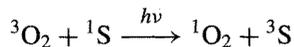and careful reasoning failed to convince his contemporaries.

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

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

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

$$H_2O_2 + ClO^- \longrightarrow Cl + H_2O + O_2(^1\Delta_g)$$
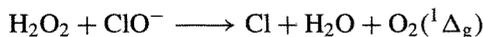
Another chemical route is by decomposition of solid adducts of ozone with triaryl and other phosphites at subambient temperatures:

$$O_3 + P(OPh)_3 \xrightarrow{-78°} O_3P(OPh)_3 \xrightarrow{-15°} O_2(^1\Delta_g)$$
$$+ OP(OPh)_3$$
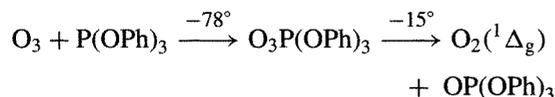
Reactions of $^1O_2$ can be classified into three types: 1,2 addition, 1,3 addition and 1,4 addition (see refs. 48–51 for details). In addition to its great importance in synthetic organic chemistry, singlet oxygen plays an important role in autoxidation (i.e. the photodegradation of polymers in air), and methods of improving the stability of commercial polymers and vulcanized rubbers to oxidation are of considerable industrial significance. Reactions of singlet oxygen also feature in the chemistry of the upper atmosphere.

14.2 Compounds of Oxygen

14.2.1 Coordination chemistry: dioxygen as a ligand

Few discoveries in synthetic chemistry during the past three decades have caused more excitement

or had more influence on the direction of subsequent work than L. Vaska's observation in 1963 that the planar 16-electron complex *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] can act as a reversible oxygen carrier by means of the equilibrium[52]

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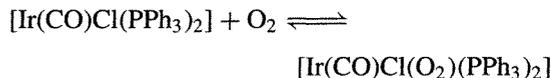
Not only were the structures, stabilities and range of metals that could form such complexes of theoretical interest, but there were manifest implications for an understanding of the biochemistry of the oxygen-carrying metalloproteins haemoglobin, myoglobin, haemerythrin and haemocyanin. Such complexes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

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

[52] L. VASKA, *Science* **140**, 809–10 (1963).

[53] J. A. CONNOR and E. A. V. EBSWORTH, *Adv. Inorg. Chem. Radiochem.* **6**, 279–381 (1964).

[54] V. J. CHOY and C. J. O'CONNOR, *Coord. Chem. Rev.* **9**, 145–70 (1972/3).

[55] J. S. VALENTINE, *Chem. Revs.* **73**, 235–45 (1973).

[56] M. J. NOLTE, E. SINGLETON and M. LAING, *J. Am. Chem. Soc.* **97**, 6396–400 (1975). An important paper showing how errors can arise even in careful single crystal X-ray studies, leading to incorrect inferences.

[57] R. W. ERSKINE and B. O. FIELD, Reversible oxygenation, *Struct. Bond.* **28**, 1–50 (1976).

[58] J. P. COLLMAN, *Acc. Chem. Res.* **10**, 265–72 (1977).

[59] A. B. P. LEVER and H. B. GRAY, *Acc. Chem. Res.* **11**, 348–55 (1978).

[60] R. D. JONES, D. A. SUMMERVILLE and F. BASOLO, *Chem. Revs.* **79**, 139–79 (1979).

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

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

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

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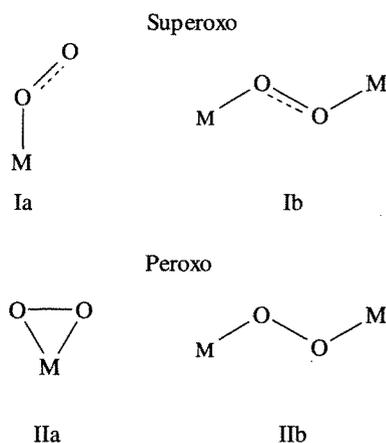
Superoxo

Ia   Ib

Peroxo

IIa   IIb

Figure 14.4 The four main types of O_2–M geometry. The bridging modes Ib and IIb appear superficially similar but differ markedly in dihedral angles and other bonding properties. See also footnote to Table 14.5 for the recently established unique μ,η^1-superoxide bridging mode.

peroxo) for reasons which will shortly become apparent (Fig. 14.4). Dioxygen can also form 1:2 complexes in which O_2 adopts a bidentate bridging geometry, labelled Ib and IIb in Fig. 14.4. Of these four classes of complex, the Vaska-type IIa peroxo complexes, are by far the most widespread amongst the transition metals, though many are not reversible oxygen carriers and some are formed by deprotonation of H_2O_2 (p. 636) rather than coordination of molecular O_2. By contrast, the bridging superoxo type Ib is known only for the green cobalt complexes formed by 1-electron oxidation of the corresponding IIb peroxo compounds. In all cases complex formation

is accompanied by a significant increase in the O–O interatomic distances and a considerable decrease in the v(O–O) vibrational stretching frequency. Both effects are more marked for the peroxo (type II) complexes than for the superoxo (type I) complexes and have been interpreted in terms of a transfer of electrons from M into the antibonding orbitals of O_2 (p. 606) thereby weakening the O–O bond. The magnitude of the effects to be expected can be gauged from Table 14.4.[60] Note that the O–O bond in O_2^+ is stronger than in O_2 but this does not mean that O_2^+ is more stable than O_2 since energy must be supplied to remove an electron from O_2 and this energy is greater than that released in forming the stronger bond: it is important not to confuse bond energy with stability. Comparative data for a wide range of dioxygen-metal complexes is in Table 14.5.[60,65] It will be noted also that the O–O distances and vibrational frequencies are rather insensitive to the nature of the metal or its other attached ligands, or, indeed, as to whether the O_2 is coordinated to 1 or 2 metal centres. Both classes of superoxo complex, however, have d(O–O) and v(O–O) close to the values for the superoxide ion, whereas both classes of peroxo complex have values close to those for the peroxide ion. (However, see footnote to Table 14.5 for an important caveat to this generalization.)

Superoxo complexes having a nonlinear M–O–O configuration are known at present only for Fe, Co, Rh and perhaps a few other transition metals, whereas the Vaska-type (IIa) complexes are known for almost all the transition metals

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[65] L. Vaska, *Acc. Chem. Res.* **9**, 175–83 (1976).

