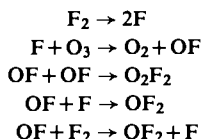
Liquid OF₂ and low-temperature solutions of OF₂ in freons¹⁸⁰ show e.s.r. absorptions after exposure to light. This free radical is, however, certainly O₂F not OF, and is possibly formed by some such reaction as



The properties of the O₂F radical will be discussed following the section on the chemistry of O₂F₂.

5.3. OXYGEN MONOFLUORIDE, OF

The previous section demonstrated the evidence for OF as an intermediate in OF₂ chemistry. Attempts to observe this species in the gas phase or in solution by such techniques as flash photolysis and e.s.r. have until very recently all failed. Further *indirect* evidence was obtained by first Schumaker and then Kirshenbaum¹⁸¹ by studying the photolysis (3650 Å) of gaseous F₂/O₃ mixtures at a variety of temperatures. At 120°K the products were O₂F₂, OF₂ and O₂ consistent with a mechanism:



The only current *proof* of OF is provided by the matrix isolation work of Arkell *et al.*¹⁸² (Although the radical was claimed^{183a} to result from the photolysis of OF₂ in CCl₃F at 77°K, the product was almost certainly^{183b} O₂F.) In Arkell's work a gaseous mixture of OF₂ in argon (or nitrogen) of composition 1 in 40 was slowly deposited on a CsBr window maintained at 4°K in a special cold cell employing liquid helium as coolant. The infrared

¹⁷⁸ G. Franz and F. Neumayr, *Inorg. Chem.* **3** (1964) 921.

¹⁷⁹ I. J. Solomon, A. J. Kacmarek and J. K. Raney, *J. Phys. Chem.* **72** (1968) 2262.

¹⁸⁰ F. I. Metz, F. E. Welsh and W. B. Rose, *Adv. Chem. Ser.* **54** (1966) 202.

¹⁸¹ E. Staricco, J. E. Sicre and H. J. Schumaker, *Z. physik. Chem. (Frankfurt)* **31** (1962) 385; A. D. Kirshenbaum, *Inorg. Nucl. Chem. Letters* **1** (1965) 121.

¹⁸² A. Arkell, R. R. Reinhard and L. P. Larson, *J. Am. Chem. Soc.* **87** (1965) 1016.

spectrum of the solid deposit showed sharp absorptions due to the OF_2 isolated in the argon matrix. Photolysis of this deposit with a 1000 W ultraviolet lamp, with appropriate filters, resulted in the development of an infrared band at 1028.5 cm^{-1} and concurrent decrease in the intensity of the OF_2 absorption. On allowing the deposit to warm to approximately 45°K , the 1028.5 cm^{-1} band disappeared and the intensity of the OF_2 bands returned to their original value; in some experiments weak absorptions due to O_2F_2 were observed on warming. On photolysis of an $^{18}\text{OF}_2$, $^{16}\text{OF}_2$ mixture two bands appeared at 1028.5 cm^{-1} and 997.4 cm^{-1} . Clearly photolysis of OF_2 generates OF and F, the latter escaping from the matrix cage of inert gas atoms—the 1028.5 cm^{-1} band is due to OF. On allowing warm-up to 45°K , the matrix becomes “diffusing” and the F and OF recombine, the small amount of O_2F_2 observed being due to the recombination $\text{OF} + \text{OF} \rightarrow \text{O}_2\text{F}_2$. More recently Arkell¹⁸⁴ has obtained a substantial increase in the quantity of OF produced by the addition of N_2O to the matrix—fluorine atoms produced photolytically from OF_2 can react with N_2O to give OF plus N_2 . With F_2 and N_2O in argon, photolysis gave OF and OF_2 and this allows a lower limit to be put on the OF bond energy of approximately 40 kcal mole^{-1} ¹⁸⁵.

In very recent work Clyne and Watson^{185a} have obtained mass spectral evidence for OF by the reaction of F atoms with O_3 . The appearance potential of OF^+ from OF is 1.6_5 eV lower than its appearance potential from OF_2 . This allows an estimate of $D(\text{FO}-\text{F})$ [$38.0 \pm 3.7\text{ kcal mole}^{-1}$] and $D(\text{OF})$ [$51.4 \pm 4.1\text{ kcal mole}^{-1}$].

The bond energy of the OF radical has been a subject of some controversy. Early electron impact studies¹⁸⁶ gave a value of $28.8 \pm 0.5\text{ kcal mole}^{-1}$ (corrected for the most recent values of other relevant thermodynamic data); matrix work suggested ~ 56 (from frequency of OF vibration) and > 40 (from $\text{F} + \text{N}_2\text{O}$ reaction). However it does now seem that the best experimental value is

$$D(\text{OF}) = 50 \pm 6\text{ kcal mole}^{-1}.$$

Theoretical estimates have ranged from 45 to 56 kcal mole^{-1} ; the most recent SCF calculations^{187a} give a value of $69 (+7-18)\text{ kcal mole}^{-1}$.

5.4. DIOXYGEN DIFLUORIDE, O_2F_2

Preparation

This compound was first prepared by Ruff and Menzel¹⁸⁸ by passage of an electric discharge through a gaseous oxygen–fluorine mixture at low pressure and with the discharge vessel maintained at liquid air temperature. Photolysis of liquid mixtures¹⁸⁹ of oxygen and fluorine produced red and yellow crystals believed to be O_3F_2 and O_2F_2 .

The common current method of preparation employs the electric discharge technique and Table 42 outlines the conditions for O_2F_2 and for the higher oxygen fluorides reported¹⁶⁹.

^{183a} F. Neumayr and N. Vanderkooi, Jr., *Inorg. Chem.* **4** (1965) 1234.

^{183b} F. E. Welsh, F. I. Metz and W. B. Rose, *J. Molec. Spectrosc.* **21** (1966) 249.

¹⁸⁴ A. Arkell, *J. Phys. Chem.* **73** (1969) 3877.

¹⁸⁵ J. S. Ogden and J. J. Turner, *J. Chem. Soc. A*, 1967, 1483.

^{185a} M. A. A. Clyne and R. T. Watson, *Chem. Phys. Letters*, in press.

¹⁸⁶ V. H. Dibeler, R. M. Reese and J. L. Franklin, *J. Chem. Phys.* **27** (1957) 1296.

¹⁸⁷ G. Glockler, *J. Chem. Phys.* **16** (1948) 604; W. C. Price, T. R. Passmore and D. M. Roessler, *Disc. Faraday Soc.* **35** (1963) 207; M. Green and J. W. Linnett, *J. Chem. Soc.* 1960, 4959.

^{187a} P. A. G. O'Hare and A. C. Wahl, *J. Chem. Phys.*, **53** (1970) 2469.

¹⁸⁸ O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.* **211** (1933) 204; **217** (1934) 85.

¹⁸⁹ S. Aoyama and S. Sakuraba, *J. Chem. Soc. Japan* **59** (1938) 1321.

It will be noted that the lower the temperature and the milder the discharge conditions, the higher the oxygen to fluorine ratio.

More recently Streng and Streng¹⁹⁰ have employed a discharge of OF₂ and O₂ rather than F₂ and O₂.

Most reports of properties of O₂F₂ describe a melting point of ~109°K for the reddish solid. Goetschel *et al.*¹⁹¹ have very recently prepared O₂F₂ by the irradiation of liquid O₂-F₂ at 77°K with 3 MeV bremsstrahlung. Higher oxides produced in this preparation were decomposed by pumping at 195°K to give oxygen and O₂F₂; the latter was a pale yellow solid with a sharp melting point at 119°K. These workers believe that the previous preparations of O₂F₂ have resulted in substantial higher oxide impurities thus lowering the melting point.

TABLE 42. CONDITIONS FOR PREPARATION OF OXYGEN FLUORIDES

O/F compound	Temp. of discharge vessel (°K)	Gas		Power
		O ₂ :F ₂ ratio	Pressure (mmHg)	
O ₂ F ₂	90	1:1	12 ± 5	25-30 mA, 2.1-2.4 kV
O ₃ F ₂	77	3:2	12 ± 5	20-25 mA, 2.0-2.2 kV
O ₄ F ₂	60-77	2:1	5-15	4.5-4.8 mA, 0.8-1.3 kV
O ₅ F ₂	60-77	5:2	0.5-8	4-6 W
O ₆ F ₂	60-77	3:1	0.5-8	4-6 W

Levy and Copeland¹⁹² have observed that O₂F₂ can be formed by the photolysis of gaseous O₂-F₂ mixtures at -42°C (no reaction at 0°C)—this reaction will be considered further under O₂F.

Physical Properties

Following Goetschel, O₂F₂ at low temperature is a pale yellow solid which melts at 119°K to give a yellow liquid. The compound is thermally unstable at room temperature, the rate of decomposition to O₂ and F₂ increasing rapidly above about 150°K.

Table 43 summarizes most of the important physical properties of O₂F₂. Certain unusual properties are of particular interest:

- (1) The O-O bond length is surprisingly short, being almost the same as in O₂ itself; the O-F bond length is considerably *longer* than in OF₂.
- (2) The infrared spectrum shows an O-O stretching vibration at 1306 cm⁻¹, which though lower in frequency than the corresponding mode in O₂F (1499 cm⁻¹) leads to a similar O-O force constant.
- (3) The ¹⁹F chemical shift is a very long way to low field of (i.e. less shielded than) CFCI₃.

¹⁹⁰ A. G. Streng and L. V. Streng, *Inorg. Nucl. Chem. Letters* **2** (1966) 107.

¹⁹¹ C. T. Goetschel, V. A. Campanile, C. D. Wagner and J. N. Wilson, *J. Am. Chem. Soc.* **91** (1969) 4702.

¹⁹² J. B. Levy and B. K. W. Copeland, *J. Phys. Chem.* **69** (1965) 408; **72** (1968) 3168.

- (4) The activation energy for the thermal decomposition (17.3 kcal mole⁻¹) is perhaps assignable to FOOF → F + OOF. Mass spectral studies suggest a value of 18 kcal mole⁻¹ for this step.

Chemical Properties

Dioxygen difluoride is a particularly powerful oxidizing agent. Because of the instability of O₂F₂, reactions must be carried out under cryogenic conditions and even then explosions

TABLE 43. PHYSICAL PROPERTIES OF DIOXYGEN DIFLUORIDE, O₂F₂

Melting point ^a	-154°C (119°K)		
Boiling point (theoretical, from extrapolation)	-57°C (216°K)		
Decomposition: $-\frac{d(O_2F_2)}{dt} = [O_2F_2] \times 10^{12.4} e^{-1700/4.57T}$			
Activation energy for thermal decomposition	17.3 kcal mole ⁻¹		
Heat of vaporization	4.583 ± 0.10 kcal mole ⁻¹		
Vapour pressure	log <i>p</i> (mmHg) = 7.515 - 1000/ <i>T</i> (<i>T</i> < 173°K)		
Heat of formation (Δ <i>H</i> _f)	4.73 ± 0.30 kcal mole ⁻¹		
<i>D</i> (FO-OF) ^b	103.5 ± 5 kcal mole ⁻¹		
<i>D</i> (F-OOF) ^b	≈ 18 kcal mole ⁻¹		
Ionization potential ^b	300-310 kcal mole ⁻¹ (13.0-13.4 eV)		
Density (liquid)	2.074-0.002 917 g cc ⁻¹ (117-186°K)		
Ultraviolet spectrum (solution in freon 13, at 77°K)	λ (Å)	3500 4000 4500 5000 6000 7000	
	ε (l mole ⁻¹ cm ⁻¹)	13.13 8.02 2.52 0.63 0.10 0.10	
Dipole moment	1.44 ± 0.04 D		
Infrared maxima (solid) (cm ⁻¹) ^c	¹⁶ O ₂ F ₂	¹⁸ O ₂ F ₂	
	1306	1239	O-O stretch
	621	595	O-F sym. stretch
	615	586	O-F asym. stretch
	457	444	O-O-F asym. bend
	369	362	O-O-F sym. bend
	205	—	torsion
Force constants ^e (mdyn Å ⁻¹)	<i>f</i> _{OF}	1.36	<i>f</i> _{oo} 10.25
	<i>f</i> _{oof}	1.17	<i>f</i> _r 0.455
	<i>f</i> _{oo-of}	1.18	<i>f</i> _{of-ooof} 0.114
Structure of gas (microwave)	<i>r</i> (O-O) = 1.217 ± 0.003 Å		
	<i>r</i> (O-F) = 1.575 ± 0.003 Å		
	OOF angle = 109° 30' ± 30'		
	dihedral angle = 87° 30' ± 30'		
Chemical shift: ¹⁹ F (v. CFCl ₃ in ppm) liquid, -865 ± 1 ^d ; dil. solution in CF ₃ Cl, -825 ± 10 ^e			
	¹⁷ O (v. H ₂ ¹⁷ O in ppm) liquid, -647 ^f		

Unless otherwise stated, data from A. G. Streng, *Chem. Revs.* **63** (1963) 607 and/or E. W. Lawless and I. C. Smith, *Inorganic High-energy Oxidisers*, Arnold, London, and Dekker, New York (1968).

^a C. T. Goetschel, V. A. Campanile, C. D. Wagner and J. N. Wilson, *J. Am. Chem. Soc.* **91** (1969) 4702.

^b T. J. Malone and H. A. McGee, Jr., *J. Phys. Chem.* **69** (1965) 4338; **70** (1966) 316.

^c K. R. Loos, C. T. Goetschel and V. A. Campanile, *Chem. Commun.* (1968) 1633; *J. Chem. Phys.* **52** (1970) 4418; D. J. Gardiner, N. J. Lawrence and J. J. Turner, *J. Chem. Soc. A* (1971) 400.

^d J. W. Nebgen, F. I. Metz and W. B. Rose, *J. Am. Chem. Soc.* **89** (1967) 3118.

^e N. J. Lawrence, J. S. Ogden and J. J. Turner, *Chem. Commun.* (1966) 102; *J. Chem. Soc. A* (1968) 3100.

^f I. J. Solomon, J. K. Raney, A. J. Kacmarek, R. G. Maguire and G. A. Noble, *J. Am. Chem. Soc.* **89** (1967) 2015.

frequently occur. A reactant can be condensed on to solid O_2F_2 at 77°K and slowly be allowed to warm to the reaction temperature; liquid O_2F_2 can be slowly dropped on to liquid or solid reactants; reactions with gases can be studied by bubbling the gases through liquid O_2F_2 or its solution in freons. Streng^{167, 193} has provided a comprehensive list of reactions, and more recent work is briefly described by Lawless and Smith¹⁶⁹.

Some violent reactions with largely uncharacterized products involve liquid O_2F_2 with organic compounds, solid NH_3 (110°K), ice (130–140°K), S (90°K), charcoal, platinum coated with PtF_4 (160°K). With liquid NO_2F and liquid N_2F_2 , O_2F_2 mixes in all proportions, but it is insoluble in liquid NF_3 .

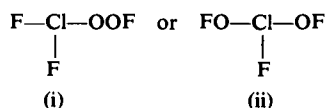
The overall result of many reactions with compounds or low fluorides is conversion into high fluorides. Streng¹⁹³ has established the stoichiometry of several such reactions and knowing the appropriate heats of formation has calculated the heats of reaction. For example:

	ΔH (kcal mole ⁻¹)
$O_2F_2 + ClF \rightarrow ClF_3 + O_2$	-30.1
$O_2F_2 + BrF_3 \rightarrow BrF_5 + O_2$	-46.1
$O_2F_2 + SF_4 \rightarrow SF_6 + O_2$	-121.5
$O_2F_2 + \frac{1}{2}HCl \rightarrow \frac{1}{2}ClF_3 + \frac{1}{2}HF + O_2$	-45.7
$O_2F_2 + \frac{1}{2}HBr \rightarrow \frac{1}{2}BrF_5 + \frac{1}{2}HF + O_2$	-58.9
$O_2F_2 + \frac{1}{2}H_2S \rightarrow \frac{1}{2}SF_6 + \frac{1}{2}HF + O_2$	-108.2

In those reactions with the smallest ΔH values it has been possible to obtain strong evidence for intermediate addition compounds. For example, if the reaction of ClF and O_2F_2 is carried out above 140°K, there is a violent reaction following the above equation; however, at lower temperatures (119–130°K), and with slow addition of ClF , a violet compound of formula O_2ClF_3 is obtained:

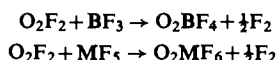


This compound can also be produced by the slow addition of Cl_2 to O_2F_2 at 130°K, by the reaction of O_2F_2 and HCl at 130–140°K and by the ultraviolet irradiation of liquid ClF_3 under a pressure of approximately 2 atm of O_2 at 195°K. The solid violet compound is stable at 195°K and is readily soluble in ClF , O_2F_2 , ClF_3 , HF ; the conductivity of non-aqueous HF is unchanged on addition of O_2ClF_3 . The most likely structures are



In view of the evidence (see below) that O_2F_2 behaves as $F + OOF$ but not $FO + OF$, (i) is the more probable. Other similar compounds proposed include O_2BrF_5 and O_2SF_6 , the evidence for the latter being sketchy.

With the avid fluoride ion acceptors BF_3 , PF_5 , AsF_5 and SbF_5 , dioxygen difluoride reacts to form O_2BF_4 and O_2MF_6 ($M = P, As, Sb$):



¹⁹³ A. G. Streng, *J. Am. Chem. Soc.* **85** (1963) 1380.

These solids are paramagnetic and almost certainly are best formulated as $O_2^+BF_4^-$ and $O_2^+MF_6^-$ (infrared, Raman and X-ray powder evidence). The boron compound has been intensively investigated. It is only slowly decomposed in the absence of moisture at 0°C, but it is an extremely active oxidizing agent; for example, benzene inflames on addition of a small particle of O_2BF_4 at room temperature. Hydrolysis of O_2BF_4 produces O_2 , O_3 , F_2 and HF .

Finally, O_2F_2 and xenon react to give XeF_2 via an unstable yellow intermediate which may be $XeOF_2$ ¹⁹⁴.

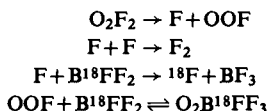
Properties Relevant to Reaction Mechanism and the OOF Radical

As mentioned above, thermal decomposition and mass spectral studies are consistent with the step $FOOF \rightarrow F + OOF$. Recent infrared matrix isolation work on O_2F_2 co-condensed from a low-temperature bath with a stream of argon or nitrogen or CO_2 at 15°K provides evidence for O_2F and O_4F_2 ¹⁹⁵.

Electron spin resonance studies on either liquid or solid O_2F_2 or solutions of O_2F_2 in freons at low temperature show the presence of a high concentration of free radical¹⁹⁶. The spectra (except for solids where free rotation is prevented) consist of a symmetrical doublet with $g \sim 2.004$ and $A \sim 12$ gauss. These spectra are identical¹⁹⁷ to that obtained by electron irradiation of liquid CF_4 containing traces of O_2 and certainly ascribable to O_2F (see below).

Direct chemical evidence that O_2F_2 behaves as $F + OOF$ has only been obtained fairly recently. At $-183^\circ C$, O_2F_2 and C_3F_6 in $CClF_3$ reacted smoothly to give a reasonable yield of a fraction containing $CF_3CF(OOF)CF_3$ and $CF_3CF_2CF_2(OOF)$ ¹⁹⁸ (cf. O_2F_2 with ClF , above).

Solomon *et al.*¹⁹⁹ have investigated the O_2F_2/BF_3 reaction using ^{18}F as a tracer; the data are consistent with the following reaction scheme:



The equilibrium in the final step was demonstrated by boron exchange of $B^{18}FF_2$ with $O_2^{10}BF_4$ at room temperature. It should also be mentioned here that O_4F_2 , which is believed to be in equilibrium with $2O_2F$, reacts with BF_3 much more readily than O_2F_2 to give the same product, O_2BF_4 .

Thus there is strong evidence that O_2F_2 reacts initially as $F + OOF$.

5.5. DIOXYGEN MONOFLUORIDE, O_2F

The above evidence suggests that O_2F exists at low temperature as a relatively stable entity. It should be noted that the observation of doublet e.s.r. spectra in condensed oxygen

¹⁹⁴ S. A. Morrow and A. R. Young, *Inorg. Chem.* **4** (1965) 759.

¹⁹⁵ D. J. Gardiner, N. J. Lawrence and J. J. Turner, *J. Chem. Soc. A* (1971) 400.

^{196a} P. H. Kasai and A. D. Kirshenbaum, *J. Am. Chem. Soc.* **87** (1965) 3069.

^{196b} F. E. Welsh, F. I. Metz and W. B. Rose, *J. Molec. Spectrosc.* **21** (1966) 249.

¹⁹⁷ R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.* **44** (1966) 434.

¹⁹⁸ I. J. Solomon, A. J. Kacmarek, J. N. Keith and J. K. Raney, *J. Am. Chem. Soc.* **90** (1968) 6557.