Table 14.4 Effect of electron configuration and charge on the bond properties of dioxygen species

Species	Bond order	Compound	d(O–O)/pm	Bond energy/ kJ mol^{-1}	v(O–O)/cm^{-1}
O_2^+	2.5	$O_2[AsF_6]$	112.3	625.1	1858
$O_2(^3\Sigma_g^-)$	2	O_2(g)	120.7	490.4	1554.7
$O_2(^1\Delta_g)$	2	O_2(g)	121.6	396.2	1483.5
O_2^- (superoxide)	1.5	$K[O_2]$	128	—	1145
O_2^{2-} (peroxide)	1	$Na_2[O_2]$	149	204.2	842
–OO–	1	H_2O_2 (cryst)	145.3	213	882

Table 14.5   Summary of properties of known dioxygen–metal complexes[a]

Complex type	O_2:M ratio	Structure	$d(O-O)$/pm (normal range)	$\nu(O-O)$/cm^{-1} (normal range)
superoxo Ia	1:1		125–135	1130–1195
superoxo Ib	1:2		126–136	1075–1122
peroxo IIa	1:1		130–155	800–932
peroxo IIb	1:1		144–149	790–884

[a] Reaction of K_2O with Al_2Me_6 in the presence of dibenzo-18-crown-6 (p. 96) yields the surprisingly stable anion $[(\mu,\eta^1\text{-}O_2)(AlMe_3)_2]^-$ in which one O of the superoxo ion bridges the 2 Al atoms (angle Al–O–Al 128°):
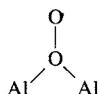
In this new type of coordination mode $d(O-O)$ is long (147 pm) and the weakness of the O–O linkage is also shown by the very low value of 851 cm^{-1} for $\nu(O-O)$, both values being more characteristic of peroxo than of superoxo complexes.[66]
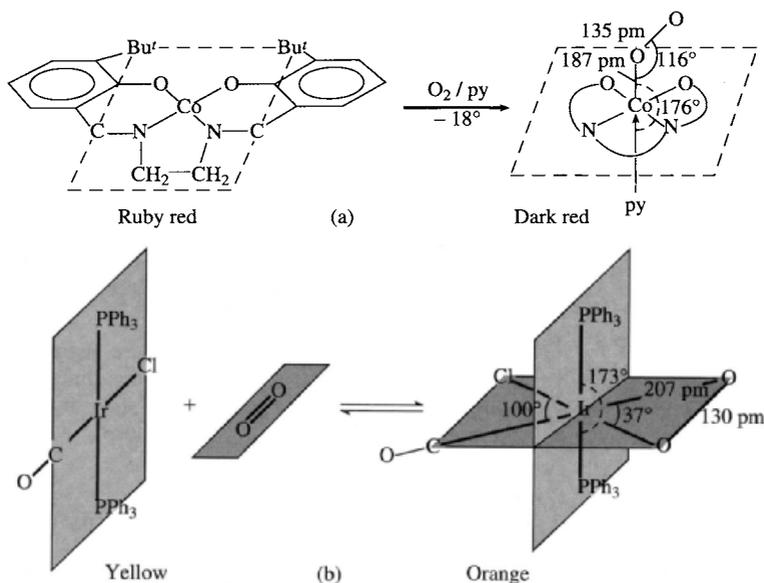

Figure 14.5   (a) Reaction of N,N'-ethylenebis(3-Bu^t-salicylideniminato)cobalt(II) with dioxygen and pyridine to form the superoxo complex [Co(3-Bu^{t}Salen)$_2$(O$_2$)py]; the py ligand is almost coplanar with the Co–O–O plane, the angle between the two being 18°.[67] (b) Reversible formation of the peroxo complex [Ir(CO)Cl(O$_2$)(PPh$_3$)$_2$]. The more densely shaded part of the complex is accurately coplanar.[68]

[66] D. C. HRNCIR, R. D. ROGERS and J. L. ATWOOD, *J. Am. Chem. Soc.* **103**, 4277–8 (1981). see also P. FANTUCCI and G. PACCHIONI, *J. Chem. Soc., Dalton Trans.*, 355–60 (1987).
[67] W. P. SCHAEFFER, B. T. HUIE, M. G. KURILLA and S. E. EALICK, *Inorg. Chem.* **19**, 340–4 (1980).
[68] S. J. LAPLACA and J. A. IBERS, *J. Am. Chem. Soc.* **87**, 2581–6 (1965).
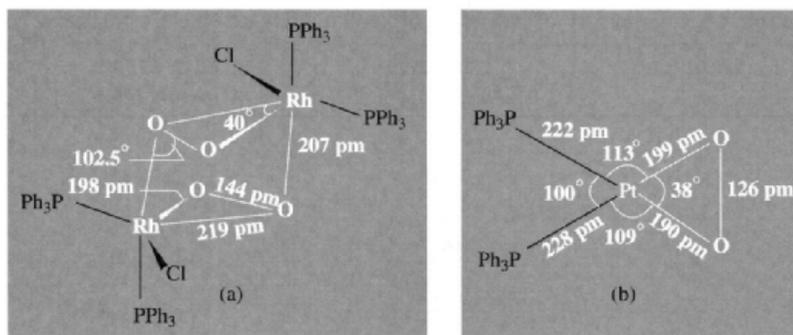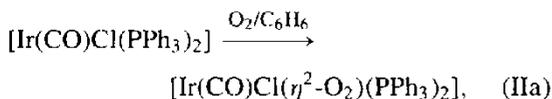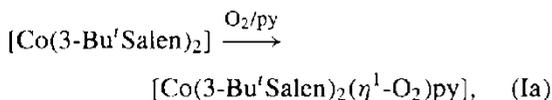
Figure 14.6   Structure and key dimensions of (a) the complex $[(Ph_3P)_2RhCl(\mu\text{-}O_2)]_2$ and (b) the complex $[Pt(O_2)(PPh_3)_2]$. The data in (b) are of poor quality because of the difficulty of growing suitable crystals and their instability in the X-ray beam (distances ± 5 pm angles $\pm 2°$).

except those in the Sc and Zn groups and possibly Mn, Cr and Fe. The two modes of formation are illustrated in Fig. 14.5 for the two reactions:

$$[Co(3\text{-}Bu^tSalen)_2] \xrightarrow{O_2/py}$$

$$[Co(3\text{-}Bu^tSalen)_2(\eta^1\text{-}O_2)py], \quad (Ia)$$

$$[Ir(CO)Cl(PPh_3)_2] \xrightarrow{O_2/C_6H_6}$$

$$[Ir(CO)Cl(\eta^2\text{-}O_2)(PPh_3)_2], \quad (IIa)$$

The sensitivity of the reaction type to the detailed nature of the bonding in the metal complex can be gauged from the fact that neither the PMe_3 analogue of Vaska's iridium complex, nor the corresponding rhodium complex $[Rh(CO)Cl(PPh_3)_2]$ react with dioxygen in this way. By contrast, the closely related red complex $[RhCl(PPh_3)_3]$ reacts readily with O_2 in CH_2Cl_2 solution with elimination of PPh_3 to give the brown dinuclear doubly bridging complex $[(Ph_3P)_2RhCl(\mu\text{-}O_2)]_2.CH_2Cl_2$ the structure of which is shown in Fig. 14.6a.[69] With $[Pt(PPh_3)_4]$ reaction also occurs with elimination of PPh_3 but the product is the yellow, planar, mononuclear complex $[Pt(\eta^2\text{-}O_2)(PPh_3)_2]$ (Fig. 14.6b).[70]
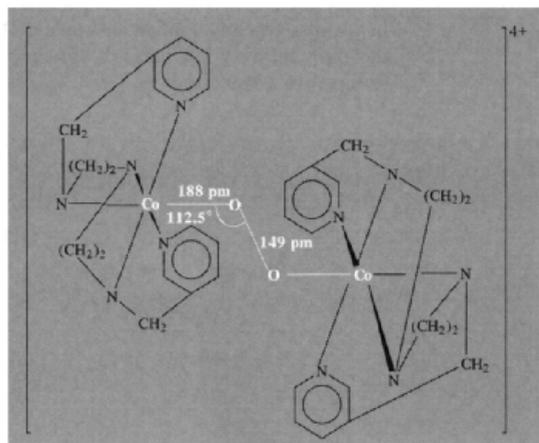

Figure 14.7   Schematic representation of the structure of the dinuclear cation in $[\{Co(pydien)\}_2O_2]L_4$ showing some important dimensions.

An example of a singly-bridging peroxo complex is the dinuclear cation $[\{Co(pydien)\}_2\text{-}O_2]^{4+}$ where pydien is the pentadentate ligand 1,9-bis(2-pyridyl)-2,5,8-triazanonane, $NC_5H_4\text{-}CH_2N(CH_2CH_2N)_2CH_2C_5H_4N$. The complex is readily formed by mixing ethanolic solutions of $CoCl_2.6H_2O$, NaI and the ligand, and then exposing the resulting solution to oxygen.[71] Some structural details are in Fig. 14.7. Such

[69] M. J. BENNETT and P. B. DONALDSON, *J. Am. Chem. Soc.* **93**, 3307-8 (1971).

[70] C. D. COOK, P.-T. CHENG and S. C. NYBURG, *J. Am. Chem. Soc.* **91**, 2123 (1969).

[71] J. H. TIMMONS, R. H. NISWANDER, A. CLEARFIELD and A. E. MARTELL, *Inorg. Chem.* **18**, 2977-82 (1979).

μ-O_2 complexes are formed generally among the "Group VIII" metals (Fe), Ru, Os; Co, Rh, Ir; Ni, Pd, Pt. A unique example from main-group element chemistry is in the doubly-bridged $R_2Sn(\mu$-O$)(\mu{:}\eta^1,\eta^1$-$O_2)SnR_2$,   (R = CH(SiMe$_3$)$_2$), in which O–O is 154 pm, Sn–O_2 201 pm, angle Sn–O–O 103.3°; Sn–O 198 pm angle Sn–O–Sn 110.3°.[72]

Many mono- and di-nuclear peroxo-type dioxygen complexes can also be made by an alternative route involving direct reaction of transition metal compounds with H_2O_2 and it is, in fact, quite arbitrary to distinguish these complexes from those made directly from O_2. Many such compounds are discussed further on p. 637 and under the chemistry of individual transition metals, but one example calls for special mention since it was the first structurally characterized peroxo derivative to feature a symmetrical, doubly bidentate (side on) bridge linking two metal centres.[73] The local coordination geometry and dimensions of the central planar {LaO$_2$La} group are shown in Fig. 14.8; the very long O–O distance is particularly notable, being substantially longer than in the O_2^{2-} ion itself (p. 616). The compound [La{N(SiMe$_3$)$_2$}$_2$(OPPh$_3$)]$_2O_2$, which is colourless, was made by treating [La{N(SiMe$_3$)$_2$}$_3$]

with Ph$_3$PO, but the origin of the peroxo group remains obscure. Similar complexes of Pr (which is also, surprisingly, colourless), Sm (pale yellow), Eu (orange-red) and Lu (colourless), were obtained in good yield either by a similar reaction or by treating [Ln{N(SiMe$_3$)$_2$}$_3$] with a half-molar proportion of (Ph$_3$PO)$_2$.H_2O_2.

The nature of the metal–oxygen bonding in the various types of dioxygen complex has been the subject of much discussion.[56,58,59,60,65,74] The electronic structure of the O_2 molecule (p. 606) makes it unlikely that coordination would be by the usual donation of an "onium" lone-pair (from O_2 to the metal centre) which forms an important component of most other donor–acceptor adducts (p. 198). Most discussion has centred on the extent of electron transfer from the metal into the partly occupied antibonding orbitals of O_2. There now seems general agreement that there is substantial transfer of electron density from the metal d$_{z^2}$ orbital into the π^* antibonding orbitals of O_2 with concomitant increase in the formal oxidation state of the metal, e.g. {Co^{II}} + $O_2 \rightarrow$ {Co^{III}(O_2^-)}. Whether the resulting bonding between dioxygen and the metal atom is predominantly ionic or partly covalent may well depend to some extent on the nature of the metal centre and is largely a semantic problem which gradually disappears the more precisely one can define the detailed MOs or the actual electron distribution,[75] cf. the discussion on p. 79.

A dramatic discovery in this area was made in 1996 when a dicopper–dioxygen adduct was found to have two isomeric forms which featured either a side-on bridging unit {Cu($\mu{:}\eta^2,\eta^2$-O_2)-Cu}$^{2+}$ or a cyclic {Cu(μ-O)$_2$Cu}$^{2+}$ core depending on whether it was crystallized from CH_2Cl_2 or thf, respectively. The two forms could be readily interconverted by reversible O–O bond cleavage and reformation, the O–O distance being ~141 pm and 229 pm in the two isomers.[75a] The

Figure 14.8   Schematic representation of the planar central portion of the μ-peroxo complex [La{N(SiMe$_3$)$_2$}$_2$(OPPh$_3$)]$_2O_2$.

[72] C. J. CARDIN, D. J. CARDIN, M. M. DEVEREUX and MAIRE A. CONVERY, *J. Chem. Soc., Chem. Commun.*, 1461–2 (1990).

[73] D. C. BRADLEY, J. S. GHOTRA, F. A. HART, M. B. HURSTHOUSE and P. R. RAITHBY, *J. Chem. Soc., Dalton Trans.*, 1166–72 (1977).
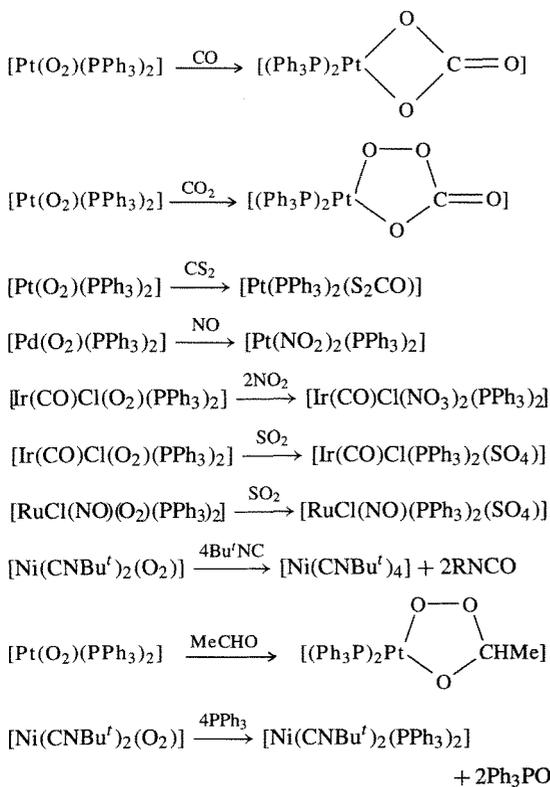
[74] R. S. DRAGO,   T. BEUGELSDIJK,   J. A. BREESE   and J. P. CANNADY *J. Am. Chem. Soc.* **100**, 5374–82 (1978).

[75] S. SAKAKI, K. HORI and A. OHYOSHI, *Inorg. Chem.* **17**, 3183–8 (1978).

[75a] W. B. TOLMAN and 7 others, *Science* **271**, 1397–400 (1996).

biochemical implications for reductive cleavage of O_2 by metalloenzymes and for O_2 evolution during photosynthesis are particularly exciting.