¹⁹⁹ J. N. Keith, I. J. Solomon, I. Sheft and H. H. Hyman, *Inorg. Chem.* **7** (1968) 230.

fluorides (OF_2 , O_2F_2 , " O_3F_2 ", O_4F_2) does not prove the existence of O_2F but merely O_nF since ^{16}O has no magnetic moment. However, Fessenden and Schuler¹⁹⁷ examined the e.s.r. spectra produced on electron irradiation of liquid CF_4 containing traces of $^{16}\text{O}_2$, $^{16}\text{O}^{17}\text{O}$ and $^{17}\text{O}_2$. The ^{17}O nucleus has a spin of $5/2$, and the presence of $^{16}\text{O}_2\text{F}$, $^{16}\text{O}^{17}\text{OF}$, $^{17}\text{O}^{16}\text{OF}$ and $^{17}\text{O}_2\text{F}$ was unequivocally demonstrated; the spectral parameters are given in Table 44, and it is now accepted that the same species is present in the condensed O/F systems. In addition, Metz *et al.*^{183b} concluded from e.s.r. work that O_2F was present in ^{17}O enriched pure liquid O_2F_2 .

TABLE 44. PHYSICAL PROPERTIES OF DIOXYGEN MONOFLUORIDE, O_2F

Ionization potential ^a	290 ± 5 kcal mole ⁻¹ (12.6 ± 0.2 eV)				
Dissociation bond energies ^a :					
<i>D</i> (O-OF)	85 kcal mole ⁻¹				
<i>D</i> (OO-F)	≈ 18 kcal mole ⁻¹				
Infrared maxima ^b (cm ⁻¹)	¹⁶ O ¹⁶ OF	¹⁶ O ¹⁸ OF	¹⁸ O ¹⁶ OF	¹⁸ O ¹⁸ OF	
	1495.0	(1453.9)	(1453.9)	1411.7	O-O stretch
	584.5	581.2	563.4	560.1	O-F stretch
	376.0	—	—	266.6	O-O-F bend
Force constants ^b (mdyn Å ⁻¹)	<i>f</i> _{OO} 10.50;	<i>f</i> _{OF} 1.32;	<i>f</i> _{OOF} 0.52;	<i>f</i> _{OO-OF} 0.300; <i>f</i> _{OF-OOF} 0.019	
Electron spin resonance data:					
(i) ^c <i>g</i> = 2.0038					
Hyperfine constants:					
	¹⁹ F 12.83 gauss (36.0 Mc/s)				
	¹⁷ O 22.17 and 14.50 gauss (62.2 and 40.7 Mc/s)				
(ii) ^d <i>g</i> ₁ = 2.0080, <i>g</i> ₂ = 2.0008, <i>g</i> ₃ = 2.0022					
Hyperfine tensors (¹⁹ F)					
	<i>A</i> ₁ ± 102.8 gauss (288.4 Mc/s)				
	<i>A</i> ₂ ∓ 50.2 gauss (141.1 Mc/s)				
	<i>A</i> ₃ ∓ 14.0 gauss (39.2 Mc/s)				
Isotropic constant	<i>A</i> - 12.8 gauss (36.0 Mc/s)				

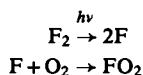
^a T. J. Malone and H. A. McGee, Jr., *J. Phys. Chem.* **69** (1965) 4338; **70** (1966) 316 (electron impact studies) the value for $D(\text{OO}-\text{F})$ assumes that $D(\text{F}-\text{OOF})$ and $D(\text{OO}-\text{F})$ are equal. The value for $D(\text{O}-\text{OF})$ assumes the same and in addition that $D(\text{OF}) = 50 \text{ kcal mole}^{-1}$.

^b Data are quoted from P. N. Noble and G. C. Pimentel, *J. Chem. Phys.* **44** (1966) 3641—photolysis of F_2 in O_2 (1:250) at 20°K . The $^{16}\text{O}^{18}\text{F}$ and $^{18}\text{O}^{16}\text{F}$ O-O stretching vibrations are calculated, using the above force constants, to be separated by only $2-3 \text{ cm}^{-1}$ and are not resolved.

^c R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.* **44** (1966) 434.

^d F. J. Adrian, *J. Chem. Phys.* **46** (1967) 1543.

Arkell²⁰⁰ and Spratley *et al.*^{201a} have obtained convincing infrared spectral evidence for O_2F by photolysis of several low temperature (4°K or 20°K) matrix mixtures, e.g. F_2 plus O_2 very dilute in argon. Presumably



and the presence of O_2F was proved by the use of $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$. For example, the band assigned to the O-F stretching vibration could be resolved under high resolution^{201b}

²⁰⁰ A. Arkell, *J. Am. Chem. Soc.* **87** (1965) 4057.

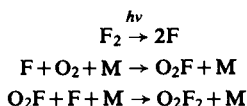
^{201a} R. D. Spratley, J. J. Turner and G. C. Pimentel, *J. Chem. Phys.* **44** (1966) 2063.

^{201b} P. N. Noble and G. C. Pimentel, *J. Chem. Phys.* **44** (1966) 3641.

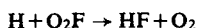
into four components, due to $^{16}\text{O}^{16}\text{OF}$, $^{16}\text{O}^{18}\text{OF}$, $^{18}\text{O}^{16}\text{OF}$ and $^{18}\text{O}_2\text{F}$ (see Table 44). On diffusion (cf. matrix work on OF) the narrow absorption at 1499 cm^{-1} changed to a broad feature at $\sim 1510\text{ cm}^{-1}$ and the rest of the spectrum remained unchanged; this is probably because diffusion results in the formation of $(\text{O}_2\text{F})_2$ which is a very weakly bonded dimer (see below).

More recently Adrian²⁰² has obtained e.s.r. spectra for O_2F by the matrix technique. These spectra are rather better than the original ones of Kasai and Kirshenbaum¹⁹⁶ from O/F compounds in solid CF_3Cl . One interesting feature of Adrian's work is the use of "forbidden" lines in which the electron spin transition is accompanied by a nuclear spin flip to obtain the relative signs of the fluorine hyperfine splitting tensor components. Theoretical work suggests that A_1 is negative, which means that the isotropic coupling constant is negative, -36.0 Mc/s .

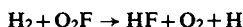
Since O_2F can be formed²⁰¹ at 4°K by the reaction $\text{F} + \text{O}_2 \rightarrow \text{O}_2\text{F}$, the activation energy for this reaction must be close to zero. Levy and Copeland¹⁹², during work on the oxygen inhibition of the H/F reaction, came to similar conclusions. As mentioned previously, at -42°C the photolysis of gaseous O_2 and F_2 gives O_2F_2 as product, presumably via



Clearly O_2F must be a relatively stable entity. [At 0°C the oxygen inhibition of the H_2/F_2 reaction does not involve what might be thought the obvious mechanism,



since the step



seems to be predominant.]

The reaction of O_2 with fluorine atoms is also presumably responsible for the very high concentrations of O_2F radicals (e.s.r. intensity evidence) which result from photolysis of liquid OF_2/O_2 mixtures²⁰³.

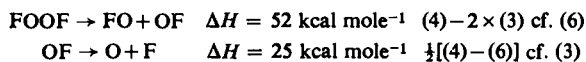
5.6. ENERGETICS AND NUCLEAR MAGNETIC RESONANCE

Before considering the chemistry of other oxygen fluorides two general topics will be considered.

Energetics of O/F Species

So far values for various energy terms have been quoted. This seems an appropriate place to point out that they are not all self-consistent.

From Table 45 we obtain:



Clearly one or more of $\Delta H_f^\circ(\text{OF}_2)$, $\Delta H_f^\circ(\text{O}_2\text{F}_2)$, $D(\text{F}-\text{OF})$, $D(\text{F}-\text{OOF})$, $D(\text{FO}-\text{OF})$ must

²⁰² F. J. Adrian, *J. Chem. Phys.* **46** (1967) 1543.

²⁰³ N. J. Lawrence, J. S. Ogden and J. J. Turner, *J. Chem. Soc. A*, 1968, 3100.

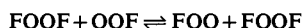
be wrong, but it is not possible to say which. However, it is clear that the O-O bonds in FOOF and OOF are particularly strong and the O-F bonds weak.

TABLE 45. SUMMARY OF SOME ΔH VALUES

	ΔH (kcal mole ⁻¹)	Method
(1) FOF \rightarrow F + O + F	90	Calorimetry
(2) FOF \rightarrow F + OF	40	Electron impact
(3) OF \rightarrow O + F	50	and kinetics
(4) FOOF \rightarrow F + O + O + F	152	(1)-(2)
(5) FOOF \rightarrow F + OOF	18	Calorimetry
(6) FOOF \rightarrow FO + OF	103	Electron impact
(7) OOF \rightarrow OO + F	18	Electron impact
(8) OOF \rightarrow O + O + F	137	(7) + D (O-O)

Free Radicals and Nuclear Magnetic Resonance

It is well known that paramagnetic species in solution can affect the position and line widths of n.m.r. signals; usually, of course, n.m.r. signals from free radicals themselves are too broad to observe. Of particular relevance to oxygen fluoride work is the paper by de Boer and Maclean²⁰⁴ on the effect of paramagnetic species exchanging with the molecule being studied. For example, in the equilibrium



the dependence of the ¹⁹F chemical shift of O₂F₂ on O₂F can be expressed by

$$\frac{\Delta H}{H} = -\frac{g\beta}{g_N\beta_N} \times a \times \frac{S(S+1)}{3kT} \times f_p \left[1 + \frac{f_d \tau_p^2 a^2 / 4}{1 + 2\tau_p T_{1e}^{-1}} \right]^{-1} \quad (5)$$

where $g\beta$ and $g_N\beta_N$ are the gyromagnetic ratios in Bohr magnetons of the electron and nucleus N (¹⁹F in this case), a is the hyperfine interaction constant, S is the nuclear spin of N ($\frac{1}{2}$ for ¹⁹F), f_p , f_d are the fractions of para- and dia-magnetic species respectively, τ_p is the lifetime of the free radical and T_{1e} is the electron longitudinal relaxation time. For this equilibrium eqn. (5) becomes

$$\frac{\Delta H}{H} = -\frac{g\beta}{g_N\beta_N} \times \frac{a}{4kT} \times \frac{f_p}{1+X}, \quad (6)$$

where X is a positive quantity. In the "slow exchange" case, X will be very large and hence $\Delta H/H = 0$, i.e. the chemical shift is unaffected by O₂F, although the line width may be affected. In the other extreme of $X = 0$, substituting for the physical constants and using the value -36 Mc/s for a ²⁰², we have

$$\frac{\Delta H}{H} \sim 10^5 \left(\frac{3f_p}{T} \right) \quad (\text{ppm}) \quad (7)$$

²⁰⁴ E. de Boer and C. MacLean, *J. Chem. Phys.* **44** (1966) 1335.

Thus at, say, 150°K , $\Delta H/H \sim 2000 f_p$. Lawrence *et al.*²⁰³ observed no change in the ^{19}F chemical shift of O_2F_2 on increasing the concentration of O_2F by an order of magnitude on addition of OF_2 —presumably f_p was very small. However, Solomon *et al.*²⁰⁵ in their studies on O_3F_2 (probably $\text{O}_2\text{F}_2 + \text{O}_4\text{F}_2 \rightleftharpoons 2\text{O}_2\text{F}$, see below) observed that the ^{19}F signal of O_2F_2 was very sensitive to temperature. *But* the explanation for this phenomenon must be more complex than the *simple* equilibrium suggested above since the ^{17}O n.m.r. signal seems to be *independent* of temperature. Substitution of the physical constants, $S = 5/2$ and $a \sim 50$ Mc/s, suggests a much *greater* ^{17}O variation with temperature. Conceivably a species $\text{O}_2\text{F} \dots \text{F}'\text{O}'\text{O}''\text{F}''$ in which a (F' or F'') is much greater than a (O' or O''), is responsible for the shifts.

5.7. TETRAOXYGEN DIFLUORIDE, O_4F_2 , AND THE EQUILIBRIUM $\text{O}_4\text{F}_2 \rightleftharpoons \text{O}_2\text{F}$

We shall first consider the preparation of O_4F_2 and some of its properties before returning to a discussion of the equilibrium with the O_2F radical.

Preparation

Table 42 (p. 753) has already outlined the discharge conditions for the preparation²⁰⁶ of O_4F_2 ; the compound has also been obtained by electrical discharge in OF_2/O_2 mixtures¹⁹⁰, and by radiolysis of liquid O_2/F_2 mixtures¹⁹¹.

The possibility that O_4F_2 was simply O_2F_2 with dissolved O_2 was eliminated by demonstrating that O_2 can be pumped off O_2F_2 ; the possibility of dissolved O_3 was eliminated by showing that O_3 can be extracted into liquid O_2 , whereas O_4F_2 in liquid O_2 shows no trace of ozone²⁰⁶.

Tetraoxygen difluoride is an even more powerful oxidizing agent than O_2F_2 , and is considerably less thermally stable, decomposing ultimately into 2O_2 and F_2 , via O_2F_2 and O_2 .

Physical Properties

The dark red-brown solid melts at -191°C (82°K) to give a similarly coloured liquid. The vapour pressure is "less than 1 mm at 90°K "²⁰⁶.

Electron spin resonance spectra^{196a, 207} of O_4F_2 show *very* intense signals due to the O_2F radical. Thus although it has been possible to obtain *some* physical data for O_2F , data for O_4F_2 must be treated with caution, and there has been no really systematic investigation of physical properties. However, since there is very strong evidence²⁰⁵ that O_3F_2 is a mixture of O_4F_2 and O_2F_2 , and several physical properties of O_3F_2 have been measured (see Table 46) it may be possible to estimate O_4F_2 properties from Tables 43 and 46—the reader is left to do this for himself.

Chemical Properties

Again there is virtually no information, but the reader can make what use seems appropriate of the descriptions of the properties of O_2F_2 (above) and O_3F_2 (below).

^{205a} I. J. Solomon, J. K. Raney, A. J. Kacmarek, R. G. Maguire and G. A. Noble, *J. Am. Chem. Soc.* **89** (1967) 2015.

^{205b} I. J. Solomon, J. N. Keith, A. J. Kacmarek and J. K. Raney, *J. Am. Chem. Soc.* **90** (1968) 5408.

²⁰⁶ A. V. Grosse, A. G. Streng and A. D. Kirshenbaum, *J. Am. Chem. Soc.* **83** (1961) 1004; A. G. Streng, *Can. J. Chem.* **44** (1966) 1476.

²⁰⁷ A. D. Kirshenbaum and A. G. Streng, *J. Am. Chem. Soc.* **88** (1966) 2434.

The Equilibrium $\text{O}_4\text{F}_2 \rightleftharpoons 2\text{O}_2\text{F}$

The ready reaction of O_4F_2 with BF_3 to give O_2BF_4 does underline its behaviour as $2\text{O}_2\text{F}$.

The e.s.r. spectrum of O_4F_2 ($\sim 3\%$ by volume) in *solid* CF_3Cl at 77°K has been interpreted on the basis of ~ 5 mole % concentration of O_2F ^{196a}. Goetschel *et al.*¹⁹¹ have reconsidered this and propose an equilibrium constant at about 80°K of 8×10^{-5} in mole fraction units. This equilibrium constant is only meaningful if the *solid* CF_3Cl readily permits diffusion, otherwise O_2F radicals may be trapped in a cage of CF_3Cl molecules. Note that in the matrix isolation studies the O_2F infrared band at 1499 cm^{-1} only disappeared after warming to the diffusion temperature (40°K). It seems reasonable to assume that at temperatures close to the melting point of CF_3Cl (92°K), it is readily diffusing. Assuming from analogous dimerizations that the standard entropy change is ~ 15 e.u., the authors calculate a standard enthalpy change of ~ 3 kcal mole⁻¹.

Fessenden and Schuler¹⁹⁷ concluded that at about 10^{-3} molar in liquid CF_4 ($\sim 100^\circ\text{K}$) the "radical does not exist largely as the dimer". These two e.s.r. observations are not irreconcilable since the great dilution in CF_4 would drive the equilibrium to the right.

To date no one has published data on the n.m.r. spectrum of O_4F_2 by examining O_4F_2 . However, Solomon *et al.*²⁰⁵ believe that they have obtained ^{19}F and ^{17}O spectra for O_4F_2 by examining liquid O_3F_2 (see below). The position of the ^{19}F signal was a sensitive function of temperature, ascribable presumably to some exchange process probably more complex than just $\text{O}_4\text{F}_2 \rightleftharpoons 2\text{O}_2\text{F}$. The situation is complicated, however, by the decomposition of O_2F , probably into O_2F_2 and O_2 , and, in fact, Solomon concludes that between 83° and 110°K the concentration of radicals *decreases* with temperature.

It is clear that because of the great difficulty in handling these compounds, the equilibrium is not yet fully understood.

5.8. TRIOXYGEN DIFLUORIDE, O_3F_2

At various times so far it has been suggested that O_3F_2 is really a mixture of O_4F_2 and O_2F_2 . Before considering the evidence for this conclusion we shall first outline the preparation and properties of this "compound".

Preparation

Trioxygen difluoride is prepared by the reactions of O_2 and F_2 in the electric discharge (see Table 42) or OF_2 and F_2 in the discharge¹⁹⁰. The assignment of the formula O_3F_2 to the compound depends only on the ratio of $\text{O}_2:\text{F}_2$ consumed and the ratio of $\text{O}_2:\text{F}_2$ obtained on thermal decomposition.

Physical Properties

Bearing in mind that O_3F_2 is probably a mixture of O_2F_2 and O_4F_2 , some of the physical properties described by Streng¹⁶⁷ are outlined in Table 46.

Chemical Properties

Not surprisingly, O_3F_2 is a potent oxidizing agent and is unstable at temperatures above its melting point although it can be stored indefinitely at 77°K in dark, dry Pyrex. It is soluble in OF_2 , O_2F_2 and O_3 although the latter solution can readily explode.

Some idea of its reactivity is demonstrated by dropping liquid O_3F_2 on to solid anhydrous ammonia at 90°K when an instantaneous flame and explosion results; its behaviour is similar with a whole range of compounds. There is some evidence for the formation of a purple species (O_2ClF_3 ?) on reaction of O_3F_2 and ClF at 77°K —at 90°K an explosion occurs.

“ O_3F_2 ” or “ $\text{O}_2\text{F}_2 + \text{O}_4\text{F}_2$ ”

Solomon *et al.*²⁰⁵ have carefully examined the ^{19}F and ^{17}O n.m.r. spectra of liquid O_3F_2 . The ^{17}O spectrum consisted of three lines, one at -647 ppm (w.r.t. H_2^{17}O) and a pair of lines of equal intensity at -971 and -1512 ppm; the first line was easily attributable to O_2F_2 by performing experiments with O_2F_2 alone. It is difficult to assign two lines of equal intensity to a molecule of such structure as FOOOF . Solomon believes this pair is due to O_4F_2 , i.e. $\text{FO}'\text{O}''\text{O}'\text{O}'\text{F}$, one line arising from O' nuclei and one from O'' nuclei. Moreover, the ^{19}F spectrum of O_3F_2 was an asymmetrical line resolved with difficulty into two overlapping lines—one presumably due to O_2F_2 and one due to O_4F_2 . The position of these ^{19}F lines, as described previously, was a sensitive function of temperature, probably due to some exchange mechanism with O_2F . Because of the apparent lack of temperature sensitivity of the ^{17}O signals, it is not possible to decide on a mechanism at this stage.

TABLE 46. PHYSICAL PROPERTIES OF TRIOXYGEN DIFLUORIDE, O_3F_2

Melting point	-190°C (83°K)
Boiling point	-60°C , decomposes (213°K)
Decomposition temperature	above m.p.
Heat of vaporization	4.581 ± 0.2 kcal mole $^{-1}$
Vapour pressure	$\log p$ (mmHg) = $6.1343 - \frac{675.57}{T}$ (79 – 114°K)
Heat of formation (ΔH_f°)	6.24 ± 0.75 kcal mole $^{-1}$
Density of liquid	$d = 2.357 - 0.00676T$ g cc $^{-1}$

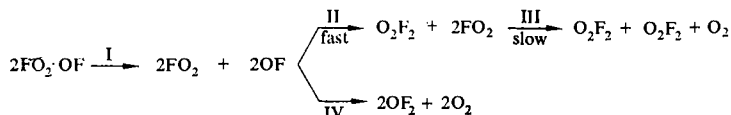
Data from A. G. Streng, *Chem. Revs.* **63** (1963) 607.

Metz *et al.*²⁰⁸ have also examined the ^{19}F n.m.r. spectra of liquid O_3F_2 . They did not resolve the signal into two components and concluded that O_3F_2 could *not* be a mixture of O_2F_2 and O_4F_2 . They did, however, on theoretical grounds reject the structure FOOOF and suggested that O_3F_2 is O_2F_2 plus “interstitial oxygen molecules” on the grounds that the only decomposition products of O_3F_2 are O_2F_2 and O_2 . These workers object to the $\text{O}_4\text{F}_2/\text{O}_2\text{F}_2$ mixture theory on the grounds that the chemical shift of *pure* O_2F_2 is insensitive to temperature and that if Solomon’s ^{19}F doublet were due to O_2F_2 and O_4F_2 the O_2F_2 signal should stay in the same place as the temperature was raised. However, as described previously, this insensitivity of O_2F_2 observed by Metz and Lawrence *et al.*²⁰³ is probably due to the very low concentration of O_2F ; in Solomon’s work the O_2F concentration was probably very high.