In addition to their great importance for structural and bonding studies, dioxygen complexes undergo many reactions. As already indicated, some of these reactions are of unique importance in biological chemistry[76] and in catalytic systems. Some of the simpler inorganic reactions can be summarized as follows: aqueous acids yield H_2O_2 and reducing agents give coordinatively unsaturated complexes. Frequently the dioxygen complex can oxidize species that do not readily react directly with free molecular O_2, e.g. CO, CO_2, CS_2, NO, NO_2, SO_2, RNC, RCHO, R_2CO, PPh_3, etc. Illustrative examples of these reactions are:

$$[Pt(O_2)(PPh_3)_2] \xrightarrow{\text{CO}} [(Ph_3P)_2Pt\langle\overset{O}{\underset{O}{}}\rangle C=O]$$

$$[Pt(O_2)(PPh_3)_2] \xrightarrow{\text{CO}_2} [(Ph_3P)_2Pt\langle\overset{O-O}{\underset{O}{}}\rangle C=O]$$

$$[Pt(O_2)(PPh_3)_2] \xrightarrow{\text{CS}_2} [Pt(PPh_3)_2(S_2CO)]$$

$$[Pd(O_2)(PPh_3)_2] \xrightarrow{\text{NO}} [Pt(NO_2)_2(PPh_3)_2]$$

$$[Ir(CO)Cl(O_2)(PPh_3)_2] \xrightarrow{2NO_2} [Ir(CO)Cl(NO_3)_2(PPh_3)_2]$$

$$[Ir(CO)Cl(O_2)(PPh_3)_2] \xrightarrow{\text{SO}_2} [Ir(CO)Cl(PPh_3)_2(SO_4)]$$

$$[RuCl(NO)(O_2)(PPh_3)_2] \xrightarrow{\text{SO}_2} [RuCl(NO)(PPh_3)_2(SO_4)]$$

$$[Ni(CNBu^t)_2(O_2)] \xrightarrow{4Bu^tNC} [Ni(CNBu^t)_4] + 2RNCO$$

$$[Pt(O_2)(PPh_3)_2] \xrightarrow{\text{MeCHO}} [(Ph_3P)_2Pt\langle\overset{O-O}{\underset{O}{}}\rangle CHMe]$$

$$[Ni(CNBu^t)_2(O_2)] \xrightarrow{4PPh_3} [Ni(CNBu^t)_2(PPh_3)_2]$$
$$+ 2Ph_3PO$$

[76] E.-I. OCHIAI, *J. Inorg. Nucl. Chem.* **37**, 1503–9 (1975). See also *Oxygen and Life: Second BOC Priestley Conference*, Roy. Soc. Chem. Special Publ. No. 39, London, 1981, 224 pp.

Explanations that have been advanced to explain the enhanced reactivity of coordinated dioxygen include:

(1) The diamagnetic nature of most O_2 complexes might facilitate reactions to form diamagnetic products which would otherwise be hindered by the requirement of spin conservation;

(2) the metal may hold O_2 and the reactant in *cis* positions thereby lowering the activation energy for oxidation, particularly with coordinatively unsaturated complexes;

(3) coordinated O_2 is usually partially reduced (towards O_2^- or O_2^{2-}) and this increased electron density might activate it.

Detailed kinetic and mechanistic studies will be required to assess the relative importance of these and other possible factors in specific instances.

14.2.2 Water

Introduction

Water is without doubt the most abundant, the most accessible and the most studied of all chemical compounds. Its omnipresence, its crucial importance for man's survival and its ability to transform so readily from the liquid to the solid and gaseous states has ensured its prominence in man's thinking from the earliest times. Water plays a prominent role in most creation myths and has a symbolic purifying or regenerating significance in many great religions even to the present day. In the religion of ancient Mesopotamia, the oldest of which we have written records (*ca.* 2000 BC), Nammu, goddess of the primaeval sea, was "the mother who gave birth to heaven and earth"; she was also the mother of the god of water, Enki, one of the four main gods controlling the major realms of the universe. In the Judaic-Christian tradition[77] "the Spirit of God moved upon the face of the waters" and creation proceeded via "a firmament in the midst of the waters" to divide heaven from

[77] Holy Bible, Genesis, Chap. 1, verses 1–10.

earth. Again, the Flood figures prominently[78] as it does in the legends of many other peoples. The activities of John the Baptist[79] and the obligatory washing practised by Muslims before prayers are further manifestations of the deep ritual significance of water.

Secular philosophers also perceived the unique nature of water. Thus, Thales of Miletus, who is generally regarded as the initiator of the Greek classical tradition of philosophy, *ca.* 585 BC, considered water to be the sole fundamental principle in nature. His celebrated dictum maintains: "It is water that, in taking different forms, constitutes the earth, atmosphere, sky, mountains, gods and men, beasts and birds, grass and trees, and animals down to worms, flies and ants. All these are but different forms of water. Meditate on water!" Though this may sound quaint or even perverse to modern ears, we should reflect that some marine invertebrates are, indeed, 96–97% water, and the human embryo during its first month is 93% water by weight. Aristotle considered water to be one of the four elements, alongside earth, air and fire, and this belief in the fundamental and elementary nature of water persisted until the epoch-making experiments of H. Cavendish and others in the second half of the eighteenth century (pp. 32, 601) showed water to be a compound of hydrogen and oxygen.[80]

Distribution and availability

Water is distributed very unevenly and with very variable purity over the surface of the earth (Table 14.6). Desert regions have little rainfall and no permanent surface waters, whereas oceans, containing many dissolved salts, cover vast tracts of the globe; they comprise 97% of the available water and cover an area of 3.61×10^8 km^2 (i.e. 70.8% of the surface of the

Table 14.6 Estimated world water supply

Source	Volume/10^3 km^3	% of total
Salt water		
Oceans	1 348 000	97.33
Saline lakes and inland seas	105[a]	0.008
Fresh water		
Polar ice and glaciers	28 200	2.04
Ground water	8 450	0.61
Lakes	125[b]	0.009
Soil moisture	69	0.005
Atmospheric water vapour	13.5	0.001
Rivers	1.5	0.0001
Total	1 385 000	100.0

[a] The Caspian Sea accounts for 75% of this.
[b] More than half of this is in the four largest lakes: Baikal 26 000; Tanganyika 20 000; Nyassa 13 000; and Superior 12 000 km^3.

earth). Less than 2.7% of the total surface water is fresh and most of this is locked up in the Antarctic ice cap and to a much lesser extent the Arctic. The Antarctic ice cap covers some 1.5×10^7 km^2, i.e. larger than Continental Europe to the Urals (1.01×10^7 km^2), the USA including Alaska and Hawaii (0.94×10^7 km^2), or Australia (0.77×10^7 km^2): it comprises some $2.5–2.9 \times 10^7$ km^3 of fresh water which, if melted, would supply all the rivers of the earth for more than 800 years. Every year some 5000 icebergs, totalling 10^{12} m^3 of ice (i.e. 10^{12} tonnes), are calved from the glaciers and ice shelves of Antarctica. Each iceberg consists (on average) of ~200 Mtonnes of pure fresh water and, if towed at 1–2 km h^{-1}, could arrive 30% intact in Australia to provide water at one-tenth of the cost of current desalination procedures.[81] Transportation of crushed ice by ship from the polar regions is an alternative that was used intermittently towards the end of the last century.

Surface freshwater lakes contain 1.25×10^5 km^3 of water, more than half of which

[78] Holy Bible, Genesis, Chaps. 6–8.

[79] Holy Bible, Gospels according to St. Matthew, Chap. 3; St. Mark, Chap. 1; St. Luke, Chap. 3, St. John, Chap. 1.

[80] J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 1, Chap. 3. pp. 122–46, Longmans Green, London, 1922.

[81] F. FRANKS, *Introduction — Water, the Unique Chemical*, Vol. 1, Chap. 1, of F. FRANKS (ed.), *Water, a Comprehensive Treatise in 7 Volumes*, Plenum Press, New York, 1972–82. Continued as F. FRANKS (ed.) *Water Science Reviews* published by Cambridge University Press: Vol. 1, 1985 etc.

is in the four largest lakes. Though these huge lacustrine sources dwarf the innumerable smaller lakes, springs and rivers of the earth, human habitation depends more on these widely distributed smaller sources which, in total, still far exceed the needs of man and the animal and plant kingdoms. Despite this, severe local problems can arise due to prolonged drought, the pollution of surface waters, or the extension of settlements into more arid regions. Indeed, droughts have been endemic since ancient times, and even pollution of local sources has been a cause of concern and the subject of legislation since at least 1847 (UK). Fortunately, it now appears that the quality of water supplies and amenities is rising steadily in most communities since the nadir of some 40 years ago, and public concern is now increasingly ensuring that funds are available on an appropriate scale to deal with the massive problems of water pollution.[82-85] (See also p. 478.)

Water purification and recycling is now a major industry.[86] The method of treatment depends on the source of the water, the use envisaged and the volume required. Luckily the human body is very tolerant to changes in the composition of drinking water, and in many communities this may contain $0.5\,\mathrm{g\,l^{-1}}$ or more of dissolved solids (Table 14.7). Prior treatment may consist of coagulation (by addition of alum or chlorinated $FeSO_4$ to produce flocs of $Al(OH)_3$ or $Fe(OH)_3$), filtration, softening (removal of

Table 14.7 World Health Organization standards for drinking water

Material	Maximum desirable conc/mg l^{-1}	Maximum permissible conc/mg l^{-1}
Total dissolved solids	500	1500
Mg	30	150
Ca	75	200
Chlorides	20	60
Sulfates	200	400

Mg^{II} and Ca^{II} by ion exchange) and disinfection (by chlorination, p. 793, or addition of ozone, p. 611). In most developed countries industrial needs for water are at least 10 times the volume used domestically. Moreover, some industrial processes require much purer water than that for human consumption, and for high-pressure boiler feedwater in particular the purity standard is 99.999 998%, i.e. no more than 0.02 ppm impurities. This is far purer than for reactor grade uranium, the finest refined gold or the best analytical reagents, and is probably exceeded only by semiconductor grade germanium and silicon. In contrast to Ge and Si, however, water is processed on a megatonne-per-day scale at a cost of only about £1 per tonne.

The beneficiation of sea water and other saline sources to produce fresh water is also of increasing importance. Normal freshwater supplies from precipitation cannot meet the needs of the increasing world population, particularly in the semi-arid regions of the world, and desalination is being used increasingly to augment normal water supplies, or even to provide all the fresh water in some places such as the arid parts of the Arabian Peninsula. The most commonly used methods are distillation (e.g. multistage flash distillation processes) and ion-exchange techniques, including electrodialysis and reverse osmosis (hyperfiltration). The enormous importance of the field can be gauged from the fact that Gmelin's volume on *Water Desalting*,[87] which reviewed 14 000 papers published up to 1973/4, has already

[82] H. B. N. HYNES, *The Biology of Polluted Waters*, Liverpool Univ. Press, 4th impression 1973, 202 pp.

[83] A. D. McKNIGHT, P. K. MARSTRAND and T. C. SINCLAIR (eds.), *Environmental Pollution Control*, Chap. 5: Pollution of inland waters; Chap. 6: The Law relating to pollution of inland waters; George, Allen and Unwin, London, 1974.

[84] C. E. WARREN, *Biology and Water Pollution Control*, Saunders, Philadelphia, 1971, 434 pp.

[85] B. COMMONER, The killing of a great lake, in *The 1968 World Book Year Book*, Field Enterprises Educ. Corp., 1968; Lake Erie water, Chap. 5 in *The Closing Circle*, London, Jonathan Cape, 1972. See also A. NISBETT *New Scientist*, 23 March 1972, pp. 650-2, who argues that B. Commoner's views are unfounded: Lake Erie is not dead but it is damaged.

[86] T. V. ARDEN, in R. THOMPSON (ed.), *The Modern Inorganic Chemicals Industry*, pp. 69-105, Chemical Society Special Publication, No. 31, 1977.

[87] *Gmelin Handbook of Inorganic Chemistry*, 8th edn. (in English), *O: Water Desalting*, 1974, 339 pp.

Table 14.8 Some physical properties of H_2O, D_2O and T_2O (at 25°C unless otherwise stated)[a]

Property	H_2O	D_2O	T_2O
Molecular weight	18.0151	20.0276	22.0315
MP/°C	0.00	3.81	4.48
BP/°C	100.00	101.42	101.51
Temperature of maximum density/°C	3.98	11.23	13.4
Maximum density/g cm^{-3}	1.0000	1.1059	1.2150
Density(25°)/g cm^{-3}	0.997 01	1.1044	1.2138
Vapour pressure/mmHg	23.75	20.51	~19.8
Viscosity/centipoise	0.8903	1.107	—
Dielectric constant ε	78.39	78.06	—
Electrical conductivity(20°C)/ohm^{-1} cm^{-1}	5.7×10^{-8}	—	—
Ionization constant $[H^+][OH^{-1}]$/mol^2 l^{-2}	1.008×10^{-14}	1.95×10^{-15}	$\sim6 \times 10^{-16}$
Ionic dissociation constant $K = [H^+][OH^-]/[H_2O]$/mol l^{-1}	1.821×10^{-16}	3.54×10^{-17}	$\sim1.1 \times 10^{-17}$
Heat of ionization/kJ mol^{-1}	56.27	60.33	—
ΔH_f°/kJ mol^{-1}	−285.85	−294.6	—
ΔG_f° kJ mol^{-1}	−237.19	−243.5	—

[a] Heavy water (p. 39) is now manufactured on the multikilotonne scale for use both as a coolant and neutron-moderator in nuclear reactors: its absorption cross-section for neutrons is much less than for normal water: σ_H 332, σ_D 0.46 mb (1 millibarn = 10^{-21} cm^2)

had to be supplemented by a further 360-page volume[88] dealing with the 4000 papers appearing during the following 4 years. A far cry from the first recorded use of desalination techniques in biblical times.[89]

Physical properties and structure

Water is a volatile, mobile liquid with many curious properties, most of which can be ascribed to extensive H bonding (p. 52). In the gas phase the H_2O molecule has a bond angle of 104.5° (close to tetrahedral) and an interatomic distance of 95.7 pm. The dipole moment is 1.84 D. Some properties of liquid water are summarized in Table 14.8 together with those of heavy water

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[88] *Gmelin Handbook of Inorganic Chemistry*, 8th edn., *O: Water Desalting*, Supplement Vol. 1, 1979, 360 pp.