²⁰⁸ J. W. Nebgen, F. I. Metz and W. B. Rose, *J. Am. Chem. Soc.* **89** (1967) 3118.

²⁰⁹ T. J. Malone and H. A. McGee, *J. Phys. Chem.* **71** (1967) 3060.

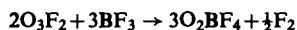
Malone and McGee²⁰⁹ have examined the variation in fragment intensity pattern with temperature in the mass spectra of O_3F_2 and O_3F_2/O_2F_2 mixtures using a cryogenic inlet system. They concluded from this variation and appearance potential data that the OF^+ ion came from OF_2 which was itself a decomposition product of O_3F_2 . They propose that O_3F_2 is best described as a loose adduct of the radicals OF and O_2F :



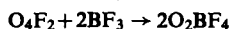
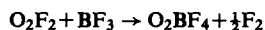
Such a mechanism explains the substantial concentration of O_2F (e.s.r. evidence) since III is slow. Moreover the authors believe the formation of O_2F_2 and O_2 would "predominate over the formation of OF_2 and O_2 ".

Malone and McGee point out that Linnett structures can be drawn for O_3F_2 , analogous to O_3 in its first excited state, and that these structures exhibit the basic features of OF and O_2F joined by a weak, single electron bond.

Solomon *et al.*^{205b} have objected to both Metz *et al.* and Malone and McGee. Firstly, they have repeated their ^{19}F work on O_3F_2 and are convinced that there are *two* signals. Secondly, they can find no n.m.r. evidence for OF_2 on allowing O_3F_2 to slowly decompose in a n.m.r. tube. Thirdly, experiments involving the reaction of BF_3 with O_4F_2 , O_3F_2 and O_2F_2 confirm that, on the basis of the ratio of BF_3 consumed to F_2 formed, the stoichiometry of the reaction with O_3F_2 ,



is consistent with the sum of the reactions with O_2F_2 and O_4F_2



If O_3F_2 were $O_2F_2 +$ "interstitial O_2 ", then presumably O_2 would be released; if it were $FO_2 \cdot OF$, then it is arguable that since O_2F_2 and O_4F_2 behave as sources of O_2F (see above), $FO_2 \cdot OF$ would act as $FO_2 + OF$ and the OF released would decompose to $O_2 + F_2$.

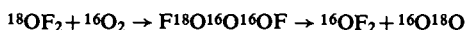
On balance, therefore, the present author supports the O_2F_2/O_4F_2 mixture hypothesis.

The absence of a molecular FOOOF compound is not surprising on energetic grounds. O_2F_2 and O_4F_2 are readily formed by the addition of fluorine atoms to O_2 molecules in the discharge or other systems, the ratio of O_2F_2 to O_4F_2 depending on the ratio of F_2 to O_2 in the gas mixture.



Molecular O_3F_2 would require oxygen atom production with its large energy requirement and, conversely, would probably be very unstable.

This, of course, does not prevent the formation of FOOOF under other conditions, and in fact Arkell²⁰⁰ obtained *some* evidence for this species in his O_2F matrix experiments. Since $^{16}OF_2$ was produced during photolysis of $^{18}OF_2$ in $^{16}O_2$ he concluded that an exchange mechanism involving O_3F_2 might be important:



Clearly such possibilities merit further exploration.

5.9. PENTAOXYGEN DIFLUORIDE, O_5F_2 , AND HEXAOXYGEN DIFLUORIDE, O_6F_2

Preparation

These two species have been reported by Streng and Grosse²¹⁰ to be formed by electric discharge at low temperature and under mild discharge conditions in O_2/F_2 gas mixtures of appropriate composition. The products were analysed by allowing them to decompose on warming and estimating the oxygen to fluorine ratio.

Properties

O_5F_2 is a reddish-brown liquid at 90°K, similar to O_4F_2 ; at 77°K, O_5F_2 forms an oil. Although stable at 77°K it decomposes at 90°K giving, finally, O_2 and F_2 . The e.s.r. spectrum is said to be substantially different from that of O_4F_2 .

O_6F_2 is a crystalline solid at 60°K with a metallic lustre. Slow warming to 90°K results in decomposition to lower oxygen fluorides and ozone; fast warming to 90°K leads to explosion; the compound even exploded on occasions when illuminated by a flashlight.

Attempts to prepare higher oxygen fluorides failed, and the authors suggest that if any are prepared it will be at temperatures below 60°K.

If the species exist as FOOOOOF and FOOOOOOF, the authors make the interesting suggestion that hydrogen atom reaction at low temperature *could* lead to cyclic O_5 and O_6 molecules.

Much more information is required about these species before molecular formulae can be determined.

5.10. OTHER OXYGEN FLUORIDE POSSIBILITIES

During Arkell's²⁰⁰ matrix work on O_2F he observed bands at 1503 and 1512 cm^{-1} on photolysis of F_2 in O_2 at 4°K. These were partially resolved sidebands on the side of the 1496 cm^{-1} band which was assigned to the O—O stretching vibration of O_2F . Arkell has suggested that these other two bands are due to O_3F and O_4F , but there is no firm evidence available yet.

Some support for the existence of such species is provided by Goetschel's²⁰¹ electron irradiation preparative work. Certain highly unstable products were obtained in small concentration, and the authors suggest the possible presence of O_4F or O_6F_2 . As well as the reaction of O_2F_2 with BF_3 to give O_2BF_4 there was *some* evidence for less stable BF_4^- salts, conceivably $O_4^+BF_4^-$ (from $O_4F + BF_3$?) and $O_6^+BF_4^-$ (from $O_6F + BF_3$?). Clearly these suggestions are highly speculative at this stage, and it is obvious that oxygen fluorine chemistry is not yet "all tied up".

5.11. COMPOUNDS OF CF_3 , FLUORINE AND OXYGEN

It would be possible to compare the properties of the oxygen fluorides with a wide range of species. However it is instructive to consider a single class of compounds which might be expected to have similar properties to oxygen fluorides—at least structurally—the CF_3 derivatives. Recently the field of C/F/O chemistry has expanded considerably and many interesting new compounds have been made. In what follows we shall concentrate simply on those species which can be theoretically derived from the corresponding O/F species

by substitution of one or more fluorine atoms by the CF₃ group. The compounds of particular interest are:



Trifluoromethyl Hypofluorite, CF₃OF

This is a stable colourless gas prepared²¹¹ by the reaction of fluorine in the presence of silver(II) fluoride catalyst with CO, CO₂, COF₂ or methanol vapour. Some physical properties are listed in Table 47.

TABLE 47. SOME PHYSICAL PROPERTIES OF CF₃OF

Melting point ^a	-215°C (58°K)
Boiling point ^a	-95°C (178°K)
Heat of formation ^b	-184.0 ± 2.5 kcal mole ⁻¹
D (CF ₃ O-F) ^c	43.5 ± 0.5 kcal mole ⁻¹

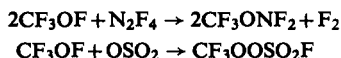
^a C. J. Hoffmann, *Chem. Revs.* **64** (1964) 91.

^b D. R. Stull, *JANAF Chemical Tables* (1964).

^c J. Czarnowski, E. Castellano and H. J. Schumacher, *Chem. Commun.* (1968) 1255.

There has also been a thorough investigation of the vibrational spectrum of CF₃OF²¹².

The important feature about CF₃OF is that it behaves as CF₃O + F not as CF₃ + OF. For example,



Photochemical behaviour also seems to be dependent on an initial step to give CF₃O + F. For example, as well as COF₂, CF₃OOCF₃ results from the gas phase photolysis of CF₃OF alone²¹³. The existence of CF₃O as intermediate is also inferred from the photochemical reaction of F₂ with COF₂ to give CF₃OF at room temperature²¹⁴.

In spite of this indirect evidence there is as yet no positive identification of the CF₃O radical. For instance, the photolysis²¹⁵ of CF₃OF in argon at 15°K with a variety of photolytic sources gives only COF₂—presumably because the CF₃O intermediate readily decays spontaneously to COF₂ + F or because the radical is more photosensitive than the parent CF₃OF.

The Trifluoromethoxide Ion, OCF₃⁻

The use of fluoride salts, especially caesium, for the preparation of several CF₃/O/F type compounds suggests a mechanism involving a fluoro anion. In fact the reaction²¹⁶ of a

²¹⁰ A. G. Streng and A. V. Grosse, *J. Am. Chem. Soc.* **88** (1966) 169.

²¹¹ See C. J. Hoffmann, *Chem. Revs.* **64** (1964) 91.

²¹² P. M. Wilt and E. A. Jones, *J. Inorg. Nucl. Chem.* **30** (1968) 2933.

²¹³ C. I. Merrill and G. H. Cady, Second International Symposium on Fluorine Chemistry, *J. Am. Chem. Soc.* **1962**, 414.

²¹⁴ P. J. Aymonino, *Proc. Chem. Soc.* **1964**, 341.

²¹⁵ R. D. Clarke, A. J. Rest and J. J. Turner, unpublished observations.

²¹⁶ M. E. Redwood and C. J. Willis, *Can. J. Chem.* **43** (1965) 1893.

heavy alkali metal fluoride (MF), suspended in CH_3CN at 20°C , with COF_2 gas leads to the isolation of $\text{M}^+(\text{OCF}_3)^-$, which anion is isoelectronic with BF_4^- . Other, less stable, salts of this kind which have been prepared include $\text{OCF}_2\text{CF}_3^-$, $\text{OCF}_2\text{CF}_2\text{CF}_3^-$ and $\text{OCF}(\text{CF}_3)_2^-$.

It is noteworthy that although F^- is easily obtained, CF_3^- does not exist, and although OF^- is not a stable entity, OCF_3^- is.

Perfluorodimethyl Peroxide, CF_3OOCF_3

Preparation. On heating equimolar quantities of CF_3OF and COF_2 to about 290°C and then cooling to room temperature, a substantial conversion to CF_3OOCF_3 resulted²¹⁷. The compound can also be produced by heating F_2 and CO_2 (2:1 ratio) to 325°C and then cooling and also by passing F_2 and CO (3:2) through a reactor containing a catalyst composed of copper ribbon coated with fluorides of silver.

Properties. CF_3OOCF_3 is a stable colourless gas (cf. FOOF) at room temperature with a boiling point $\sim -37^\circ\text{C}$. The compound begins to decompose at about 225°C .

In its chemistry CF_3OOCF_3 behaves as $(\text{CF}_3\text{O})_2$ not $\text{CF}_3 + \text{OOCF}_3$. In fact there is no evidence for the OOCF_3 radical. The dissociation into CF_3O radicals is greatly helped by photolysis with ultraviolet light.

There is little structural information on this compound but the infrared spectrum²¹⁸ does suggest that the C–O and O–O bonds are ordinary single bonds; certainly there is no evidence for the very strong O–O bond found in O_2F_2 .

Trifluoromethyl Trioxide, CF_3OOO

Vanderkooi and Fox²¹⁹ studied the e.s.r. spectra of photolysed solutions of CF_3OF and CF_3OOCF_3 in NF_3 as solvent at low temperature. They assigned the six line spectra produced in both cases to CF_3OO ; a freely rotating CF_3 group would produce a 1:3:3:1 quartet, and the authors explained the doublet of triplets observed on the basis of restricted rotation. (^{19}F hyperfine splittings = 6.72 and 0.54 gauss.) More recently, Fessenden²²⁰ has examined the photolysis of CF_3OOCF_3 (and $\text{CF}_3^{17}\text{OOCF}_3$) in NF_3 solution at -196°C in the presence of traces of oxygen and ^{17}O enriched oxygen. These results demonstrate that the radical produced is not CF_3OO , but CF_3OOO with $g = 2.00373 \pm 0.00001$ and ^{17}O hyperfine constants 23.3, 14.0 (CF_3OOO), 3.59 (CF_3OOO) gauss. The point is also made that the g value is markedly different from other RO_2 radicals and provides a further reason for rejecting CF_3OO . However, the two larger ^{17}O hyperfine constants and the g value are very close to those of O_2F . Presumably, therefore, the CF_3O radical produced on photolysis immediately reacts with an O_2 molecule to give $(\text{CF}_3\text{O})\text{O}_2$ in precisely the same way as fluorine atoms react with O_2 to give O_2F . It is tempting therefore to postulate that the terminal O–O band in CF_3OOO is likely to be very strong and that when comparing the chemistry of fluorine with CF_3 species the unit of comparison should be CF_3O rather than CF_3 .

²¹⁷ R. S. Porter and G. H. Cady, *J. Am. Chem. Soc.* **79** (1957) 5628.

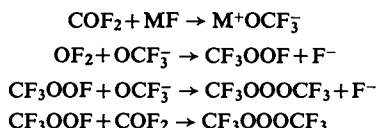
²¹⁸ A. J. Arvia and P. J. Aymonino, *Spectrochim. Acta* **18** (1962) 1299; D. W. Wertz and J. R. Durig, *J. Mol. Spectrosc.* **25** (1968) 467.

²¹⁹ N. Vanderkooi and W. B. Fox, *J. Chem. Phys.* **47** (1967) 3634.

²²⁰ R. W. Fessenden, *J. Chem. Phys.* **48** (1968) 3725.

Bis (Trifluoromethyl) Trioxide, CF₃OOOCF₃

Preparation. Although this compound can be obtained by the direct fluorination^{221a} of salts of trifluoroacetic acid, it is best prepared^{221b} by the reaction of OF₂ with COF₂ over a caesium fluoride catalyst. The postulated mechanism for this reaction,



has received support from ¹⁷O tagging experiments^{221c}.

Properties. CF₃OOOCF₃ is a stable material with a melting point of -138°C and a normal boiling point of -16°C. It begins to decompose in glass at about 70°C to give CF₃OOCF₃ and O₂ along with trace amounts of COF₂ and SiF₄.

CF₃OOOCF₃ reacts with N₂F₄, SF₄, SO₂, etc., to give simple CF₃O products (CF₃ONF₂, CF₃OSF₄OCF₃, etc.) which can also be obtained by starting with CF₃OOCF₃ or CF₃OF²²². However, the reactions are cleaner and more controllable than corresponding reactions with CF₃OF and proceed with higher yield and at lower temperature.

Electron spin resonance experiments similar to those with CF₃OF and CF₃OOCF₃ in NF₃ demonstrated²²² the production of the same radical. It seems unlikely, in view of its chemical behaviour, that CF₃OOO results from CF₃ loss from CF₃OOOCF₃ but rather that CF₃O is first produced and this then reacts with traces of O₂.

A further important point is that the infrared spectrum²²² suggests that the C-O and O-O bonds are normal single bonds.

This might at first sight seem rather surprising since the CF₃OOO radical appears to have a very strong terminal O-O bond. In other words since FOOF and OOF both have strong O-O bonds, so should CF₃OOOCF₃ and CF₃OOO. However, if we again consider the unit CF₃O, the molecule which should possess the strong O-O bond is CF₃O·O=O·OCF₃ rather than CF₃OOOCF₃. Unfortunately the only report of CF₃OOOOCF₃ is that it may be produced as an impurity in the preparation of the trioxide^{221a}. Similarly, the only published information on CF₃OOF whose properties would be particularly interesting for a comparison of CF₃, CF₃O and F groups, is the chemical shift of the OOF fluorine: -291 ppm v. CFCF₃. This is the same as the chemical shift of FSO₂OOF, and is a long way to high field of O₂F₂ (-825 ppm). It is tempting to suggest that CF₃OOF is analogous to FOF (i.e. CF₃O-O-F), but that the fluorine resonance of CF₃OOOF, if it is prepared, will be to very low fields.

5.12. SOME COMMENTS ON THE BONDING IN OXYGEN FLUORIDES

Table 48 lists some relevant physical properties. It is important to emphasize that the use of force constants to predict bond energies is not reliable; note particularly that the F₂ force constant is greater than that for Cl₂ but that F₂ has a weaker bond than Cl₂. Generally,

^{221a} P. G. Thompson, *J. Am. Chem. Soc.* **89** (1967) 4316.

^{221b} L. R. Anderson and W. B. Fox, *J. Am. Chem. Soc.* **89** (1967) 4313.

^{221c} Private communication from I. J. Solomon to W. B. Fox.

²²² W. B. Fox, private communication; R. P. Hirschmann, W. B. Fox and L. R. Anderson, *Spectrochim. Acta A* **25** (1969) 811.

TABLE 48. SOME PHYSICAL PROPERTIES OF OXYGEN FLUORIDES AND RELATED SPECIES

Bond length ^a (Å)			Force constants ^b (mdyne/Å)				Bond dissociation energies ^c	
	r_{OH}	r_{OF}	r_{OO}	f_{OH}	f_{OF}	f_{OCl}	f_{OO}	(ΔH° kcal mole ⁻¹)
OH	0.97			7.1				OH → O + H 102
OF					5.42			OF → O + F 50
OCi	1.57					6.4 ^d		OCi → O + Cl 64
O ₂			1.21				11.43	O ₂ → 2O 119
OH ₂	0.96			7.66				HOH → H + O + H 2 × 111
								HO + H 120
OF ₂		1.41			3.95			FOF → F + O + F 2 × 45
OCl ₂						2.75 ^e		ClOCI → Cl + O + Cl 2 × 54
O ₂ H				6.46			6.2 ^f	OOH → O ₂ + H 47
								O + O + H 166
O ₂ F					1.32		10.50	O + OH 64
O ₂ Cl						1.29	9.7 ^g	OOH → O ₂ + H 18
								O + OF 87
O ₂ H ₂	0.95		1.48	7.4			4.6	HOOH → H + O ₂ + H 2 × 68
								H + OOH 88
								H + O
								+ O + H 256
								HO + OH 52
O ₂ F ₂		1.575	1.22		1.36		10.25	FOOF → FO + OF 52
								F + O ₂ F 18
								F + O + O + F 152
H ₂		($r = 0.75$)			($f = 5.13$)			H ₂ → 2H 104
F ₂		($r = 1.42$)			($f = 4.45$)			F ₂ → 2F 38
Cl ₂		($r = 1.99$)			($f = 3.20$)			Cl ₂ → 2Cl 58

^a Values from readily available books except for O₂F₂ (see Table 43) and OCi, A. Carrington, P. N. Dyer and D. H. Levy, *J. Chem. Phys.* **47** (1967) 1756.

^b Values from readily available books or this chapter except for those stated.

^c Values from NBS circulars *Selected Values of Thermodynamic Properties*, 270-1 (1965), 270-2 (1966); data for O/F compounds from previous tables.

^d Based on ν 995 cm⁻¹ (L. Andrews and J. I. Raymond, *J. Chem. Phys.* **55** (1971) 3087).

^e M. M. Rochkind and G. C. Pimentel, *J. Chem. Phys.* **42** (1965) 1361.

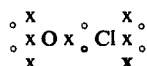
^f D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **38** (1963) 2627.

^g A. Arkell and I. Schwager, *J. Am. Chem. Soc.* **89** (1967) 5999. (N.B.—This is OOCI not OCiO and is produced by photolysis of OCiO in argon at 4°K.)

however, substantial differences in force constants imply considerable differences in bond energy in the same direction. It is also important to realize that bond dissociation energies do not necessarily bear any relation to the "intrinsic" energy of a bond. For example, in the reaction $\text{HOOH} \rightarrow \text{H} + \text{O}_2 + \text{H}$ one cannot infer an intrinsic bond energy of 68 kcal mole⁻¹ for the O–H bond since ΔH for the reaction is much affected by the formation of an O–O double bond.

The O-X Bond in OX, OX₂

The bond lengths, force constants and bond energy terms indicate that the O-H bond has the same properties in OH and OH₂. This is not surprising since there is no possibility of π -bonding or "non-bonding electron repulsion". By contrast the striking difference in the O-Cl bond in OCl and OCl₂ suggests the presence of π -bonding in OCl which would have a nominal bond order of $1\frac{1}{2}$. Linnett's²²³ double-quartet structure for OCl



is consistent with this picture since the formal charge of $+\frac{1}{2}$ on the Cl atom is acceptable.

The bond energies and force constants for OF and OF₂ suggest a slightly stronger O-F bond in OF. Simple molecular orbital theory predicts a bond order of $1\frac{1}{2}$ for OF, but the formal charge of $+\frac{1}{2}$ on the fluorine atom in the Linnett structure is not allowed.

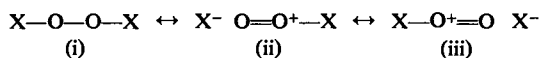
The O-X Bond in O₂X, O₂X₂

There is *some* evidence that the O-H bond in O₂H is slightly weaker than the presumably ordinary single bond in OH, OH₂ and O₂H₂. There is, however, no doubt that the O-F and O-Cl bonds in O₂F, O₂F₂ and O₂Cl are considerably weaker than the nominally single bonds in OF₂ and OCl₂. It is interesting to note that Rochkind and Pimentel²²⁴ obtained *some* matrix evidence for ClOOCl which was described as a weak dimer of OCl, i.e. the O-Cl bond was comparable with that in the OCl radical.