[89] Holy Bible, Exodus, Chap. 15, verses 22–25: "... so Moses brought the sons of Israel from the Red Sea and they went into the desert of Sur. And they marched three days in the wilderness and found no water to drink. And then they arrived at Merra and they could not drink from the waters of Merra because they were bitter. ... And the people murmured against Moses saying: What shall we drink? And Moses cried unto the Lord. And the Lord showed him a wood and he put it into the water and the water became sweet".

D_2O and the tritium analogue T_2O (p. 41). The high bp is notable (cf. H_2S, etc.) as is the temperature of maximum density and its marked dependence on the isotopic composition of water. The high dielectric constant and measurable ionic dissociation equilibrium are also unusual and important properties. The ionic mobilities of $[H_3O]^+$ and $[OH]^-$ in water are abnormally high (350×10^{-4} and 192×10^{-4} cm s^{-1} per V cm^{-1} at 25° compared with 50–75×10^{-4} cm^2 V^{-1} s^{-1} for most other ions). This has been ascribed to a proton switch and reorientation mechanism involving the ions and chains of H-bonded solvent molecules. Other properties which show the influence of H bonding are the high heat and entropy of vaporization (ΔH_{vap} 44.02 kJ mol^{-1}, ΔS_{vap} 118.8 J deg^{-1} mol^{-1}), high surface tension (71.97 dyne cm^{-1}, i.e. 71.97 mN m^{-1}) and relatively high viscosity. The strength of the H bonds has been variously estimated at between 5–50 kJ per mol of H bonds and is most probably close to 20 kJ mol^{-1}. The structured nature of liquid water in which the molecules are linked to a small number of neighbours (2–3) by H bonds also accounts for its anomalously low density compared with a value of ~1.84 g cm^{-3} calculated for

a normal close-packed liquid with molecules of similar size and mass. Details of the structure of liquid water have been probed for more than six decades since the classic paper of J. D. Bernal and R. H. Fowler proposed the first plausible model.[90] Despite extensive work by X-ray and neutron diffraction, Raman and infrared spectroscopy, and the theoretical calculation of thermodynamic properties based on various models, details are still controversial and there does not even appear to be general agreement on whether water consists of a mixture of two or more species of varying degrees of polymerization or whether it is better described on a continuous model of highly bent H-bond configurations.[91]

When water freezes the crystalline form adopted depends upon the detailed conditions employed. At least nine structurally distinct forms of ice are known and the phase relations between them are summarized in Fig. 14.9. Thus, when liquid or gaseous water crystallizes at atmospheric pressure normal hexagonal ice I_h forms, but at very low temperatures ($-120°$ to $-140°$) the vapour condenses to the cubic form, ice I_c. The relation between these structures is the same as that between the tridymite and cristobalite forms of SiO_2 (p. 342), though in both forms of ice the protons are disordered.

Many of the high-pressure forms of ice are also based on silica structures (Table 14.9) and in ice II, VIII and IX the protons are ordered, the last 2 being low-temperature forms of ice VII and III respectively in which the protons are disordered. Note also that the high-pressure polymorphs VI and VII can exist at temperatures as high as $80°C$ and that, as expected, the high-pressure forms have substantially greater densities than that for ice I. A vitreous form of ice can be obtained by condensing water vapour at temperatures of $-160°C$ or below.

In "normal" hexagonal ice I_h each O is surrounded by a nearly regular tetrahedral arrangement of 4 other O atoms (3 at 276.5 pm and 1, along the c-axis, at 275.2 pm). The O–O–O angles are all close to $109.5°$ and neutron diffraction shows that the angle H–O–H is close to $105°$, implying that the H atoms lie slightly off the O–O vectors. The detailed description of the disordered H atom positions is complex. In the proton-ordered phases II and IX neutron diffraction again indicates an angle H–O–H close to $105°$ but the O–O–O angles are now $88°$ and $99°$ respectively. More details are in the papers mentioned in ref. 92.

Table 14.9   Structural relations in the polymorphs of ice[92]

Polymorph	Analogous silica polymorph	$d/(\text{g cm}^{-3})$	Ordered (O) or disordered (D) positions
I_h	Tridymite	0.92	D
I_c	Cristobalite	0.92	D
II	—	1.17	O
III⎱ IX⎰	Keatite Keatite	1.16	D⎱ O⎰
IV	See footnote[a]	—	—
V	No obvious analogue	1.23	D
VI	Edingtonite[b,c]	1.31	D
VII⎱ VIII⎰	Cristobalite[c] Cristobalite[c]	1.50	D⎱ O⎰

[a]Metastable for H_2O, but firmly established for D_2O.
[b]Edingtonite is $BaAl_2Si_3O_{10}.4H_2O$ (see p. 1037 of ref. 93).
[c]Structure consists of two interpenetrating frameworks.
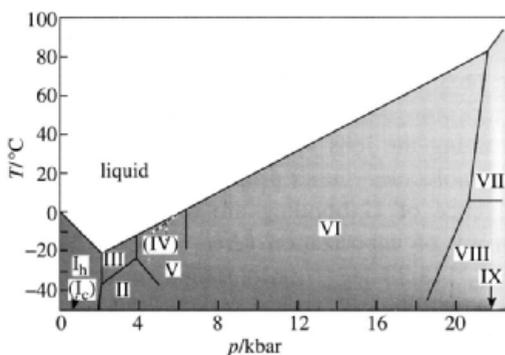

Figure 14.9   Partial phase diagram for ice (metastable equilibrium shown by broken lines).

90 J. D. BERNAL and R. H. FOWLER, *J. Chem. Phys.* **1**, 515–48 (1933).

91 P. KRINDEL and I. ELIEZER, *Coord. Chem. Rev.* **6**, 217–46 (1971).

92 A. F. WELLS, Water and hydrates, Chap. 15 in *Structural Inorganic Chemistry*, 5th edn., pp. 653–98, Oxford University Press, Oxford, 1984.

As indicated in Tables 14.8 and 14.9, ice I_h is unusual in having a density less than that of the liquid phase with which it is in equilibrium (a property which is of crucial significance for the preservation of aquatic life). When ice I_h melts some of the H bonds (possibly about 1 in 4) in the fully H-bonded lattice of 4-coordinate O atoms begin to break, and this process continues as the liquid is warmed, thereby enabling the molecules to pack progressively more closely with a consequent *increase* in density. This effect is opposed by the thermal motion of the molecules which tends to expand the liquid, and the net result is a maximum in the density at 3.98°C. Further heating reduces the density, though only slowly, presumably because the effects of thermal motion begin to outweigh the countervailing influence of breaking more H bonds. Again the qualitative explanation is clear but quantitative calculations of the density, viscosity, dielectric constant, etc., of H_2O, D_2O and their mixtures remain formidable.

It was previously thought that pure ice had a low but measurable electrical conductivity of about 1×10^{-10} ohm^{-1} cm^{-1} at -10°C. However, this conductivity is now thought to arise almost exclusively from surface defects, and when these have been removed ice is essentially an insulator with an immeasurably small conductivity.[93]

Water of crystallization, aquo complexes and solid hydrates

Many salts crystallize from aqueous solution not as the anhydrous compound but as a well-defined hydrate. Still other solid phases have variable quantities of water associated with them, and there is an almost continuous gradation in the degree of association or "bonding" between the molecules of water and the other components of the crystal. It is convenient to recognise five limiting types of interaction though the boundaries between them are vague

and undefined and many compounds incorporate more than one type.