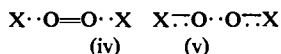
The O-O Bond in O₂, O₂X and O₂X₂

It is clear that the O-O bonds in O₂F, O₂F₂ and O₂Cl are practically the same as the double bond in O₂ itself. In O₂H the force constant suggests an O-O bond between O₂ and O₂H₂ in properties—the O-O force constant in O₃ is 7.3 mdyn Å⁻¹. Interestingly, if spectroscopic evidence²²⁴ is reliable, the O-O bond in O₂Cl₂ is very weak.

Any successful bonding model must be able to explain these phenomena plus the observations on CF₃ compounds. Simple valence-bond theory can make good sense of the difference between, say, O₂H₂ and O₂F₂:



When X = F, (ii) and (iii), which increase the O-O bond strength and decrease the O-X bond strength, can make a substantial contribution because of the electronegativity of fluorine. When X = H, this does not happen, and structure (i) predominates. Similarly, FOOOOF is predicted to have weak O-F bonds, strong terminal O-O bonds and a weak central O-O bond. However, FOOF is also predicted to be a stable entity, and "strongish" central bonds are predicted for CF₃OOCF₃ and ClOOCl. It is, of course, possible to say that whether a molecule adopts structure (iv) or (v)

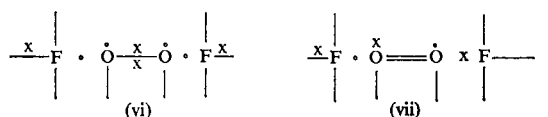


²²³ J. W. Linnett, *The Electronic Structure of Molecules*, Methuen, London, and Wiley, New York (1964).

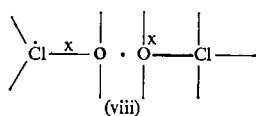
²²⁴ M. M. Rochkind and G. C. Pimentel, *J. Chem. Phys.* **46** (1967) 4481.

depends on relative bond strengths. Rochkind and Pimentel²²⁴ argued that the weak dimer [i.e. (v)] structure for ClOOCl is due to the high bond energy of the OCl radical. It is difficult to argue this way in the case of CF_3OOCF_3 since there is no reason why the C-O bond in the OCF_3 radical should be any stronger than a normal single bond. One difference between the CF_3 group and the halogen atoms is that there is no possibility of π -bonding to oxygen, and this may be important.

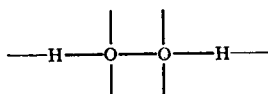
Linnett²²³ has discussed the structure of O_2F_2 and concludes that the preponderance of structures (vi) and (vii) is responsible for the long O-F and short O-O bonds.



These structures are particularly favoured because they place formal charges of $-\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$ (vi), and $-\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$ (vii) on the four atoms. It is possible that in O_2Cl_2 there is a considerable contribution from



and its mirror image; in (viii) the formal charges are $\frac{1}{2}$, 0, $-\frac{1}{2}$, 0 [which is acceptable in this case but forbidden in O_2F_2 because of the $\frac{1}{2}$ on the end halogen], and there is a weak O-O and strong O-Cl bonds. For O_2H_2 the only really likely structure is



Linnett structures are readily drawn for O_4F_2 , suggesting a loose O_2F dimer, but in the case of O_3F_2 , the only satisfactory^{208, 209} Linnett structures imply $\text{O}_2\text{F} \cdot \text{OF}$. The method can be extended to O_2X species with results in broad agreement with experimental observation. In particular a structure involving a one-electron O-O bond in O_2Cl places a formal charge of $-1\frac{1}{2}$ on the terminal oxygen which is not acceptable. Presumably structures involving a strong O-O bond then become dominant.

A quite different model was introduced by Jackson²²⁵ and subsequently extended by Pimentel *et al.*²²⁶. In the species O_2X (or O_2X_2) the X lone electron is considered to interact with one of (or both) the antibonding π -orbitals of the O_2 molecule—a [p (or s) $-\pi^*$] σ -bond. The more electron density flows from X to O_2 , the weaker the O_2 bond and the stronger the O-X bond. Consequently, in O_2F , because of electronegativity differences, it is not surprising that O-F is weak and O-O strong. In O_2H , the O-O bond order will be approximately $1\frac{1}{2}$ because of the non-interacting O_2 π system. This idea can be extended to systems

²²⁵ R. H. Jackson, *J. Chem. Soc.* 1962, 4585.

where the non-interacting π -antibonding orbital has either *two* (XNO) or *no* (XCO) electrons²²⁶. In particular, a detailed molecular orbital study²²⁷ on FNO supports such a simplified model. In O_2F_2 the model predicts strong O–O and weak O–F bonds and *similarly* for O_2Cl , contrary to the experimental evidence.

Other theoretical treatments have been suggested²²⁸ but it is probably too much to hope that any one simple model will explain such a diversity of experimental fact.

6. HYDROGEN PEROXIDE²²⁹

6.1. HISTORY

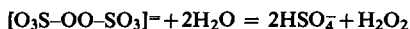
Hydrogen peroxide was first reported²³⁰ by Thenard in 1818. He treated barium peroxide with acid, and after removing other ions from the solution by precipitation he obtained an aqueous solution of hydrogen peroxide; he removed water by evaporation under reduced pressure, and was able in this way to prepare H_2O_2 that was almost anhydrous. He found that his product evolved oxygen when treated with a catalyst such as MnO_2 , and from the volume of gas given off he concluded that the compound must contain twice as much oxygen as does water.

6.2. SYNTHESIS

Oxygen in hydrogen peroxide is in the oxidation state (–1); the compound may be obtained either by oxidizing oxygen from the (–2) state, or by reducing molecular oxygen, and processes based on reactions of both of these types have been used on an industrial scale. The oxidative route starts from aqueous sulphuric acid or sulphate, which is oxidized electrolytically at high current densities between platinum electrodes. The oxidative step may be represented:



The perdisulphate formed is hydrolysed in acid solution:



Hydrogen peroxide may be removed from the hydrolysate with steam, and sulphate is regenerated. The conditions must be carefully controlled to avoid side-reactions leading to the formation of O_2 rather than H_2O_2 . The earliest process for manufacturing hydrogen peroxide was based on the reduction of atmospheric oxygen with barium metal, giving barium peroxide, from which (as Thenard found) hydrogen peroxide may be obtained by treatment with acid. Since 1945 processes have been developed that make use of the autoxidation of certain organic substrates; atmospheric oxygen is reduced to H_2O_2 , and the oxidized substrate may then be reduced to its original state quickly and cheaply, often by catalytic

²²⁶ R. D. Spratley and G. C. Pimentel, *J. Am. Chem. Soc.* **88** (1966) 2394; J. S. Shirk and G. C. Pimentel, *ibid.* **90** (1968) 3349.

²²⁷ S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta* **9** (1967) 103.

²²⁸ S. J. Turner and R. D. Harcourt, *Chem. Commun.* (1967) 4; N. J. Lawrence, thesis, Cambridge (1967).

²²⁹ W. L. Schumb, C. N. Satterfield and R. L. Wentworth, *Hydrogen Peroxide*, Reinhold (1955).

²³⁰ L. J. Thenard, *Ann. chim. phys.* **8** (1818) 306.

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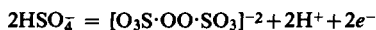
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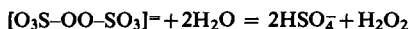
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²²⁶ R. D. Spratley and G. C. Pimentel, *J. Am. Chem. Soc.* **88** (1966) 2394; J. S. Shirk and G. C. Pimentel, *ibid.* **90** (1968) 3349.

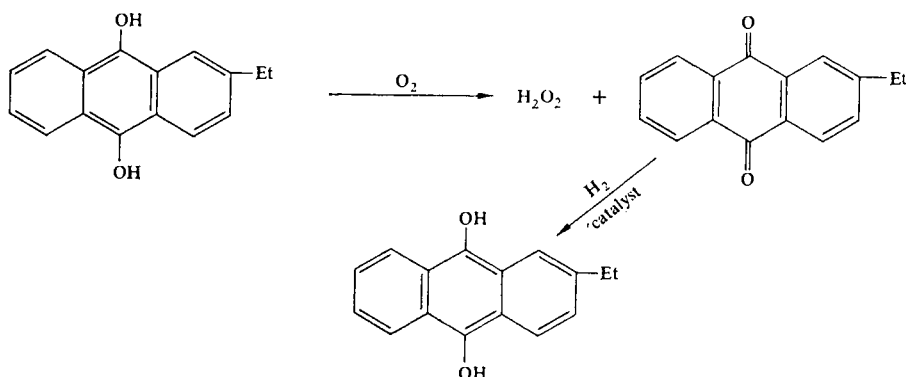
²²⁷ S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta* **9** (1967) 103.

²²⁸ S. J. Turner and R. D. Harcourt, *Chem. Commun.* (1967) 4; N. J. Lawrence, thesis, Cambridge (1967).

²²⁹ W. L. Schumb, C. N. Satterfield and R. L. Wentworth, *Hydrogen Peroxide*, Reinhold (1955).

²³⁰ L. J. Thenard, *Ann. chim. phys.* **8** (1818) 306.

hydrogenation. The only reagents consumed are atmospheric oxygen and hydrogen gas. One widely used substrate is 2-ethylanthraquinol²³¹:



The primary product of all these processes is aqueous H_2O_2 , which is an important industrial material. The liquid can be concentrated to *ca.* 98% by weight by fractional distillation at low pressure; very pure and anhydrous H_2O_2 is obtained by fractional crystallization or by extraction with organic solvents. The same methods may be used to produce anhydrous H_2O_2 in the laboratory from commercial aqueous H_2O_2 ; hydrogen peroxide is not normally synthesized in the laboratory although the preparation of D_2O_2 on a laboratory scale from D_2O and $K_2S_2O_8$ has been described²³², and H_2O_2 ²³³ has been prepared²³⁴ from hydroxylamine and molecular oxygen in alkaline perchlorate solution at room temperature.

The greatest care is needed when H_2O_2 is purified by extraction with organic solvents; explosive compounds are all too easily formed, as are mixtures that may detonate.

6.3. MOLECULAR STRUCTURE AND SPECTRA

The structure of H_2O_2 is represented by $HOOH$; the isomeric $H_2O:O$ has not been detected (but see section 7). The four atoms are not normally coplanar. In crystalline H_2O_2 (space group²³⁵ $D_4^8P4_32,2$; four molecules in the unit cell) the dihedral angle is just over 90° , and each oxygen atom is linked by hydrogen bonds to three other molecules. In the vapour the vibration-rotation spectrum can be accounted for²³⁶ in terms of a dihedral angle of 111.5° (though an earlier study²³⁷ led to a value of 119.8°); in the peroxy-hydrate of sodium oxalate, $Na_2C_2O_4 \cdot H_2O_2$, the H_2O_2 molecule is constrained²³⁸ into a planar configuration. Thus the dihedral angle is easily deformed. The other molecular parameters

²³¹ *Industrial Chemist* 1959.

²³² M. Schulz, A. Rieche and K. Kirschke, *Chem. Ber.* **100** (1967) 370.

²³³ F. Fehér, *Ber.* **72** (1939) 1789.

²³⁴ M. Anbar, Z. Baruch and D. D. Meyerstein, *Int. J. Appl. Radiation Isotopes* **17** (1966) 256.

²³⁵ W. R. Busing and H. A. Levy, *J. Chem. Phys.* **42** (1965) 3054.

²³⁶ R. M. Hunt, R. A. Leacock, C. W. Peters and K. Hecht, *J. Chem. Phys.* **42** (1965) 1931.

²³⁷ R. L. Redington, W. B'Olson and P. C. Cross, *J. Chem. Phys.* **36** (1962) 1311.

²³⁸ B. F. Pedersen and B. Pedersen, *Acta Chem. Scand.* **18** (1964) 1454.

(see Table 49) are much less sensitive to environment, though $d(\text{O}-\text{O})$ may be rather less in the crystal than in the vapour.

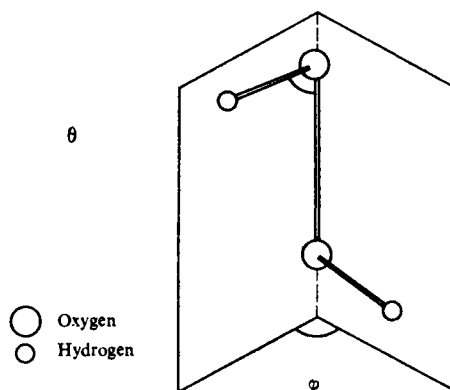


FIG. 7. Diagrammatic representation of the arrangement of the atoms in H_2O_2 . $\angle\theta = 94.8^\circ$, $\angle\phi$ (dihedral angle) = 111.5° for vapour.

The fundamental vibration frequencies are relatively easily identified, with the exception of the torsional mode ν_4 . Gaseous H_2O_2 gives a complicated vibration-rotation spectrum between 11 and 680 cm^{-1} ; all the bands observed have been accounted for by an analysis using torsional barriers²³⁶ $V_{\text{cis}} = 2460\text{ cm}^{-1}$ and $V_{\text{trans}} = 386\text{ cm}^{-1}$, and a similar analysis has been used for the spectrum of gaseous D_2O_2 . The low-frequency spectra of condensed phases are harder to account for in detail; in a matrix of N_2 , ν_4 has been given the value²³⁹ of 385 cm^{-1} . The ultraviolet absorption of H_2O_2 increases with decreasing wavelength; for aqueous solutions there is a maximum just above 2000 \AA that has been assigned to a charge transfer transition²⁴⁰.

In terms of simple theory, H_2O_2 may be described as a saturated molecule, with single bonds between the hydrogen and the oxygen atoms, and between the two oxygen atoms. The σ -bonds from oxygen are described as between pure p and sp^3 in character. A number of more sophisticated calculations of the electronic structure have been made, using²⁴¹ LCAO SCF MO and other²⁴² methods; particular attention has been paid to the origin and magnitude of the torsional barrier, for H_2O_2 is the simplest molecule to show restriction of rotation about a single bond.

6.4. OTHER PHYSICAL PROPERTIES

The pure liquid is syrupy and colourless or nearly so. Like water, it is extensively associated, and the Trouton constant indicates that this association persists even near the

²³⁹ E. Catalano and R. H. Sanborn, *J. Chem. Phys.* **38** (1963) 2273.

²⁴⁰ J. Jortner and G. Stein, *Bull. Res. Co. Israel* **6 A** (1957) 239.

²⁴¹ W. H. Fink and L. C. Allen, *J. Chem. Phys.* **46** (1967) 2261.

²⁴² S. J. Turner and R. D. Harcourt, *Chem. Commun.* 1967, 4.

boiling point. Hydrogen peroxide is miscible in all proportions in the liquid phase with water, with which it forms a compound $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ that is congruently melting and almost completely dissociated in the liquid phase. The vapour-pressure curve for mixtures of H_2O_2 and H_2O shows no maxima or minima. Hydrogen peroxide is soluble in many organic solvents, including alcohols, ethers, esters and amines (see note about hazards). Other physical properties are given in Table 49.

TABLE 49. PHYSICAL PROPERTIES OF H_2O_2 *Molecular properties and structure*

	Vapour (vib.-rot. spectrum)	Crystal (neutron diffraction) ^c
$r(\text{O}-\text{O})$, Å	1.475 ^a	1.453 ± 0.007
$r(\text{OH})$, Å	0.950 ^a	0.988 ± 0.005 (1.008 ± 0.005 after thermal correction)
<OOH Dihedral angle	94.8° ^a 111.5 ± 0.5 ^b	102.7 ± 3° 90.2 ± 0.6°

Fundamental vibration frequencies (cm ⁻¹)	Vapour (IR) ^{a, b}	Liquid ^d	Crystal (-190°) (IR) ^d
$\nu(\text{OH})$, ν_1	3599	3400 (IR, R)	3285
$\delta(\text{OH})$, ν_2	(1380)	1400 (R)	1407
$\nu(\text{O}-\text{O})$, ν_3	880	880 (IR, R)	882
Torsion, ν_4	242.8, 370.7	?	? ? 690
$\nu(\text{OH})$, ν_5	3608	3400 (IR, R)	3192
$\delta(\text{OH})$, ν_6	1266	? 1350 (IR)	1385

Rotational barriers ^b $V_{\text{trans}} = 386 \pm 4 \text{ cm}^{-1}$; $V_{\text{cis}} = 2460 \text{ cm}^{-1}$ Ultraviolet absorption (aqueous solution) ^e $\lambda_{\text{max}} = 2165 \pm 5 \text{ Å}$, $\epsilon_{\text{max}} = 460$ Dipole moment (vapour; Stark effect) ^f

2.1–2.3 D

*Thermodynamic properties and bond strengths*Formation thermodynamics ^a: ΔG_f° , 298-25.24 kcal mole⁻¹ ΔH_f° , 298-32.58 kcal mole⁻¹ S° 55.6 cal mole⁻¹ °K⁻¹ C_p (solid) (273°K > T > 220°K)0.0722 + 0.001 2397 cal gm⁻¹ C_p (liquid), 0–27°C0.628 cal gm⁻¹ D (HO–OH) (298°)48.8 kcal mole⁻¹ ^h D (H–OOH) (298°)89.6 kcal mole⁻¹ (electron impact) ^hIonization potential ^h

10.92 ± 0.05 eV

Other bulk properties

Melting point	-0.43°
Boiling point	150.2°
Vapour pressure ¹	$\log p_{\text{mm}} = -\frac{3\,140.594\,30}{T} + 9.827\,689 - 0.007\,436\,0T + 0.000\,004\,151\,6T^2$
$\Delta H_{\text{fus}}, 0^\circ$	87.84 cal gm ⁻¹
$\Delta H_{\text{subl}}, 0^\circ$	457.8 cal gm ⁻¹
$\Delta H_{\text{vap}}, 1 \rightarrow v, 0^\circ$	370.2 cal gm ⁻¹
Trouton's constant	26.5 cal mole ⁻¹ °K ⁻¹
Density: solid	1.6434 gm cm ⁻³ at -4.45°
liquid ¹ , ρ	$1.5970 + 0.000\,078\,4T - 0.00\,000\,197\,0T^2$
Mean coefficient of cubical expansion for liquid	(0-25°) 7.9×10^{-4} °C ⁻¹ (25-96°) 8.58×10^{-4} °C ⁻¹
Viscosity (20°)	0.01249 poise
Surface tension (20°)	80.4 dyne cm ⁻¹
Dielectric constant, ϵ	$84.2 - 0.62t + 0.0032t^2$ (t in °C)
Refractive index, n_D^{20}	1.40774
Polarizability, $\alpha \times 10^{24}$	2.30 cm ³ molecule ⁻¹
Specific conductance (99.9%)	3.9×10^{-7} ohm ⁻¹ cm ⁻¹
Magnetic susceptibility, χ_r	-0.50×10^{-6} c.g.s. e.m.u. g ⁻¹ at 10°C
Verdet constant (5461 Å)	13.32×10^{-3} min oe ⁻¹ cm ⁻¹

Data from W. C. Schumb, C. N. Satterfield and R. L. Wentworth, *Hydrogen Peroxide*, Reinhold (1955), unless otherwise stated.

^a R. L. Redington, W. B. Olson and P. C. Cross, *J. Chem. Phys.* **36** (1962) 1311.

^b R. M. Hunt, R. A. Leacock, C. W. Peters and K. T. Hecht, *J. Chem. Phys.* **42** (1965) 1931.

^c W. R. Busing and H. A. Levy, *J. Chem. Phys.* **42** (1965) 3054.

^d R. L. Miller and D. F. Hornig, *J. Chem. Phys.* **34** (1961) 265.

^e In alkaline solution; assigned to HO₂⁻; aqueous H₂O₂ gives no maxima at $\lambda > 2000$ Å; J. Jortner and G. Stein, *Bull. Res. Co. Israel* **6A** (1957) 239.

^f J. T. Massey and D. R. Bianco, *J. Chem. Phys.* **22** (1954) 442.

^g NBS Technical Note 270-3 (1968).

^h S. N. Foner and R. L. Hudson, *J. Chem. Phys.* **36** (1962) 2676, 2681. P. A. Giguère, *J. Chem. Phys.* **30** (1959) 322.

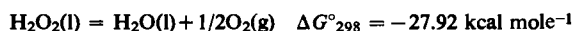
ⁱ A. L. Tsykalo and A. G. Tabachnikov, *Teplofiz. Svoistva Veshchestv, Akad. Nauk Ukr. SSR, Respub. Mezhdovedom* (1968) 120.

^j A. L. Tsykalo and A. G. Tabachnikov, *Teor. Eksp. Khim.* **2** (1966) 837.

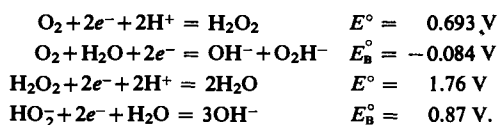
6.5. CHEMICAL PROPERTIES

Hydrogen peroxide has an extensive redox chemistry, and also shows hydroxylic properties, derived from the two OH groups. The redox properties will be considered first.

The compound is stable with respect to its elements (see Table 49), but is unstable with respect to decomposition into water and molecular oxygen in the solid, the liquid or the vapour phases, or in aqueous solution:

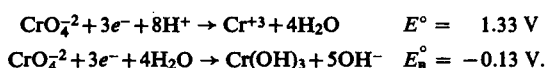


This instability with respect to disproportionation is reflected in the standard potentials:



In the vapour phase, decomposition, a first-order process, is associated with dissociation into radicals such as OH or OOH; photolysis or decomposition of H_2O_2 by X-rays have been shown by e.s.r. to produce radicals like these²⁴³. In all phases decomposition is very sensitive to homogeneous or heterogeneous catalysis by metals, metal oxides or metal ions, and in homogeneous systems it is probable that peroxy-compounds of metals are formed as intermediates. In the absence of catalysts the pure liquid is stable indefinitely at room temperature and may be distilled at low pressures without decomposition, but concentrated solutions are usually stabilized by the addition of compounds such as sodium stannate or 8-hydroxyquinoline, which inhibit catalysts. These very concentrated solutions are normally stored and handled in apparatus made from very pure (>99.5%) aluminium, stainless steel, glass, porcelain, or plastic such as polyvinyl chloride, polyethylene or PTFE.

Since oxygen in H_2O_2 is in an intermediate oxidation state (-1), hydrogen peroxide can act either as an oxidizing or as a reducing agent; the appropriate potentials are given above. Its behaviour is very much influenced by kinetic factors, for its reactions are not simple electron-transfer processes. Some clearly involve free radicals; indeed, the system $\text{Ti}^{+3}/\text{H}_2\text{O}_2$ has been studied extensively in recent years in connection with free radical oxidations of organic compounds. The reactions of Fenton's reagent (a mixture of H_2O_2 and Fe^{+2}) are also free radical oxidation processes. Other reactions may proceed by two-electron transfer steps; in all systems involving transition metal ions the formation of metal peroxy-complexes may be important. The mechanisms and the products of the reactions of H_2O_2 in aqueous solution are very sensitive to pH, as illustrated by the system $\text{H}_2\text{O}_2/\text{Cr(III)}/\text{Cr(VI)}$. The potentials for $\text{Cr(VI)}/\text{Cr(III)}$ are:



Thus in acid solution H_2O_2 is capable of oxidizing Cr(III) to Cr(VI) , and of reducing Cr(VI) to Cr(III) . It is the reduction that predominates; but in alkaline solution chromate is reduced to the Cr(V) species $\text{Cr(O}_2)_4^{3-}$, which decomposes to regenerate chromate. Aqueous H_2O_2 exchanges oxygen with water immeasurably slowly²⁴⁴ in the presence of HClO_4 , and extremely slowly in the presence of hydroxide ion or of sulphuric acid; exchange is faster with water containing nitric acid, and kinetic analysis suggests that peroxynitric acid is formed by reaction between H_2O_2 and N_2O_5 in the solution. The small but measurable exchange²⁴⁵ between H_2O_2 and H_2O ²⁴⁷ both in evolved O_2 and in residual H_2O_2 in the presence of such species as Fe^{+2} or ClO^- has also been explained in terms of intermediate formation of unstable peroxy-species.

Besides these reactions, hydrogen peroxide oxidizes a number of organic compounds, and is useful in the preparation of epoxides and of sulphones; α -halo-hydroperoxides have been prepared by treatment of olefins with halogens and hydrogen peroxide^{246, 247}. It is also an intermediate in many biological oxidation processes.

As a hydroxy-compound, hydrogen peroxide can, in principle, act as an acid or as a base. For the acid dissociation²⁴⁷ of H_2O_2 in water, the equilibrium favours the formation of H_3O^+ :

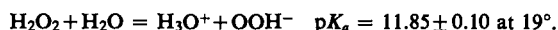
²⁴³ B. G. Ershov and A. K. Pikaev, *Izvest. Akad. Nauk SSSR, Ser. Khim.* 1964, 922.

²⁴⁴ M. Anbar and S. Guttman, *J. Am. Chem. Soc.* **83** (1961) 2035.

²⁴⁵ M. Anbar, *J. Am. Chem. Soc.* **83** (1961) 2031.

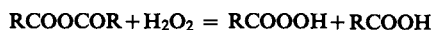
²⁴⁶ K. Weissmehl and M. Lederer, *Chem. Ber.* **96** (1963) 77.

²⁴⁷ J. Jortner and G. Stein, *Bull. Res. Co. Israel* **6A** (1957) 239.

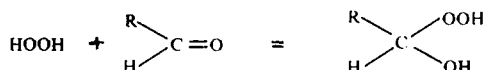


This shows that H_2O_2 is rather more acidic than water. Derivatives of H_2O_2 analogous to hydroxides and oxides—that is, hydroperoxides and peroxides—are discussed in the next section. Hydrogen peroxide is much less basic than water (“at least one millionth” less basic²⁴⁸); the lower conductivity of, for example, perchloric acid in $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ than in water may be connected with the difficulty of protonating H_2O_2 , which perhaps interferes with proton mobility²⁴⁹. The ion H_3O_2^+ may be formed²⁵⁰ in solutions of H_2O_2 in HBF_4 , but its salts have not been characterized. The specific conductivity of 99.9% H_2O_2 is very low, so self-ionization is not extensive.

Other “hydroxylic” reactions of H_2O_2 follow those of water. Acid anhydrides gives peroxy-acids:



aldehydes²⁵¹ gives peroxy-aldols:



Again like water, hydrogen peroxide forms adducts with many salts and compounds such as triphenyl phosphine. These adducts are presumably held together by hydrogen bonds. The crystal structures of some have been determined, and in each case are consistent with the presence of molecules of H_2O_2 within the crystal lattice.

6.6. ANALYTICAL CHEMISTRY

Hydrogen peroxide is normally estimated with potassium permanganate, which it reduces quantitatively. The strengths of solution of hydrogen peroxide are often expressed in terms of “volumes”, which means “the volume of gaseous oxygen at n.t.p. produced by one volume-unit of liquid”. Thus 100-volume H_2O_2 gives 100 ml (at n.t.p.) of O_2 for each millilitre of liquid completely decomposed, meaning that each millilitre of liquid must contain about 9 mmol H_2O_2 , so that “100-volume” H_2O_2 must contain about 30% by weight of H_2O_2 .

6.7. USES OF HYDROGEN PEROXIDE

Hydrogen peroxide is of considerable importance in connection with the catalysis of polymerization reactions and in the production of epoxides; it is used to oxidize organic nitrogen compounds and organic and inorganic sulphur compounds, and in the synthesis of organic peroxides and peroxyacids and of sodium perborate, all of which are significant commercial products. Hydrogen peroxide has been extensively used to bleach many different materials, among them cellulose, textiles, leather, furs, human and animal hair,

²⁴⁸ A. G. Mitchell and W. F. K. Wynne-Jones, *Trans. Faraday Soc.* **52** (1954) 824.

²⁴⁹ M. Kilpatrick, *Can. J. Chem.* **37** (1959) 163.

²⁵⁰ R. W. Alder and M. C. Whiting, *J. Chem. Soc.* 1964, 4707.

²⁵¹ E. G. Sander and W. P. Jenks, *J. Am. Chem. Soc.* **90** (1968) 4377.

tripe, sausage-skin and headstones; it has been used as a source of oxygen in rocket fuels and in submarines, and as an aerating agent. In dilute form it is a mild disinfectant and antiseptic. In qualitative and quantitative analysis its specific colour-reaction with certain metals is useful, and it has been used in pregnancy testing.

Toxicity. In low concentrations H_2O_2 is not physiologically dangerous, but in high concentrations it is; it attacks the eyes and skin.

7. PEROXIDES AND RELATED COMPOUNDS

This section is concerned with other compounds containing at least one pair of linked oxygen atoms, but no oxygen chains with more than two atoms. They are of several types:

- (1) Salts of the ion O_2^+ .
- (2) Ionic superoxides, containing the ion O_2^- .
- (3) Ionic peroxides, containing the ion O_2^{2-} , and hydroperoxides, containing the ion O_2H^- .
- (4) Solid, non-stoichiometric peroxides.
- (5) Compounds containing the peroxy-group linked by directed bonds to other atoms.
- (6) Oxygen carriers.

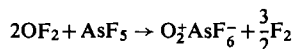
7.1. DIOXYGENYL SALTS

Though the electronic spectrum of the O_2^+ ion was analysed many years ago, the first salt of this species, $\text{O}_2^+\text{PtF}_6^-$, was not reported²⁵² until 1962. It was obtained by fluorinating platinum in glass or silica apparatus; since then, dioxygenyl salts of the anions MF_6^- ($\text{M} = \text{P}, \text{As}, \text{Sb}$), SnF_6^{2-} and BF_4^- have been prepared from the highest fluoride of the appropriate element by one or more of the following routes:

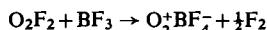
- (1) Treatment with a mixture of fluorine and oxygen, either at high temperature²⁵³ or in daylight²⁵⁴:



- (2) Treatment with OF_2 at temperatures greater than 150° :²⁵³



- (3) Treatment with dioxygenyl difluoride at low ($\sim -190^\circ$) temperatures^{255, 256}:



The compounds are all paramagnetic; some properties of the O_2^+ ion are given in Table 50. The fluoroborate and the fluorophosphate decompose slowly at 0° , but the hexafluoroarsenate and antimonate are stable under an inert atmosphere at temperatures up to 100° . All the compounds are powerful oxidizing and fluorinating agents. The fluoroantimonate

²⁵² N. Bartlett and D. H. Lohmann, *Proc. Chem. Soc.* 1962, 115.

²⁵³ J. B. Beal, C. Pupp and W. E. White, *Inorg. Chem.* **8** (1969) 828.

²⁵⁴ J. Shamir and J. Binenboym, *Inorg. Chim. Acta* **2** (1968) 37.

²⁵⁵ A. R. Young, T. Hirata and S. I. Morrow, *J. Am. Chem. Soc.* **86** (1964) 20.

²⁵⁶ D. V. Bantov, V. F. Sukhoverkhov and Yu. N. Mikhailov, *Izv. Sib. Otdel. Akad. Nauk SSSR, Ser. Khim. Nauk* 1968, 84.

tripe, sausage-skin and headstones; it has been used as a source of oxygen in rocket fuels and in submarines, and as an aerating agent. In dilute form it is a mild disinfectant and antiseptic. In qualitative and quantitative analysis its specific colour-reaction with certain metals is useful, and it has been used in pregnancy testing.

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- (6) Oxygen carriers.

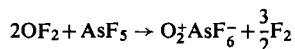
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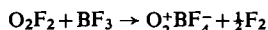
- (1) Treatment with a mixture of fluorine and oxygen, either at high temperature²⁵³ or in daylight²⁵⁴:



- (2) Treatment with OF_2 at temperatures greater than 150° :²⁵³



- (3) Treatment with dioxygenyl difluoride at low ($\sim -190^\circ$) temperatures^{255, 256}:



The compounds are all paramagnetic; some properties of the O_2^+ ion are given in Table 50. The fluoroborate and the fluorophosphate decompose slowly at 0° , but the hexafluoroarsenate and antimonate are stable under an inert atmosphere at temperatures up to 100° . All the compounds are powerful oxidizing and fluorinating agents. The fluoroantimonate

²⁵² N. Bartlett and D. H. Lohmann, *Proc. Chem. Soc.* 1962, 115.

²⁵³ J. B. Beal, C. Pupp and W. E. White, *Inorg. Chem.* **8** (1969) 828.

²⁵⁴ J. Shamir and J. Binenboym, *Inorg. Chim. Acta* **2** (1968) 37.

²⁵⁵ A. R. Young, T. Hirata and S. I. Morrow, *J. Am. Chem. Soc.* **86** (1964) 20.

²⁵⁶ D. V. Bantov, V. F. Sukhoverkhov and Yu. N. Mikhailov, *Izv. Sib. Otdel. Akad. Nauk SSSR, Ser. Khim. Nauk* 1968, 84.

is soluble in excess of SbF_5 and the fluoroarsenate reacts with NO_2 , giving the nitronium salt of the same anion; all the salts react very violently with water, giving oxygen and ozone.

TABLE 50. SOME PROPERTIES OF THE IONS O_2^+ , O_2^- AND O_2^{2-}

	O_2^+	O_2^-	O_2^{2-}
$d(\text{O}-\text{O}) (\text{\AA})$	1.17 ± 0.17^a	$1.32-1.35^b$	$1.48-1.49^c$
$\nu(\text{O}-\text{O}) (\text{cm}^{-1})$	$1858 (\text{O}_2\text{AsF}_6)^d$	$1145 (\text{KO}_2)^e$	$\left. \begin{matrix} 738 \\ 794 \end{matrix} \right\} (\text{Na}_2\text{O}_2)^f$
$\mu_{\text{eff}} (\text{BM}) (300^\circ\text{K})$	1.57^g	2.04^h	—
g_{av}	1.9980 ± 0.0002^i	$2.058 (\text{Na}_2\text{O}_2)^j$	—

^a N. Bartlett and D. H. Lohmann, *Proc. Chem. Soc.* 1962, 115. This agrees within error with the value 1.1227 ± 0.0001 from spectroscopy (see Table 12, p. 702).

^b F. Halverson, *Phys. Chem. Solids* **23** (1962) 207.

^c N.-G. Vannerberg, *Progr. Inorg. Chem.* (ed. F. A. Cotton) **4** (1963) 125.

^d J. Shamir, J. Binenboym and H. H. Claasen, *J. Am. Chem. Soc.* **90** (1968) 6223. The frequency is not significantly different for O_2SbF_6 dissolved in liquid SbF_5 .

^e J. A. Creighton and E. R. Lippincott, *J. Chem. Phys.* **40** (1964) 1779. This frequency varies between 1120 and 1145 cm^{-1} in alkali metal halide lattices (J. Rolfe, W. Holzen, W. E. Murphy and H. J. Bernstein, *J. Chem. Phys.* **49** (1968) 963).

^f For the anhydrous compound. For $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$, $\nu(\text{O}-\text{O})$ is 842 cm^{-1} (J. C. Evans, *J. Chem. Soc. D*, 1969, 682).

^g N. Bartlett and I. P. Beaton, *Chem. Commun.* 1966, 167.

^h L. Pauling, *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, New York (1960), p. 351.

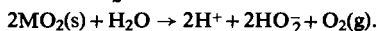
ⁱ J. Shamir and J. Binenboym, *Inorg. Chim. Acta* **2** (1968) 37.

^j In KCl , $g_{\text{av}} = 2.1140$ (P. W. Atkins and M. C. R. Symons, *The Structure of Inorganic Radicals*, Elsevier, Amsterdam (1967), p. 111).

7.2. IONIC SUPEROXIDES²⁵⁷

Superoxides of the alkali metals may be prepared by direct reaction between the metal and oxygen (except for lithium), or by oxygenation of solution of the metal in liquid ammonia; superoxides are also formed by dissociation of hydrogen peroxide adducts of metal hydroperoxides. The superoxide ion is present in the crystal lattice; those superoxides whose structures have been studied in detail are polymorphic, but in all the bond length in O_2^- is greater than in O_2 , consistent with an electronic structure in which there is one more π_g^* electron than in O_2 . Some structural parameters are given in Table 50. Superoxides are coloured and paramagnetic; changes in magnetic susceptibility and colour appear to be associated with phase changes. Besides the superoxides, mixed peroxides-superoxides (such as $\text{K}_4(\text{O}_2)(\text{O}_2)_2$) are known.

When heated, superoxides decompose into the metal oxide and molecular oxygen; the electron affinity of O_2 is barely exothermic (see Table 10, p. 698), and the ion is stabilized by the lattice energy. Superoxides are powerful oxidizing agents; they react with water to give oxygen and the unstable ion HO_2^- :



²⁵⁷ N.-G. Vannerberg, *Progr. Inorg. Chem.* (ed. F. A. Cotton), Interscience, **4** (1963) 125.

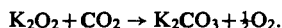
²⁵⁸ L. Andrews, *J. Chem. Phys.* **50** (1969) 4288.

They react with CO_2 to give oxygen and the metal carbonate through an intermediate peroxycarbonate.

Molecules of alkali metal superoxides, trapped in matrices at low temperatures, have recently been detected by infrared spectroscopy.²⁵⁸

7.3. IONIC PEROXIDES²⁵⁷

Peroxides containing the ion O_2^{2-} are formed by the alkali metals and the alkaline earth metals; they are formally derived from H_2O_2 by deprotonation. They may be prepared by oxygenation of the metal or of solutions of the metal in liquid ammonia, or by treatment of the metal or some compound with H_2O_2 . Ionic peroxides are white, and contain the O_2^{2-} ion, which is diamagnetic and isoelectronic with F_2 ; some structural parameters are given in Table 50. The additional π^* electron leads to a longer bond in O_2^{2-} than in O_2^- , and to a substantially lower stretching frequency. Ionic peroxides decompose when heated into the metal oxide and molecular oxygen; they react with acids to give H_2O_2 , and with water to give H_2O_2 and HO_2^- ; they are, of course, powerful oxidizing agents. The reaction with CO_2 , liberating oxygen, is of some importance in maintaining artificial atmospheres:



Peroxides form a large number of hydrates and of peroxyhydrates (which contain H_2O_2 of crystallization). Ionic hydroperoxides, containing the ion O_2H^- , are also known and are formally related to ionic peroxides.

7.4. NON-STOICHIOMETRIC PEROXIDES²⁵⁹

Treatment of solutions of salts of thorium or of some actinide elements with H_2O_2 leads to the formation of rather ill-defined solids containing metal ions, peroxide, other anions and water. It has been suggested that some at least of these compounds contain layers of metal ions and of peroxy-groups, with the other species held between the layers; the proportion of the various components depends on the conditions of preparation of the sample concerned and upon its previous history.

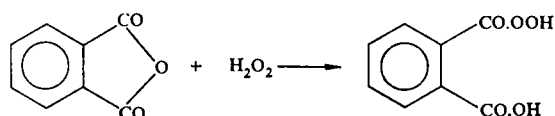
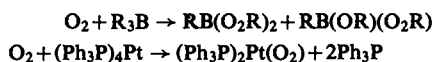
7.5. PEROXIDES CONTAINING DIRECTED BONDS

There is an enormous range of compounds in which peroxy- or similar groups are directly bound to atoms other than hydrogen. The peroxy-group may replace an oxygen atom as a bridge between two other groups, giving compounds such as $\text{Me}_3\text{SnOOSnMe}_3$, $\text{K}_2[\text{O}_3\text{SOOSO}_3]$ or $\text{F}_3\text{CO}\cdot\text{OO}\cdot\text{COCF}_3$; it may replace the oxygen atom of a hydroxy-group in a hydroxide, an alcohol or an acid, giving such compounds as Me_3SnOOH , $\text{C}_4\text{H}_9\text{OOH}$ or $\text{CH}_3\text{CO}\cdot\text{OOH}$; it may replace an oxygen atom linked to another atom by a formal double bond, as in the ion $[\text{HCr}(\text{O})_2(\text{O}_2)_2]^-$. The compounds of these different

²⁵⁹ J. A. Connor and E. A. V. Ebsworth, *Advances in Inorganic Chemistry and Radiochemistry* (ed. H. J. Emeléus and A. G. Sharpe), Wiley (1964), Vol. 6.

classes are vastly different in structure and in chemistry²⁶⁰⁻²⁶². Many, as the organic peroxides, are easily recognized, but it is sometimes very hard to distinguish between solids containing bound peroxide and others that contain H₂O₂ of crystallization. Chemical tests, of which the best-known is the Riesenfeld-Liebhaufsky test (based on oxidation of buffered aqueous I⁻), have been devised to distinguish between true peroxides and peroxy-hydrates, but these tests have not proved reliable. They depend on differences in reactivity between H₂O₂ itself and bound peroxide, and so cannot distinguish between a peroxy-hydrate and a compound containing bound peroxide that is hydrolysed very rapidly. Recently, criteria have been based on n.m.r.²⁶³, or e.s.r.²⁶⁴, and on Raman spectroscopy²⁶⁵, where the (O-O) stretching mode of H₂O₂ has proved particularly useful.

In general, peroxides may be prepared by reduction of molecular oxygen (autoxidation) or ozone, or by treatment of an appropriate compound with H₂O₂ or an ionic peroxide:



Almost all preparative routes start from some compound already containing the O-O group; an important exception is the preparation of peroxydisulphate, $[\text{O}_3\text{S} \cdot \text{O}_2 \cdot \text{SO}_3]^{-2}$, by the anodic oxidation of acid sulphate solution.

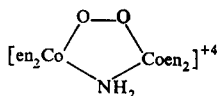
7.5.1. Stereochemistry

The geometry of the peroxy-group in these compounds is very varied. In ether-type peroxides QOOQ the following types of structure may be distinguished (Fig. 8).