(a) *H_2O coordinated in a cationic complex.* This is perhaps the most familiar class and can be exemplified by complexes such as $[Be(OH_2)_4]SO_4$, $[Mg(OH_2)_6]Cl_2$, $[Ni(OH_2)_6](NO_3)_2$, etc.; the metal ion is frequently in the $+2$ or $+3$ oxidation state and tends to be small and with high coordination power. Sometimes there is further interaction via H bonding between the aquocation and the anion, particularly if this derives from an oxoacid, e.g. the alums $\{[M(OH_2)_6]^+[Al(OH_2)_6]^{3+}[SO_4]_2^{2-}\}$ and related salts of Cr^{3+}, Fe^{3+}, etc. The species H_3O^+, $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$ are a special case in which the cation is a proton, i.e. $[H(OH_2)_n]^+$, and are discussed on p. 630.

(b) *H_2O coordinated by H bonding to oxoanions.* This mode is relatively uncommon but occurs in the classic case of $CuSO_4.5H_2O$ and probably also in $ZnSO_4.7H_2O$. Thus, in hydrated copper sulfate, 1 of the H_2O molecules is held much more tenaciously than the other 4 (which can all be removed over P_4O_{10} or by warming under reduced pressure); the fifth can only be removed by heating the compound above 350°C (or to 250° *in vacuo*). The crystal structure shows that each Cu atom is coordinated by $4H_2O$ and $2SO_4$ groups in a *trans* octahedral configuration (Fig. 14.10) and that the fifth H_2O molecule is not bound to Cu but forms H (donor) bonds to 2 SO_4 groups on neighbouring Cu atoms and 2 further H (acceptor) bonds with *cis*-H_2O molecules on 1 of the Cu atoms. It therefore plays a cohesive role in binding the various units of the structure into a continuous lattice.

(c) *Lattice water.* Sometimes hydration of either the cation or the anion is required to improve the size compatibility of the units comprising the lattice, and sometimes voids in the lattice so formed can be filled by additional molecules of water. Thus, although LiF and NaF are anhydrous, the larger alkali metal fluorides can form definite hydrates $MF.nH_2O$ ($n = 2$ and 4 for K; $1\frac{1}{2}$ for Rb; $\frac{2}{3}$ and $1\frac{1}{2}$ for Cs). Conversely, for the chlorides: KCl, RbCl and CsCl are always anhydrous whereas LiCl can form hydrates with

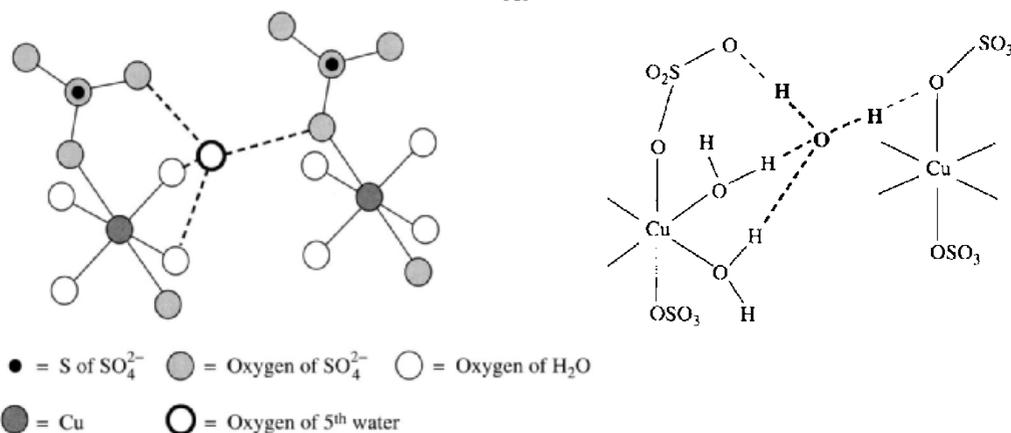^{93} A. VON HIPPEL, *Mat. Res. Bull.* **14**, 273–99 (1979).

● = S of SO_4^{2-} ◔ = Oxygen of SO_4^{2-} ○ = Oxygen of H_2O

● = Cu   ◯ = Oxygen of 5th water

Figure 14.10   Two representations of the repeating structural unit in $CuSO_4.5H_2O$ showing the geometrical distribution of ligands about Cu and the connectivity of the unique H_2O molecule.

1, 2, 3 and $5H_2O$, and $NaCl.2H_2O$ is also known. The space-filling role of water molecules is even more evident with very large anions such as those of the heteropoly acids (p. 1013), e.g. $H_3[PW_{12}O_{40}].29H_2O$.

(d) *Zeolitic water*. The large cavities of the framework silicates (p. 354) can readily accommodate water molecules, and the lack of specific strong interactions enables the "degree of hydration" to vary continuously over very wide ranges. The swelling of ion-exchange resins and clay minerals (p. 353) are further examples of non-specific hydrates of variable composition.

(e) *Clathrate hydrates*.[94] The structure motif of zeolite "hosts" accommodating "guest" molecules of water can be inverted in an intriguing way: just as the various forms of ice (p. 624) are formally related to those of silica (p. 342), so $(H_2O)_n$ can be induced to generate various cage-like structures with large cavities, thereby enabling the water structure itself to act as host to various guest molecules. Thus, polyhedral frameworks, sometimes with cavities of more than one size, can be generated from unit cells containing $12H_2O$, $46H_2O$, $136H_2O$, etc. In
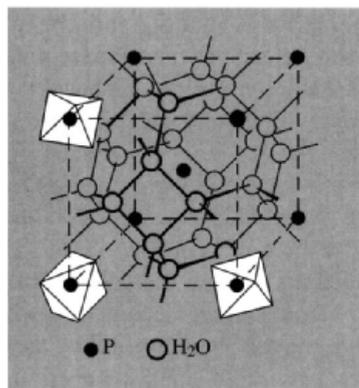

●P   ○H_2O

Figure 14.11   Crystal structure of $HPF_6.6H_2O$ showing the cavity formed by 24 H_2O molecules disposed with their O atoms at the vertices of a truncated octahedron. The PF_6 octahedra occupy centre and corners of the cubic unit cell, i.e. one PF_6 at the centre of each cavity.[92]

the first of these (Fig. 14.11) there is a cubic array of 24-cornered cavities, each cavity being a truncated octahedron with square faces of O atoms and each H_2O being common to 2 adjacent cavities (i.e. $24/2 = 12H_2O$). There is space for a guest molecule G at the centre of each cavity, i.e. at the centre of the cube and at each corner resulting in a stoichiometry $G(8G)_{1/8}.12H_2O$, i.e. $G.6H_2O$ as in $HPF_6.6H_2O$. The structure should

94 E. BERECZ and M. BALLA-ACHS, *Gas Hydrates*, Elsevier, Amsterdam, 1983, 343 pp.

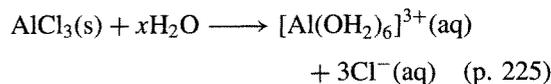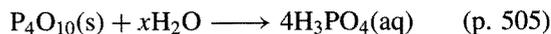be compared with the aluminosilicate framework in ultramarine (p. 358).