Planar, trans-QOOQ. This arrangement is found in the perdisulphate ion²⁶⁶ and in the paramagnetic species²⁶⁷ $[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5]^{+5}$, which from the short (O-O) distance (1.31 Å) has been described as a superoxo-complex.

Non-planar, QOOQ. This is the type of structure adopted by H₂O₂. Dihedral angles vary widely, from 146° in diamagnetic²⁶⁸ $[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5]^{+4}$ (described as a peroxo-complex because the (O-O) distance is 1.47 Å) to 64° in the cyclic anion²⁶⁹ $[\text{B}_2(\text{O}_2)_2(\text{OH})_4]^{-}$.

Near-planar, cis QOOQ. The paramagnetic cobalt complexes²⁷⁰



²⁶⁰ A. G. Davies, *Organic Peroxides*, Butterworths, London (1962).

²⁶¹ G. Sosnovsky and J. H. Brown, *Chem. Rev.* **66** (1966) 528.

²⁶² E. G. E. Hawkins, *Organic Peroxides*, Spon, London (1961).

²⁶³ T. M. Connor and R. E. Richards, *J. Chem. Soc.* 1958, 289.

²⁶⁴ I. F. Franchuk, *Teor. Eksperim. Khim.* **1** (1965) 531.

²⁶⁵ W. P. Griffith and J. D. Wickens, *J. Chem. Soc. A*, 1968, 397.

²⁶⁶ W. H. Zachariasen and R. C. L. Mooney, *Z. Krist.* **88** (1934) 63.

²⁶⁷ R. E. Marsh and W. P. Schaeffer, *Acta Cryst.* **24** (1968) 246.

²⁶⁸ W. P. Schaeffer, *Inorg. Chem.* **7** (1968) 725.

²⁶⁹ A. Hansson, *Acta Chem. Scand.* **15** (1961) 934.

²⁷⁰ U. Thewalt and R. Marsh, *J. Am. Chem. Soc.* **89** (1967) 6364.

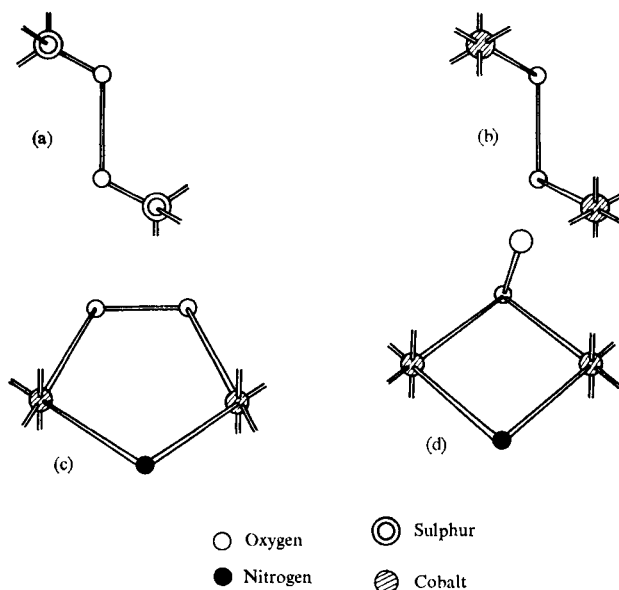
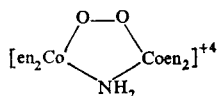


FIG. 8. Configurations in peroxides.

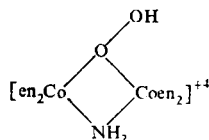
(a) *Trans*, planar in $\text{S}_2\text{O}_8 = (\text{K salt})$.

(b) Skew, non-planar in $[(\text{NH}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5]^{+4}$.

(c) *Cis*, near-planar, in



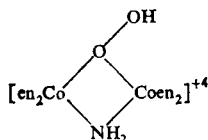
(d) Isomeric, in



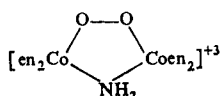
All from X-ray studies.

adopt this configuration; these compounds, with $d(\text{O}-\text{O})$ 1.31–1.32 Å, are described as superoxo-complexes.

Isomeric $\text{Q}_2\text{O}:\text{O}$. The only compound so far proved to have this type of structure is a salt of the red, diamagnetic cation²⁷⁰



In solution this cation is formed from a diamagnetic species believed to be



which isomerizes when the peroxy-bridge is protonated; the activation energy for isomerization is of the order of 15–20 kcal mole⁻¹, and the process is reversible²⁷¹.

In peroxy-derivatives in which the two oxygen atoms are bound to a single metal, the two metal–oxygen distances in all compounds so far studied are about equal, though there are some small deviations from symmetry that may be significant. Compounds of this type are so far only known for transition elements (though the vibrational spectra of alkali metal peroxide and superoxide molecules trapped in matrices at low temperatures suggest that the MOO systems here too may form isocetes triangles²⁵⁸). The peroxy-group is in effect doubly bound to the metal; the bonding has been discussed in terms of donation to the metal²⁶⁰ from π - and π^* -orbitals of O_2^{-2} , and also by using the equivalent orbital approach²⁷². In most peroxy-complexes the (O–O) distance is in the range 1.4–1.5 Å, though it is rather shorter in the paramagnetic cobalt complexes, but in one series of compounds the (O–O) bond length is remarkably sensitive to small changes in the rest of the molecule. In the species *trans*-ClIr(Ph₃P)₂(CO)(O₂), *trans*-IIr(Ph₃P)₂(CO)(O₂) and (diphos)₂Ir(O₂)⁺BF₄⁻, the (O–O) distances are respectively^{273–274} 1.30 ± 0.03 Å, 1.51 ± 0.03 Å and 1.66 ± 0.03 Å.

Other Physical Properties

The (O–O) bond dissociation energy has been determined in a number of ether-type organic peroxides; the values are in the range 30–50 kcal mole⁻¹. In H₂O₂ and in many peroxy-complexes of transition metals the (O–O) stretching modes are found²⁶⁵ near 800–900 cm⁻¹. The infrared spectra of adducts of O₂ with compounds such as (Ph₃P)₂Ni also contain bands in this region that have been shown by isotopic substitution to be associated with the (O–O) group and are assigned to the (O–O) stretching mode²⁷⁵. It is remarkable that in the three iridium complexes described above the band assigned to ν (O–O) is almost unchanged in frequency, despite the very large change in the (O–O) distance.

Chemical Properties

Organic peroxides decompose readily to give free radicals, and have been extensively studied and used in connection with the initiation and progress of free radicals reactions in organic chemistry. They are important in many industrial oxidation processes, including the production of epoxides. Peroxy-disulphuric acid and its salts are very important as

²⁷¹ M. Mori and J. A. Weil, *J. Am. Chem. Soc.* **89** (1967) 3732.

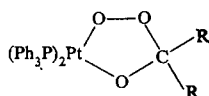
²⁷² W. P. Griffith, *J. Chem. Soc.* 1964, 5248.

²⁷³ S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.* **87** (1965) 2581; J. A. McGinnety, R. J. Doedens and J. A. Ibers, *Inorg. Chem.* **6** (1967) 2243.

²⁷⁴ J. A. McGinnety and J. A. Ibers, *Chem. Commun.* 1968, 235.

²⁷⁵ K. Hirota, M. Yamamoto, S. Otsuka, A. Nakamura and Y. Tatsuno, *Chem. Commun.* 1968, 533.

unusually powerful oxidizing agents in inorganic chemistry^{276, 277}. Many transition metal peroxides are dangerously explosive, and relatively little is known about their chemistry. The oxygen adduct $(\text{Ph}_3\text{P})_2\text{Pt}(\text{O}_2)$ reacts with ketones²⁷⁸ to give peroxy-derivatives:



the reaction with CO_2 leads to the formation of a carbonato-complex, but a peroxy-carbonato species is apparently formed first, and the reaction with CS_2 may also give a peroxy-species²⁷⁹. The peroxy-compounds of transition metals (Table 51) are important in analytical chemistry (many of them are coloured), in connection with the catalytic decomposition of H_2O_2 , and as models for natural oxygen-carriers.

TABLE 51. SOME OF THE ELEMENTS FORMING PEROXY-COMPOUNDS

Ionic superoxides	Alkali metals, alkaline earths ? Ti, Zr, Hf; Fe; Co, Ag, etc.
Ionic peroxides and hydroperoxides	Alkali metals, alkaline earths; Zn-Hg
Solid non-stoichiometric	Rare earths, Th, Pa
"Ether"-type peroxides	Be, B, Al, Ga; C-Pb; F, ? Cl
"alcohol"-type hydroperoxides	
Peroxyacids, peroxy salts	? B, C, ? N, P, S; V, Nb, Ta; Cr, Mo, W; Mn; U
Peroxy complexes (neutral or cations)	Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Re; ? Fe, Ru; Co, Rh, Ir; Ni, Pd, Pt; Cu; U
Oxygen carriers	Fe, Co, Ir, Cu

7.6. OXYGEN CARRIERS²⁸⁰

Certain compounds combine reversibly with molecular oxygen. The naturally bearing oxygen carriers include haemoglobin and haemocyanin; the simplest synthetic oxygen carrier is Vaska's compound, *trans*- $\text{ClIr}(\text{Ph}_3\text{P})_2\text{CO}$. These compounds, when oxygenated, are closely related to peroxy-derivatives of transition elements; indeed, they really represent a special class of peroxides rather than a class of compounds that is quite distinct. While the oxygen adduct of Vaska's compound gives up its oxygen reversibly, the oxygen adduct of the very similar *trans*- $\text{Ir}(\text{Ph}_3\text{P})_2\text{CO}$ does not, so the iodide cannot be regarded as an oxygen carrier. The configuration of oxygen in the oxygen adduct of haemoglobin is still unknown.

7.7. RELATIONSHIPS BETWEEN BOND LENGTH AND BOND ORDER IN PEROXIDES AND RELATED COMPOUNDS

If bond energies are plotted against bond lengths for the simple O_2^+ , O_2 , O_2^- and O_2^{2-} peroxy-species, a smooth curve is obtained²⁸¹; a smooth curve is also obtained if $(\text{O}-\text{O})$

²⁷⁶ D. A. House, *Chem. Rev.* **62** (1962) 185.

²⁷⁷ J. Burgess, *Ann. Rep. Chem. Soc.* **65A** (1968) 398.

²⁷⁸ R. Ugo, F. Conti, S. Cenini, R. Mason and G. Robertson, *Chem. Commun.* 1968, 1498.

²⁷⁹ P. J. Hayward, D. M. Blake, C. J. Nyman and G. Wilkinson, *Chem. Commun.* 1969, 987.

²⁸⁰ L. H. Vogt, H. M. Faigenbaum and S. Wiberley, *Chem. Rev.* **63** (1963) 269.

stretching frequencies are plotted against $d(\text{O}-\text{O})$ for O_2 in its ground and excited states²⁸², as well as for O_2^- and O_2^{2-} . However, the very wide variation in $d(\text{O}-\text{O})$ in complex peroxides, coupled with the apparent constancy in $\nu(\text{O}-\text{O})$, makes these relationships of doubtful value in assessing $(\text{O}-\text{O})$ bond orders. The reactivity of bound O_2 has been discussed²⁸³ in terms of its resemblance to electronically excited O_2 .

8. OZONE AND RELATED SPECIES

8.1. OZONE

During the past decade two factors have contributed to the increased attention paid by chemists and others to the behaviour of ozone; these factors are, on the one hand, chemical aeronomy and, on the other, the recognition of the strong oxidizing power of ozone.

A summary of physical data relating to ozone is given in Table 52. In the solid state, ozone is blue-black in colour, melting to a deep blue liquid and boiling to give a blue, thermally unstable gas.

Ozone, O_3 , is normally prepared in the laboratory by passing an electric discharge through oxygen gas. Machines for the production of ozone, known as ozonizers, are marketed commercially. More generally, ozone is formed whenever oxygen is subjected to intense radiation, whether photochemical or electrical: thus studies have been carried out on ozone produced by pulse radiolysis²⁸⁴, flash photolysis²⁸⁴, mercury-sensitized photolysis²⁸⁵ and $^{60}\text{Co}-\gamma$ radiolysis²⁸⁶ of oxygen.

The growing interest in physical phenomena of the upper atmosphere (thermosphere), together with problems associated with atmospheric pollution in large cities²⁸⁷, has produced a large volume of fundamental work on the rates of reaction of atoms with simple molecules²⁸⁸. Many of these reactions occur with concomitant emission of light (chemiluminescence). Examples of these fundamental rate studies which involve ozone as one component include the following:

$\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	ref. 289	(1)
$\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	290	(2)
$\text{SO} + \text{O}_3 \rightarrow \text{SO}_2 + \text{O}_2$	291	(3)
$\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2$	292	(4)
$\text{M} + \text{O}_3 \rightarrow \text{M} + \text{O}_2 + \text{O}$	293	(5)
$\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$	294	(6)
$\text{H}_2\text{S} + \text{O}_3 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$	295	(7)

²⁸¹ D. G. Tuck, *J. Inorg. Nucl. Chem.* **26** (1964) 1525.

²⁸² J. C. Evans, *J. Chem. Soc. D*, 1969, 682.

²⁸³ R. McWeeny, R. Mason and A. D. C. Towl, *Disc. Faraday Soc.* **47** (1969) 20.

²⁸⁴ C. J. Hochanadel, J. A. Ghormley and J. W. Boyle, *J. Chem. Phys.* **48** (1968) 2416.

²⁸⁵ R. J. Fallon, J. T. Vanderslice and E. A. Mason, *J. Phys. Chem.* **64** (1960) 505.

²⁸⁶ J. T. Sears and J. W. Sutherland, *J. Phys. Chem.* **72** (1968) 1166.

²⁸⁷ R. P. Wayne and J. N. Pitts, *J. Chem. Phys.* **50** (1969) 3644.

²⁸⁸ M. Nicolet, *Disc. Faraday Soc.* **37** (1964) 7 *et seq.*

²⁸⁹ D. Garvin, H. P. Broida and H. J. Kostkowski, *J. Chem. Phys.* **32** (1960) 880.

²⁹⁰ L. F. Phillips and H. I. Schiff, *J. Chem. Phys.* **36** (1962) 1509.

²⁹¹ C. J. Halstead and B. A. Thrush, *Proc. Roy. Soc.* **295** (1966) A, 380.

²⁹² P. N. Clough and B. A. Thrush, *Trans. Faraday Soc.* **65** (1969) 23.

²⁹³ W. M. Jones and N. Davidson, *J. Am. Chem. Soc.* **84** (1962) 2868.

²⁹⁴ W. Kaufmann and J. R. Kelso, *J. Chem. Phys.* **47** (1967) 4541.

²⁹⁵ R. D. Cadle and M. Ledford, *Air Water Pollution* **10** (1966) 25.

stretching frequencies are plotted against $d(\text{O}-\text{O})$ for O_2 in its ground and excited states²⁸², as well as for O_2^- and O_2^{2-} . However, the very wide variation in $d(\text{O}-\text{O})$ in complex peroxides, coupled with the apparent constancy in $\nu(\text{O}-\text{O})$, makes these relationships of doubtful value in assessing $(\text{O}-\text{O})$ bond orders. The reactivity of bound O_2 has been discussed²⁸³ in terms of its resemblance to electronically excited O_2 .

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$\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2$	292	(4)
$\text{M} + \text{O}_3 \rightarrow \text{M} + \text{O}_2 + \text{O}$	293	(5)
$\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$	294	(6)
$\text{H}_2\text{S} + \text{O}_3 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$	295	(7)

²⁸¹ D. G. Tuck, *J. Inorg. Nucl. Chem.* **26** (1964) 1525.

²⁸² J. C. Evans, *J. Chem. Soc. D*, 1969, 682.

²⁸³ R. McWeeny, R. Mason and A. D. C. Towl, *Disc. Faraday Soc.* **47** (1969) 20.

²⁸⁴ C. J. Hochanadel, J. A. Ghormley and J. W. Boyle, *J. Chem. Phys.* **48** (1968) 2416.

²⁸⁵ R. J. Fallon, J. T. Vanderslice and E. A. Mason, *J. Phys. Chem.* **64** (1960) 505.

²⁸⁶ J. T. Sears and J. W. Sutherland, *J. Phys. Chem.* **72** (1968) 1166.

²⁸⁷ R. P. Wayne and J. N. Pitts, *J. Chem. Phys.* **50** (1969) 3644.

²⁸⁸ M. Nicolet, *Disc. Faraday Soc.* **37** (1964) 7 *et seq.*

²⁸⁹ D. Garvin, H. P. Broida and H. J. Kostkowski, *J. Chem. Phys.* **32** (1960) 880.

²⁹⁰ L. F. Phillips and H. I. Schiff, *J. Chem. Phys.* **36** (1962) 1509.

²⁹¹ C. J. Halstead and B. A. Thrush, *Proc. Roy. Soc.* **295** (1966) A, 380.

²⁹² P. N. Clough and B. A. Thrush, *Trans. Faraday Soc.* **65** (1969) 23.

²⁹³ W. M. Jones and N. Davidson, *J. Am. Chem. Soc.* **84** (1962) 2868.

²⁹⁴ W. Kaufmann and J. R. Kelso, *J. Chem. Phys.* **47** (1967) 4541.

²⁹⁵ R. D. Cadle and M. Ledford, *Air Water Pollution* **10** (1966) 25.

TABLE 52. PHYSICAL DATA FOR OZONE

Molecular weight, M	48
Melting point ($^{\circ}\text{K}$)	80.5
Boiling point ($^{\circ}\text{K}$)	161.3
Critical data:	
Temperature, T_c ($^{\circ}\text{K}$)	261.1
Pressure, P_c (atm)	54.6
Volume, V_c (cc mole $^{-1}$)	147.1
Density:	
Gas at 273 $^{\circ}\text{K}$, 760 mmHg (g l $^{-1}$)	2.144
Liquid at 77.4 $^{\circ}\text{K}$, 760 mmHg (g cc $^{-1}$)	1.614
Solid at 77.4 $^{\circ}\text{K}$, 760 mmHg (g cc $^{-1}$)	1.728
Surface tension at 90 $^{\circ}\text{K}$ (dyne cm $^{-1}$)	38.4
Viscosity at 90 $^{\circ}\text{K}$ (centipoise)	1.57
Dielectric constant at 90 $^{\circ}\text{K}$	4.75 \pm 0.02
Dipole moment, D	0.58
Ionization potentials (eV):	
1	12.3 \pm 0.1
2	12.52 \pm 0.05
3	13.52 \pm 0.05
4	16.4–17.4
5	19.2 \pm 0.1
Electron affinity (kcal mole $^{-1}$)	+44 \pm 10
Enthalpy of formation:	
ΔH_f° (g) (kcal mole $^{-1}$)	+34.1
ΔH_f° (aq) (kcal mole $^{-1}$)	+32.2
Free energy of formation, ΔG° (g)	+39.0
Entropy, S° (cal mole $^{-1}$ deg $^{-1}$)	57.1
Molecular dimensions:	
r (O–O) (\AA)	1.278(3)
α (OOO) (deg)	116 $^{\circ}$ 45'
Redox potentials (V):	
(a) $\text{O}_3 + 2\text{H}^+ + 2e \rightarrow \text{O}_2 + \text{H}_2\text{O}$	+2.07
(b) $\text{O}_3 + \text{H}_2\text{O} + 2e \rightarrow \text{O}_2 + 2\text{OH}^-$	+1.24
Point group, C_{2v}	
Vibrational frequencies (cm $^{-1}$):	
ν_1 IR, Raman (pol)	1110
ν_2 IR, Raman (pol)	705
ν_3 IR	1043
Force constants (mdyn \AA^{-1})	
f_d 5.70 f_{α/d^2}	1.28
f_{dd} 1.52 $f_{\alpha\alpha/d^2}$	0.33

From studies of the kinetics of thermal decomposition of ozone in the gas phase, it is generally agreed that the process²⁹⁶ occurs in two stages²⁹⁷ as shown in eqns. (5) and (6). The photochemical decomposition of ozone,



has been studied in detail²⁹⁸.

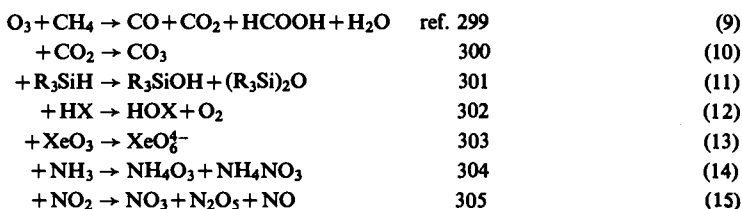
The reactions of ozone with more complicated systems provide examples of its considerable oxidizing power. The redox potential, E_0 , of ozone is such as to place it in a class

²⁹⁶ S. W. Benson and A. E. Axworthy, *J. Chem. Phys.* **42** (1965) 2614.

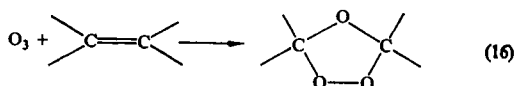
²⁹⁷ M. F. R. Mulcahy and D. J. Williams, *Trans. Faraday Soc.* **64** (1968) 59.

²⁹⁸ R. G. W. Norrish and R. P. Wayne, *Proc. Roy. Soc. A*, **288** (1965) 200, 361.

with molecular fluorine, the hydroxyl radical and atomic oxygen, all of which are very strong oxidizing agents:



The reactions of ozone with organic compounds have been reviewed³⁰⁶⁻³⁰⁸. Particular interest attaches to the reaction with alkenes. The end product of the reaction



is termed an ozonide (but see following section). The ozonide may be destroyed ($\text{Zn}/\text{H}_2\text{O}$; MeOH/I^-), leaving the organic product which is either an aldehyde or a ketone. This reaction is useful as a means of determining the position of unsaturated linkages in organic compounds, for example:



The exact mechanism of the reaction leading to the formation of the ozonide, eqn. (16), is the subject of controversy; however, the current view³⁰⁹ appears to favour the initial formation of a π -complex between an ozone molecule and an olefin molecule. Ozone may be regarded as a 1,3-dipolar molecule.

An interesting contrast has been shown³¹⁰ in the rate of reaction between ozone and the simple olefins ethylene, propylene and butene-2, on the one hand, and their perfluorinated analogues, on the other hand. This difference has been taken to illustrate the effect of fluorination upon the $\text{C}=\text{C}$ bond strength of olefins.

²⁹⁹ F. J. Dilleuth, D. R. Skidmore and C. C. Schubert, *J. Phys. Chem.* **64** (1960) 1496.

³⁰⁰ N. G. Moll, D. R. Clutter and W. E. Thompson, *J. Chem. Phys.* **45** (1965) 4469.

³⁰¹ L. Spialter and J. D. Austin, *Inorg. Chem.* **5** (1966) 1975. J. D. Austin and L. Spialter, *Adv. Chem. Ser.* **77** (1968) 26.

³⁰² I. Schwager and A. Arkell, *J. Am. Chem. Soc.* **89** (1967) 6006.

³⁰³ T. M. Spittler and B. Jaselskis, *J. Am. Chem. Soc.* **88** (1966) 2942.

³⁰⁴ I. J. Solomon, K. Hattori, A. J. Kacmarek, G. M. Platz and M. J. Klein, *J. Am. Chem. Soc.* **84** (1962) 34.

³⁰⁵ W. B. De More and N. Davidson, *J. Am. Chem. Soc.* **81** (1959) 5869.

³⁰⁶ P. S. Bailey, *Chem. Rev.* **58** (1958) 925.

³⁰⁷ A. T. Menyailo and M. V. Pospelov, *Russ. Chem. Rev.* **36** (1967) 284.

³⁰⁸ F. D. Gunstone, *Educ. Chem.* **5** (1968) 166.

³⁰⁹ S. Fliszár and J. Carles, *J. Am. Chem. Soc.* **91** (1969) 2637; R. W. Murray, *Accounts Chem. Res.* **1** (1968) 313.

³¹⁰ J. Heicklen, *J. Phys. Chem.* **70** (1966) 477.

Various theoretical studies have been made of the ozone molecule. Both *ab initio* SCF MO³¹¹ and INDO³¹² calculations produce estimates of the bond angle, $\widehat{\text{OOO}}$ which are in satisfactory agreement with the experimental value. Ozone is a 24(18) electron molecule, isoelectronic with NO_2^- and NOCl .

A number of different methods are available for the quantitative estimation of ozone. The simplest chemical method involves the oxidation of KI to give iodine which can then be titrated with thiosulphate. The reaction



is quantitative. Ozone can also be determined photometrically by measurement at the maximum absorption in the ultraviolet region³¹³ (λ_{max} 2537 Å; ϵ 135 cm⁻¹). This band in the ultraviolet spectrum of ozone is known as the Hartley band.

Largely as a consequence of its oxidizing power, ozone produces technological problems by causing rubbers to crack and the general deterioration of textile fibres. Extensive studies have been carried out to determine ways in which such deleterious effects can be inhibited by treatment of the substances with chemical agents such as diamines.

In addition to the simple reactions shown in eqns. (1)–(7), some of which are chemiluminescent, the reactions between ozone and CO, CS₂ and a wide range of organic compounds give rise to chemiluminescence³¹⁴, which in certain cases may be very intense.

8.2. OZONIDES

In the previous section it was noted that ozone is a 24(18) electron molecule. Addition of one electron to this entity produces the ozonide ion, O_3^- , which is isoelectronic with the 33(19) electron molecule ClO_2 . The angle ($\widehat{\text{OClO}}$) in ClO_2 is 117°³¹⁵; in O_3^- the angle ($\widehat{\text{OOO}}$) is 100°³¹⁶.

The literature on ozonides has been reviewed on a number of occasions^{317–320}. Ozonides have been intensively investigated in recent years as potential sources of oxygen because of the aerospace industrial interest in non-regenerative air revitalization agents and propellant materials of high specific impulse.

Although the parent acid, HO_3 , is unknown, ozonide salts of the alkali metals³²¹, the alkaline earth metals³²² and both the ammonium³²³ and tetramethylammonium³²¹ cations

³¹¹ S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.* **47** (1967) 1953.

³¹² J. A. Pople, D. L. Beveridge and P. A. Dobosh, *J. Chem. Phys.* **47** (1967) 2026.

³¹³ W. B. De More and O. F. Raper, *J. Phys. Chem.* **68** (1964) 412.

³¹⁴ R. L. Bowman and N. Alexander, *Science* **154** (1966) 1454.

³¹⁵ R. F. Curl, J. L. Kinsey, J. G. Baker, J. C. Baird, G. R. Bird, R. F. Heidleberg, T. M. Sugden, D. R. Jenkins and C. R. Kenney, *Phys. Rev.* **121** (1961) 1119.

³¹⁶ L. V. Azárov and I. Corvin, *Proc. Nat. Acad. Sci. US* **49** (1963) 1.

³¹⁷ N. G. Vannerberg, *Prog. Inorg. Chem.* **4** (1962) 125.

³¹⁸ A. W. Petrocelli and R. V. Chiarenzelli, *J. Chem. Educ.* **39** (1962) 557.

³¹⁹ I. I. Vol'nov, *Usp. Khim.* **34** (1965) 2111.

³²⁰ I. I. Vol'nov, *Peroxides, Superoxides and Ozonides of Alkali and Alkaline Earth Metals* (English translation), Plenum Press, New York (1966).

³²¹ I. J. Solomon, A. J. Kacmarek, J. M. McDonough and K. Hattori, *J. Am. Chem. Soc.* **82** (1960) 5640.

³²² I. I. Vol'nov, S. A. Tokareva, V. N. Belevskii and G. P. Pilipenko, *Izvestia Akad. Nauk SSSR, Ser. Khim.* 1967, 416.

³²³ I. J. Solomon, K. Hattori, A. J. Kacmarek, G. M. Platz and M. J. Klein, *J. Am. Chem. Soc.* **84** (1962) 34.

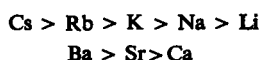
have been described. The reaction between ozone and an alkali metal hydroxide in solution was first described in 1866³²⁴, when it was noted that a red colour was produced in the solution. Subsequently it was found that the reaction between a powered alkali metal hydroxide and gaseous ozone in an oxygen carrier at room temperature or below, produces the ozonide of the metal, and the presence of the O_3^- anion was established³²⁵.

A detailed study of the mechanism of formation of potassium ozonide, KO_3 , using $K^{18}OH$, has shown that the overall stoichiometry of the reaction is given by the equation³²⁶



where $H^\circ = -158 \text{ kcal mole}^{-1}$. The reaction by which ozonide salts in general are formed is catalysed by ammonia³²⁷, and the ozonide, once formed, is often isolated by extraction into liquid ammonia. Alkali metal ozonides are soluble in liquid ammonia, methylamine and dimethylformamide³²¹. Although ozonides of all the alkali metals are known, lithium ozonide is known only in the form of its ammonia adduct, $LiO_3 \cdot 4NH_3$ ³²⁷. Calculations of the heat of formation, ΔH_f° , and the lattice energy of the hypothetical LiO_3 have suggested³²⁸ that it will not be stable with respect to decomposition to a lower oxide in the free (non-solvated) state.

The thermal stability of an ozonide is largely determined by the cation present. Thus among the alkali metals and the alkaline earth metals, the following order of decreasing thermal stability is observed:



which is in agreement with calculations of the thermodynamic stability of these systems^{322, 329}. The enthalpy of formation of various ozonides has been measured, and the results shown in Table 53 obtained.

TABLE 53. ENTHALPY OF FORMATION OF SOLID OZONIDES (kcal mole^{-1})

$LiO_3 \cdot 4NH_3$	-135 ± 5	Ref. 327	$Ca(O_3)_2$	-69	Ref. 322
KO_3	-62.1 ± 0.9	330	$Sr(O_3)_2$	-68	322
Me_4NO_3	-49.5 ± 4.5	321	$Ba(O_3)_2$	-67	322

$$\Delta H_f^\circ (O_3^-, g) = -11 \pm 10 \text{ (ref. 328).}$$

In the solid state, ozonides of the alkali and alkaline earth metals are coloured. Both NaO_3 and KO_3 are dichroic, while crystallographic studies have shown that both have a body-centred tetragonal unit cell ($I4/mcm$) with the following lattice parameters:

³²⁴ C. F. Schönbein, *J. Prakt. Chem.* **45** (1866) 469.

³²⁵ I. A. Kazarnovskii, G. P. Nikolskii and T. A. Abletsova, *Doklady Akad. Nauk SSSR* **64** (1949) 69.

³²⁶ I. I. Vol'nov, V. N. Chamova and E. I. Latysheva, *Izvestia Akad. Nauk SSSR, Ser. Khim.* **1967**, 1183.

³²⁷ A. J. Kacmarek, J. K. McDonough and I. J. Solomon, *Inorg. Chem.* **1** (1962) 659.

³²⁸ R. L. Wood and L. A. D'Orazio, *J. Phys. Chem.* **69** (1965) 2562.

³²⁹ G. P. Nikolskii, Z. A. Bagdasar'yan and I. A. Kazarnovskii, *Doklady Akad. Nauk SSSR* **77** (1951) 69.

	<i>a</i>	<i>c</i>	Ref.
NaO ₃	11.61	7.66	331
KO ₃	8.597	7.080	316

The structure of KO₃ is related to that of KN₃. A monoclinic form of KO₃ related to KNO₂ has been described³³². From this data the lattice energy and Madelung constant of KO₃ have been calculated³²⁸ for two possible models of the charge distribution of the ozonide ion thus:

Model <i>a</i>	charge distribution	O ⁻¹ O ⁻¹ O ⁻¹
Model <i>b</i>	charge distribution	O ⁻¹ O ⁺¹ O ⁻¹
	Model <i>a</i>	Model <i>b</i>
Lattice energy (kcal mole ⁻¹)	166.7	178.4
Madelung constant	2.1012 ± 0.03 %	2.2554 ± 0.08 %

This data has been used to calculate the electron affinity of ozone (44 ± 10 kcal mole⁻¹) and thermodynamic functions (Δ*H*[°], Δ*G*[°]) of other alkali metal ozonides.

When ozone is passed over ammonia at -130°, ammonium ozonide, NH₄O₃, is produced³²³. From a study of the infrared spectrum of NH₄O₃ at temperatures below -90°, the following values of the fundamental frequencies of the O₃⁻ ion were obtained³³³ as *v*₁ 1260, *v*₂ 800, *v*₃ 1140 cm⁻¹. The values of the structural parameters of the ozonide ion obtained from spectroscopic³³³ and crystallographic³¹⁶ measurements together with values calculated³³⁴ by comparison with NO₂, NO₂⁻ and O₃ are presented in Table 54. The corresponding values for ozone are provided for comparison

TABLE 54. STRUCTURAL PARAMETERS OF O₃⁻ ION

Method	<i>r</i> (O-O) Å	(∠OOO) (deg)	Ref.
X-ray	1.19	100	316
Infrared	1.22	~100	333
Calculation	1.34	110 ± 5	334
O ₃ microwave	1.278	116.8	335

In addition to the methods mentioned above, the ozonide ion may be produced in solution as a result of pulse radiolysis³³⁶, flash photolysis³³⁷ or γ-irradiation³³⁸ of such substances

³³⁰ G. P. Nikolskii, L. J. Kazarnovskaya, Z. A. Bagdasar'yan and I. A. Kazarnovskii, *Doklady Akad. Nauk SSSR* **72** (1950) 713.

³³¹ S. N. Tokareva, M. S. Dobrolyubova and S.Z. Makarov, *Khim. Perekisnykh Soedin. Akad. Nauk SSSR, Inst. Obshch i Neorg. Khim.* 1963, 188; *Chem. Abs.* **60** (1964) 12884a.

³³² I. J. Solomon and A. J. Kacmarek, *J. Phys. Chem.* **64** (1960) 168.

³³³ K. Herman and P. A. Giguere, *Can. J. Chem.* **43** (1965) 1946.

³³⁴ P. Smith, *J. Phys. Chem.* **60** (1956) 1471.

³³⁵ R. H. Hughes, *J. Chem. Phys.* **24** (1956) 131.

³³⁶ G. Czapski, *J. Phys. Chem.* **71** (1967) 1683.

³³⁷ L. Dogliotti and E. Hayon, *J. Phys. Chem.* **71** (1967) 2511.

³³⁸ K. Tagaya and T. Nogaito, *J. Phys. Soc. Japan* **23** (1967) 70.

as H_2O_2 , the persulphate ion, AgNO_3 and KClO_4 . In these experiments the presence of the ozonide ion has been established from its characteristic visible absorption which shows λ_{max} at 4300 Å. This value should be compared with that found in the ozonide salts³²³, all of which show a maximum absorption at ~ 4500 Å, together with five subsidiary maxima at the following approximate wavelengths; 5020, 4850, 4660, 4330, 4300 Å. The spectra of these salts all show a slight solvent dependence.

The ozonide ion is paramagnetic. The moment of KO_3 (μ) was found³²⁵ to be 1.63 BM. The e.s.r. spectra of several ozonides have been studied³¹⁷ in order to determine the g -value of the unpaired electron and the following results have been obtained^{325, 339}.

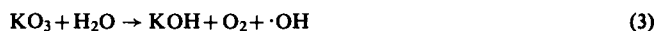
	g -value		g -value
NaO_3	2.012	NH_4O_3	2.0119
KO_3	2.0124	Me_4NO_3	2.0144

From these data it has been concluded that there is considerable spin-orbit coupling in the ozonide ion.

The application of e.s.r. spectroscopy in a study³⁴⁰ of the hydrolysis of KO_3 has shown that, although the overall process may be described³²⁵ by the equation



free hydroxyl radicals, $\cdot\text{OH}$, are produced as intermediates in the reaction thus:



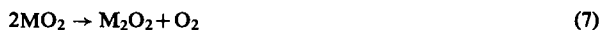
Thermal decomposition of ozonide salts^{319, 341} has been studied by a variety of methods, particularly by d.t.a. The reaction is complex, but in its most simple form may be described by the equations



so that the overall process is described by



Further thermal decomposition of the superoxide, MO_2 , according to



can also occur, so that the general decomposition reaction is³⁴²



³³⁹ A. D. McLachlan, M. C. R. Symons and M. G. Townsend, *J. Chem. Soc.* 1959, 952.

³⁴⁰ I. A. Kazarnovskii, N. P. Lipikhin and N. N. Bubnov, *Izvestia Akad. Nauk SSSR, Ser. Khim.* 1966, 2247.

³⁴¹ C. B. Riolo and T. F. Soldi, *Chim. Ind. (Milan)* 48 (1966) 846.

³⁴² E. I. Sokovnin, *Izvestia Akad. Nauk SSSR, Ser. Khim.* 1963, 181.

The reaction between potassium superoxide, KO_2 , and ozone in oxygen in a fluorocarbon solvent at -100° to -60° , leads³⁴³ to the formation of KO_3 by a process similar to that described by the reverse of eqn. (6). The peculiar advantage of this method is that it avoids the use of liquid ammonia.

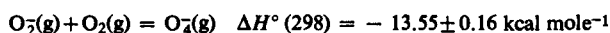
9. OTHER SPECIES CONTAINING O_3 AND O_4 GROUPS

9.1. O_4

In 1924 G. N. Lewis explained the drop in paramagnetic susceptibility of O_2 on condensation and on cooling by postulating³⁴⁴ the formation of $(\text{O}_2)_2$ dimers, with a heat of formation of $128 \text{ cal mole}^{-1}$; since then his suggestion has been supported by evidence drawn from measurements of magnetic susceptibility³⁴⁵, from electronic spectroscopy³⁴⁶ and from a preliminary study of the crystal structure of oxygen³⁴⁷. Thorough analysis of the structures of α -, β - and γ - O_2 , however³⁴⁸⁻³⁵⁰, shows that dimers are not present in these phases; the antiferromagnetism has been accounted for in terms of long- and short-range magnetic ordering³⁵¹, which probably persists in the liquid; thus most of the evidence on which the suggestion of dimerization was based has lost its force. There are electronic transitions in all phases that are clearly associated with co-operative effects, but in the vapour and the liquid phases it is not clear whether the polymolecular species is longer lived than a collision complex³⁵². Calculations based on the second virial coefficient, using a Lennard-Jones potential³⁵³, suggest that the concentration of dimers in O_2 at 300°K and 1 atm pressure is $6.4 \times 10^{-4} \text{ dimers mole}^{-1}$, but experiments with a mass spectrometer indicate that the concentration is much lower³⁵⁴. It should be noted that in gaseous argon or krypton under the same conditions the concentration of dimers is higher.

9.2. CHARGED O_4 SPECIES

The molecule ions O_4^+ and O_4^- have both been detected by mass spectrometry^{355, 356}, and the e.s.r. spectra of irradiated nitrates at low temperatures contain signals that have been assigned³⁵⁷ to O_4^- . In the gas phase the heats of formation of the two ions are³⁵⁶:



³⁴³ I. I. Volnov, S. A. Tokareva, V. I. Klimanov and G. P. Pilipenko, *Izvestia Akad. Nauk SSSR, Ser. Khim.* 1966, 1267.

³⁴⁴ G. N. Lewis, *J. Am. Chem. Soc.* **46** (1924) 2027.

³⁴⁵ L. N. Mulay and L. K. Keys, *J. Am. Chem. Soc.* **86** (1964) 4489.

³⁴⁶ V. I. Dianov-Klovov, *Optics Spectrosc.* **20** (1966) 530

³⁴⁷ L. Vegard, *Nature* **136** (1935) 720.

³⁴⁸ C. S. Barrett, L. Meyer and J. Wassermann, *J. Chem. Phys.* **47** (1967) 592.

³⁴⁹ R. A. Alikhanov, *Soviet Physics JETP* **18** (1964) 556.

³⁵⁰ T. A. Jordan, W. E. Streib and W. N. Lipscomb, *Acta Cryst.* **17** (1964) 777.

³⁵¹ M. F. Collins, *Proc. Phys. Soc.* **89** (1966) 415.

³⁵² R. P. Blickensderfer and G. E. Ewing, *J. Chem. Phys.* **47** (1967) 331.

³⁵³ D. E. Stogryn and J. Hirschfelder, *J. Chem. Phys.* **31** (1959) 1531; **33** (1960) 942.

³⁵⁴ T. A. Milne and F. T. Greene, *J. Chem. Phys.* **47** (1967) 3668.

³⁵⁵ R. E. Voshall, J. G. Pack and A. V. Phelps, *J. Chem. Phys.* **43** (1965) 990.

³⁵⁶ D. C. Conway and L. E. Nesbitt, *J. Chem. Phys.* **48** (1968) 509.

³⁵⁷ R. Kikuchi, T. Nogaito, K. Tagaya and K. Matsumo, *Mem. Inst. Sci. Ind. Res. Osaka Univ.* **24** (1967)

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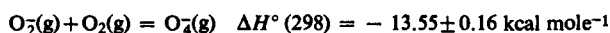
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³⁴⁸ C. S. Barrett, L. Meyer and J. Wassermann, *J. Chem. Phys.* **47** (1967) 592.

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³⁵³ D. E. Stogryn and J. Hirschfelder, *J. Chem. Phys.* **31** (1959) 1531; **33** (1960) 942.

³⁵⁴ T. A. Milne and F. T. Greene, *J. Chem. Phys.* **47** (1967) 3668.

³⁵⁵ R. E. Voshall, J. G. Pack and A. V. Phelps, *J. Chem. Phys.* **43** (1965) 990.

³⁵⁶ D. C. Conway and L. E. Nesbitt, *J. Chem. Phys.* **48** (1968) 509.

³⁵⁷ R. Kikuchi, T. Nogaito, K. Tagaya and K. Matsumo, *Mem. Inst. Sci. Ind. Res. Osaka Univ.* **24** (1967)

The rate constant for the former reaction has been determined³⁵⁸. The heats of formation are in reasonable agreement with calculations by the modified Hückel method assuming that the molecule ions are planar.

9.3. HYDROGEN SUPEROXIDES³⁵⁹

The formation of superoxides H_2O_3 and H_2O_4 has been postulated to explain the delay in oxygen evolution when H_2O_2 is oxidized by potassium permanganate; the compounds may also be formed in H-O flames and in irradiated aqueous H_2O_2 . Some of the observations have been questioned, and for others there are other possible explanations. There is much evidence relating to the possible formation of hydrogen superoxides from studies at low temperatures of the products of the action of an electric discharge on H_2O or H_2O_2 , or of the reaction between ozone or oxygen and hydrogen atoms. On warming the products to 160°K, heat and oxygen are evolved; the molar ratio of evolved O_2 to residual H_2O_2 is said for the system hydrogen atoms/liquid ozone to be 1:1, and it has been suggested that the evolved oxygen comes from decomposition of H_2O_4 . The melting point of the condensate is lower than the lowest point in the $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ eutectic; the X-ray and electron diffraction patterns are different from those given by mixtures of H_2O and H_2O_2 , the product is diamagnetic below 160°K (indicating the absence of radicals) and there are bands in the infrared spectra that have been assigned to modes of H_2O_4 because no other plausible assignment could be devised. This evidence has been vehemently contested³⁶⁰. The spectroscopic assignments have been questioned³⁶¹; other explanations have been put forward for most of the observations. If H_2O_3 or H_2O_4 is formed, it is clear that they are unstable at normal temperatures; either or both may be formed at low temperatures, but the evidence so far available is by no means decisive.

9.4. OTHER TRIOXIDES AND TETROXIDES

When t-butyl hydroperoxide is treated with lead tetraacetate in CH_2Cl_2 at low temperatures, a substance is formed which appears stable at temperatures below -30° , but which evolves oxygen rapidly at higher temperatures; it is believed to be di(t-butyl) trioxide³⁶². An earlier claim to have prepared the compound³⁶³ has been discounted³⁶⁴. From the constancy of the e.s.r. signal assigned to t-butyl peroxy-radicals (formed by photolysis of di-t-butyl peroxycarbonate at -70°) in the temperature range -110° to -85° , it is suggested³⁶⁵ that in that temperature range there is appreciable dimerization to form di(t-butyl peroxide). Neither of these compounds is stable enough to have been isolated in a pure form.

³⁵⁸ D. A. Dundas, P. Kerbarle and A. Good, *J. Chem. Phys.* **50** (1969) 805.

³⁵⁹ M. Venugopalan and R. G. Jones, *Chem. Rev.* **66** (1966) 133; *The Chemistry of Dissociated Water Vapour and Related Systems*, Interscience (1968).

³⁶⁰ P. A. Giguère, *J. Am. Chem. Soc.* **90** (1968) 7181.

³⁶¹ K. Herman and P. A. Giguère, *Can. J. Chem.* **46** (1968) 2649.

³⁶² P. D. Bartlett and P. Günther, *J. Am. Chem. Soc.* **88** (1966) 3288.

³⁶³ N. A. Milas and F. G. Arzoumanidis, *Chem. Ind.* 1966, 66.

³⁶⁴ R. D. Youssefyeh and R. W. Murray, *Chem. Ind.* 1966, 1531.

³⁶⁵ P. D. Bartlett and G. Guaraldi, *J. Am. Chem. Soc.* **89** (1967) 4799.

The perfluoroalkyl trioxides $\text{CF}_3\text{OOOCF}_3$ and $\text{CF}_3\text{OOOC}_2\text{F}_5$, on the other hand, have been isolated and characterized by infrared, n.m.r. and mass spectrometry, and by measurements of vapour density. The compounds were prepared by the direct fluorination of metal salts of trifluoroacetic acid³⁶⁶ and by the reaction between dioxygen difluoride and carbonyl fluoride³⁶⁷. Besides these, the trioxide radical CF_3OOO has been identified by e.s.r. spectroscopy³⁶⁸ among the photolysis products of $\text{CF}_3\text{OOOCF}_3$ (see section 5.11, under *Bis* (trifluoromethyl trioxide, $\text{CF}_3\text{OOOCF}_3$)).

³⁶⁶ P. G. Thompson, *J. Am. Chem. Soc.* **89** (1967) 4316.

³⁶⁷ L. R. Anderson and W. B. Fox, *J. Am. Chem. Soc.* **89** (1967) 4313.

³⁶⁸ R. W. Fessenden, *J. Chem. Phys.* **48** (1968) 3725.

Contents of Comprehensive Inorganic Chemistry

VOLUME 1

The element Hydrogen, ortho- and para-Hydrogen, atomic Hydrogen

K M MACKAY *University of Waikato*

Hydrides

K M MACKAY *University of Waikato*

Deuterium and Tritium

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F O SLADKY *University of Innsbruck*

Lithium and its compounds

W A HART & O F BEUMEL Jr *Foote Mineral Co, Pennsylvania*

Sodium, Potassium, Rubidium, Cesium and Francium

T P WHALEY *International Minerals and Chemical Corp, Illinois*

Beryllium

D A EVEREST *National Physical Laboratory, Teddington*

Magnesium, Calcium, Strontium, Barium and Radium

R D GOODENOUGH & V A STENGER *The Dow Chemical Co, Michigan*

Boron

N N GREENWOOD *University of Leeds*

Aluminium, Gallium, Indium and Thallium

K WADE & A J BANISTER *University of Durham*

Carbon

A K HOLLIDAY, G HUGHES & S M WALKER *University of Liverpool*

An introduction to the organic chemistry of the metallic elements

M L H GREEN *University of Oxford* & P POWELL *Royal Holloway College*

Silicon

E G ROCHOW *Harvard University*

Index

VOLUME 2

Germanium

E G ROCHOW, *Harvard University*

Tin

E W ABEL *University of Exeter*

Lead

E W ABEL *University of Exeter*

Nitrogen

K JONES *University of Manchester Inst. of Science & Technology*

Phosphorus

A D F TOY *Stauffer Chemical Co, New York*

Arsenic, Antimony and Bismuth

J D SMITH *University of Sussex*

Oxygen

E A V EBSWORTH *University of Edinburgh*,

J A CONNOR *University of Manchester*, &

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Sulphur

M SCHMIDT & W SIEBERT *University of Wurzburg*

Selenium, Tellurium and Polonium

K W BAGNALL *University of Manchester*

Fluorine

T A O'DONNELL *University of Melbourne*

Chlorine, Bromine, Iodine and Astatine

A J DOWNS & C J ADAMS *University of Oxford*

Index

VOLUME 3

Copper

A G MASSEY *University of Technology, Loughborough*

Silver

N R THOMPSON *ICI, Runcorn Heath Laboratory, Cheshire*

Gold

B F G JOHNSON *University of Cambridge*

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Scandium, Yttrium and Lanthanum

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D C BRADLEY & P THORNTON *Queen Mary College, London*

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The chemistry of Niobium and Tantalum

D BROWN *Atomic Energy Research Establishment, Harwell*

Chromium, Molybdenum and Tungsten

C L ROLLINSON *University of Maryland*

Manganese

R D W KEMMITT *University of Leicester*

Technetium

R D PEACOCK *University of Leicester*

Rhenium

R D PEACOCK *University of Leicester*

Iron

D NICHOLLS *University of Liverpool*

Cobalt

D NICHOLLS *University of Liverpool*

Nickel

D NICHOLLS *University of Liverpool*

The 2nd and 3rd row elements of group

VIII, A, B and C

S E LIVINGSTONE *University of New South Wales*

Index

VOLUME 4

The Lanthanides

T MOELLER *Arizona State University*

Carbonyls, Cyanides, Isocyanides and Nitrosyls

W P GRIFFITH *Imperial College of Science & Technology London*

Compounds of the transition elements involving metal-metal bonds

D L KEPERT *University of Western Australia*

& K VRIEZE *University of Amsterdam*

Transition metal hydrogen compounds

J C GREEN & M L H GREEN *University of Oxford*

Non-stoichiometric compounds: an introductory essay

D J M BEVAN *The Flinders University of South Australia*

Tungsten bronzes, Vanadium bronzes and related compounds

P HAGENMULLER *University of Bordeaux*

Isopolyanions and heteropolyanions

D L KEPERT *University of Western Australia*

Transition metal chemistry

B F G JOHNSON *University of Cambridge*

Organo-transition metal compounds and related aspects of homogeneous catalysis

B L SHAW & N I TUCKER *University of Leeds*

Index

VOLUME 5

The Actinides

J A LEE & J A MARPLES

G W C MILNER & G PHILLIPS

P G MARDON

Atomic Energy Research Establishment, Harwell

C KELLER *Kernforschungszentrum, Karlsruhe*

S H EBERLE *Universität Karlsruhe*

D BROWN, R M DELL & P E POTTER *AERE, Harwell*

K W BAGNALL *University of Manchester*

J RYDBERG & J O LILJENZIN *Chalmers University of Technology*

S ÅHRLAND *University of Lund*

Master Index

INDEPENDENT OPINION

"These books are attractively bound and have clear print. Since the length and cost are not prohibitive, this set of books should be well within the budget of most libraries. Not only will the professional chemist find these books useful, but students and other readers will find them a valuable reference source. (Comprehensive Inorganic Chemistry) should be found in every undergraduate and graduate library, as well as industrial libraries. Many professional chemists may even consider them for personal libraries. Highly recommended."

Choice—A publication of the Association of College and Research Libraries.

INDEPENDENT OPINION

Volume 1 1467 pp + index

"This covers the chemistry of hydrogen, the noble gases, and of the elements of Groups IA, IIA, IIIB, carbon and silicon. The first three chapters deal with hydrogen, hydrides, deuterium and tritium and the fourth is an interesting discussion of the proton, protonic acids and the hydrogen bond. Two chapters follow on the inert gases, including interesting and extensive recent knowledge about their compounds set out by N. Bartlett and F. O. Sladky. Four chapters on the alkalis and alkaline earths contain a wealth of detail, although perhaps along traditional lines. N. N. Greenwood has written an excellent account on boron chemistry of book length in itself, and another chapter deals at length with much new information about aluminium, gallium, indium and thallium. Chapters 13 and 15 deal with carbon and silicon. Here it might have been expected that more would have been included on the high pressure chemistry of carbon and silicates, and mineral chemistry. Chapter 14 by M. L. H. Green and P. Powell is a useful introduction to the organic chemistry of the metallic elements, along modern lines of ligand field theory and ideas about metal complexes.

Throughout this volume, with its different authors, it is perhaps inevitable that there is some lack of uniformity in the extent of detail given. There are also a few lapses in symbolism, notation, and uniformity of units. Yet the whole must be regarded as a highly commendable collection of material which will be valuable to chemists of all kinds."

Professor Sir Harold Thompson FRS
Oxford

Volume 2 1594 pp + index

"Volume 2 is concerned with the chemistry of the elements of Groups IV, V, VI, VII. The general impression on reading the various chapters of this volume is the great effectiveness in reporting a considerable amount of chemistry in a very digestible form. The systematic presentation applied to each chapter allows a rapid assessment of the appropriate chemical information, and the text is well documented with reference to the original literature plus good review articles for a more detailed coverage. Perhaps a minor criticism of this work lies in the indexing; the subject index is relatively sparse for a text of such magnitude and it would have been of considerable utility to have a formulae index to the text.

The area of chemistry covered by this work is obviously very great, but it does appear to have

dealt with it in a very succinct manner for the majority of the text, which extends to approximately 1500 pages. The two major chapters in the book are associated with the chemistry of nitrogen, approximately 240 pages, and the chemistry of the halogens (excepting fluorine), approximately 500 pages. The book thus encompasses in one volume what would normally be a series of books. Both of the above mentioned chapters are admirable and the authors, K. Jones on nitrogen with A. J. Downs and C. J. Adams on the halogens, are to be commended on both the presentation and coverage. The chapter on the halogens illustrates the real strength of the series, in that detailed chemical information is not only presented but discussed in physico-chemical theoretical terms. A scientific compendium of this size often suffers from the "catalogue" approach, but the present text presents the chemistry in critical mode with a realistic assessment of the various physical methods used in property determination. Thus the properties of the halogens are discussed in terms of bond energies, bond lengths, vibrational properties, e.s.r., n.m.r., n.q.r. and Mossbauer spectroscopy, electronic and magnetic properties and dipole moments allowing a detailed appraisal of the use of various modern methods in studying the chemical properties reviewed.

Considering the magnitude of the task undertaken, it is extremely pleasing to note the number of chapters referring to papers in the 1971 period—a truly great commendation on the overall editorship of these volumes. Perhaps a general note in each volume stating the period covered by the references would have been of help. In general this work provides a welcome and unique addition to the inorganic literature."

Professor J. Lewis FRS
Cambridge

Volume 3 1370 pp + index

"This volume covers the chemistry of the elements of the d-block of the Periodic Table (the transition elements), with the exception of the Lanthanide elements (Vol. 4), the Actinide elements (Vol. 5) and some special aspects which are common to many of the transition elements (Vol. 4). The volume is therefore concerned specifically with the three elements which characterize each of the ten transition groups, and the chapters are mostly grouped in this way. However, the six platinum metals are treated in one chapter which is the best way to fit these similar elements into the overall scheme which is standard for all five volumes. There are altogether 17 chapters, written by 14 authors who are internationally

recognized 1370 pages of text and a useful 17 page index.

The five volumes are quite remarkable, in that they can justifiably claim to be comprehensive, yet at the same time remain interesting and readable; they are probably unique in this respect. Volume 3 serves as an excellent source-book for the essential physical constants of all important compounds (simple and complex) of the transition metals. These are arranged so that significant comparisons are made wherever possible, and there are extensive references. It says much for the ingenuity of the editors, authors, and particularly the printers that the presentation of such an amount of information has been possible, while still maintaining the readability of the text. Throughout the volume chemical properties and reactions are discussed and interpreted rather than listed. The need for skilled correlation of data is particularly important in Volume 3, since it is in the area of the transition elements that a major part of the research work in inorganic chemistry has been published in recent years, and in this area also there has been a major interaction of inorganic with theoretical chemistry.

This volume must surely become the first point of reference for research workers and teachers alike. The transition elements play an important role in Pure and Applied Chemistry, Physics, Materials Science and Biology, and the authors clearly intend their chapters to be of value to this wide audience. Teachers at any level will also appreciate the very high quality of the general presentation, discussion, formulae and diagrams. Apart from reference to the original literature, few scientists will find it necessary to look outside this volume for their material."

Professor C. C. Addison FRS
Nottingham

Volume 4 994 pp + index

"Volume 4 is concerned with the general chemistry of the lanthanides and some special topics in transition metal chemistry.

Therold Moeller has packed a great amount of the fundamental chemistry of the lanthanides into his 101 pages in an interesting and scholarly manner with tables of essential data. Important recent developments in their organometallic chemistry have come too late to be included, but the chapter provides a useful fairly detailed first reference to their inorganic chemistry.

The subjects of the surveys are topical and obviously bear the mark of the late Sir Ronald Nyholm. They vary considerably in detail of treatment, interest and authority. Generally they emphasize recent work until about 1969-70 but rarely show a sense of history. They vary in length from 60 to 200 pages, mostly around 100 pages. They are authoritative and useful surveys all giving numerous references to recent reviews and

original work. The authors are well known chemists whose style and subject matter are familiar to most inorganic chemists. There are eight surveys as follows:—

Carbonyls, cyanides, isocyanides and nitrosyls by W. Griffith. Compounds of the transition elements involving metal-metal bonds by D. L. Kepert and K. Vrieze. Transition metal hydrogen compounds by J. C. Green and M. L. H. Green. Non-stoichiometric compounds: an introductory essay by D. J. M. Bevan. Tungsten bronzes, vanadium bronzes and related compounds by P. Hagenmuller. Isopolyanions and heteropolyanions by D. L. Kepert. Transition metal chemistry by B. F. G. Johnson. Organo-transition metal compounds and related aspects of homogeneous catalysis by B. L. Shaw and N. I. Tucker.

This volume has its own subject index of sixteen and a half pages, and is well produced with numerous tables of data and references provided at the foot of each page."

Professor J. Chatt FRS
Sussex

Volume 5 635 pp + Master index

"Volume 5 is devoted to the Actinides (635 pp) and the Master Index (78 pp). The latter serves little purpose since it merely indicates the sub-sections of CIC, and thus repeats the indexes in each individual volume. Indeed, as the treatment of each element or series of elements follows a standard pattern, the volumes are essentially self-indexing anyway. A one-page table of contents at the beginning of Volume 5 would have been more helpful and is a curious omission. The running headings at the top of each double page are also singularly uninformative, only three being used: 'The Elements' for 102 pages, 'Compounds' for 361 pages and 'Solution Chemistry' for the remaining 171 pages.

The treatment of actinium and the actinides (elements 89-103) is both readable and authoritative. Nine of the contributors are from AERE, Harwell, and the other five (with one exception) are from nuclear chemistry institutes in Sweden and Germany. In reviewing these 5f elements it is salutary to recall that the majority have been synthesized for the first time within the last 30 years—yet the number of compounds known and the amount of information on them has already outstripped the more limited chemistry of their 4f congeners, the lanthanides. The authors have done a magnificent job in assembling, collating, assessing, and systematizing a vast amount of data on the physical and chemical properties of these elements and their numerous compounds. The work, which is extensively referenced, will undoubtedly remain the standard first source of information in this area for many years to come."

Professor N. N. Greenwood FRIC
Leeds

INDEX

- Brin process 697
- Bronzes 735
- Cristobalite 739
- Dioxygen
 - difluoride 752
 - bonding 769
 - chemical properties 754
 - OO[•]F radical 756
 - physical properties 753, 754
 - preparation 752
 - monofluoride 756
 - bonding 769
 - physical properties 757
- Dioxygenyl salts 778
- Fenton's reagent 776
- Haemocyanin 710
- Hexaoxygen difluoride 764
- Hydrogen peroxide 771
 - analysis 777
 - history 771
 - molecular structure 772, 774
 - properties
 - chemical 775
 - physical 773
 - thermodynamic 774
 - synthesis 771
 - uses 777
 - vibrational spectra 773
- Hydroxylases 711
- Laccase 711
- Oxides 722
 - allotropy 739
 - complex
 - structures 732
 - geometrical effects 740
 - simple 722
 - acid-base character 722
 - structures 730
 - structures 729
 - chain lattices 736
- Oxides (*cont.*)
 - cryolite structure 734
 - infinite three-dimensional lattices 730
 - layer lattices 735
 - molecular units 737
 - perovskite structure 734
 - thermodynamic considerations 739
- Oxygen 685
 - analysis 717
 - atomic 719
 - production 720
 - biological properties 717
 - bonding 686
 - additional α -bonds 688
 - angles 689
 - internal π -bonding 688
 - carriers 784
 - crystal structure 699
 - difluoride 748
 - bonding 769
 - chemical properties 748
 - OF radical 750
 - physical properties 748, 749
 - preparation 748
 - discovery 685
 - electronic structure
 - atomic 686
 - atomic energy levels 686
 - molecular 698
 - extraction 696
 - fluorides 747
 - bonding 767
 - energetics 758
 - free radicals 750, 756, 759
 - nmr 759
 - physical properties 768
 - ion-molecule reactions 721
 - isotopes 691
 - O¹⁷ 694
 - O¹⁸ 692
 - radioactive 691
 - stable 691
 - magnetic properties 705
 - molecular structure 699
 - monofluoride 751
 - bonding 769

Oxygen (*cont.*)

occurrence 696

O₄ 792

charged species 792

physical properties 687

liquid 707

molecules 706

solid 708

production 718

reactions 710

autoxidation 711

chemisorption 712

deoxygenation 716

electrochemical 715

heterogenous catalysis of 712

homogeneous catalysis of 712

oxygenation 710

photochemical oxygenation 714

singlet O₂ 714

spectroscopic properties 701

electronic spectra 701

esr spectra 704

microwave spectra 704

vibrational spectra 703

structural properties 698

uses 718

Oxygenases 710

Ozone 785

physical properties 786

preparation 785

reactions 786

Ozonides 788

physical properties 791

preparation 789

Pentaoxygen difluoride 764

Perfluorodimethyl peroxide 766

Perovskite structure 734

Peroxides 778

bond energies 784

ionic 780

non-stoichiometric 780

with directed bonds 710

chemical properties 783

Peroxides (*cont.*)

physical properties 783

stereochemistry 781

Phlogiston 685

Quartz 739

Riesenfeld-Liebhafsky test 781

Superoxides

ionic 779

Tetraoxygen difluoride 760

chemical properties 760

equilibrium with monomer 761

physical properties 760

preparation 760

Tridymite 739

Trifluoromethyl compounds 764

bis trioxide 767, 794

hypofluorite 765

ion 765

trioxide 766, 794

Trioxygen difluoride 761

chemical properties 761

composition 762

physical properties 762

preparation 761

Vaska's compound 784

Water 741

anomalous 746

dimensions 742

nmr spectrum 743

phase diagram 745

properties

chemical 747

physical 741

thermodynamic 743

ultraviolet absorption 743

vibrational frequencies 742

Winkler method 717