With the more complicated framework of $46H_2O$ there are 6 cavities of one size and 2 slightly smaller. If all are filled one has $46/8H_2O$ per guest molecule, i.e. $G.5\frac{3}{4}H_2O$ as in the high-pressure clathrates with $G = Ar$, Kr, CH_4 and H_2S. If only the larger cavities are filled, the stoichiometry rises to $G.7\frac{2}{3}H_2O$: this is approximated by the classic chlorine hydrate phase discovered by Humphry Davy and studied by Michael Faraday. The compound is now known to be $Cl_2.7\frac{1}{4}H_2O$, implying that up to 20% of the smaller guest sites are also occupied.

With the $136H_2O$ polyhedron there are 8 larger and 16 smaller voids. If only the former are filled, then $G.17H_2O$ results $(17 = 136/8)$ as in $CHCl_3.17H_2O$ and $CHI_3.17H_2O$, whereas if both sets are filled with molecules of different sizes, compounds such as $CHCl_3.2H_2S.17H_2O$ result. Many more complicated arrays are possible, resulting from partial filling of the voids or partial replacement of H_2O in the framework by other species capable of being H-bonded into the network, e.g. $[NMe_4]F.4H_2O$, $[NMe_4]OH.5H_2O$, $Bu_3^nSF.20H_2O$ and $[N(i-C_5H_{11})_4]F.38H_2O$. Further structural details are in ref. 92, and industrial applications are discussed in the comprehensive ref. 94.

Chemical properties

Water is an excellent solvent because of its high dielectric constant and very strong solvating power. Many compounds, whether hydrated or anhydrous, dissolve to give electrolytic solutions of hydrated cations and anions. However, detailed treatments of solubility relations, free energies and enthalpies of ionic hydration, temperature dependence of solubility and the influence of dissolved ions on the H-bonded structure of the solvent, fall outside the scope of the present treatment. Even predominantly covalent compounds such as $EtOH$, $MeCO_2H$, Me_2CO, $(CH_2)_4O$, etc. can have high solubility or even complete miscibility with water due to H-bonded interaction with the solvent. Again, covalent compounds such as HCl can dissolve to give ionic solutions by heterolytic cleavage (e.g. to aquated $H_3O^+Cl^-$), and the process of dissolution sometimes also results in ionic cleavage of the solvent itself, e.g. $[H_3O]^+[BF_3(OH)]^-$ (p. 198). Because of the great affinity that many elements have for oxygen, solvolytic cleavage (hydrolysis) of "covalent" or "ionic" bonds frequently ensues, e.g.:

$$P_4O_{10}(s) + xH_2O \longrightarrow 4H_3PO_4(aq) \quad (p.\ 505)$$

$$AlCl_3(s) + xH_2O \longrightarrow [Al(OH_2)_6]^{3+}(aq)$$
$$+ 3Cl^-(aq) \quad (p.\ 225)$$

Such reactions are discussed at appropriate points throughout the book as each individual compound is being considered. A particularly important set of reactions in this category is the synthesis of element hydrides by hydrolysis of certain sulfides (to give H_2S), nitrides (to give NH_3), phosphides (PH_3), carbides (C_nH_m), borides (B_nH_m), etc. Useful reviews are available on hydrometallurgy (the recovery of metals by use of aqueous solutions at relatively low temperatures),[94a] hydrothermal syntheses[94b] and the use of supercritical water as a reaction medium for chemistry.[94c]

Another important reaction (between H_2O, I_2 and SO_2) forms the basis of the quantitative determination of water when present in small amounts. The reaction, originally investigated by R. Bunsen in 1835, was introduced in 1935 as an analytical reagent by Karl Fischer who believed, incorrectly, that each mole of I_2 was equivalent to 2 moles of H_2O:

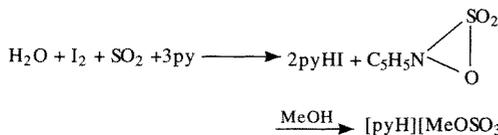$$2H_2O + I_2 + SO_2 \underset{}{\overset{MeOH/py}{\rightleftharpoons}} 2HI + H_2SO_4$$

In fact, the reaction is only quantitative in the presence of pyridine, and the methanol solvent

[94a] F. HABASHI, *Chem. and Eng. News*, 8 Feb. 1982, pp. 46–58.

[94b] A. RABENAU, *Angew. Chem. Int. Edn. Engl.* **24**, 1026–40 (1985).

[94c] R. W. SHAW, T. B. BRILL, A. A. CLIFFORD, C. A. ECKERT and E. U. FRANCK, *Chem. and Eng. News*, 23 Dec. 1991, pp. 26–39.

is also involved leading to a 1:1 stoichiometry between I_2 and H_2O:

$$H_2O + I_2 + SO_2 + 3py \longrightarrow 2pyHI + C_5H_5N\overset{SO_2}{\underset{O}{\diagdown}}$$

$$\xrightarrow{\text{MeOH}} [pyH][MeOSO_3]$$

The stability of the reagent is much improved by replacing MeOH with $MeOCH_2CH_2OH$, and this forms the basis of the present-day Karl Fischer reagent.[95]

In addition to simple dissolution, ionic dissociation and solvolysis, two further classes of reaction are of pre-eminent importance in aqueous solution chemistry, namely acid-base reactions (p. 48) and oxidation–reduction reactions. In water, the oxygen atom is in its lowest oxidation state (-2). Standard reduction potentials (p. 435) of oxygen in acid and alkaline solution are listed in Table 14.10[96] and shown diagramatically in the scheme opposite. It is important to remember that if H^+ or OH^- appear in the electrode half-reaction, then the electrode potential will change markedly with the pH. Thus for the first reaction in Table 14.10: $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$, although $E^° = 1.229\,V$, the actual potential at 25°C will be given by

$$E/\text{volt} = 1.229 + 0.05916\log\{[H^+]/mol\,l^{-1}\} \times$$
$$\{P_{O_2}/\text{atm}\}^{\frac{1}{4}}$$

which diminishes to 0.401 V at pH 14 (Fig. 14.12). Likewise, for the half-reaction

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[95] E. SCHOLZ, *Karl Fischer Titration Determination of Water*, Springer Verlag, Berlin, 1984, 150 pp.

[96] G. MILAZZO and S. CAROLI, *Tables of Standard Electrode Potentials*, p. 229, Wiley-Interscience, New York, 1978.

$H^+ + e^- \rightleftharpoons \frac{1}{2}H_2$, $E^°$ is zero by definition at pH 0, whereas at other concentrations

$$E/\text{volt} = -0.05916\log\{P_{H_2}/\text{atm}\}^{\frac{1}{2}}/$$
$$\{[H^+]/mol\,l^{-1}\}$$

and the value falls to -0.828 at pH 14. Theoretically no oxidizing agent whose reduction potential lies above the O_2/H_2O line and no reducing agent whose reduction potential falls below the H^+/H_2 line can exist in thermodynamically stable aqueous solutions. However, for kinetic reasons associated with the existence of over-potentials, these lines can be extended by about 0.5 V as shown by the dotted lines in Fig. 14.12, and these are a more realistic estimate of the region of stability of oxidizing and reducing agents in aqueous solution. Outside these limits more strongly oxidizing species (e.g. F_2, $E^°$ 2.866 V) oxidize water to O_2 and more strongly reducing agents (e.g. K_{metal}, $E^°$ -2.931 V) liberate H_2. Sometimes even greater activation energies have to be overcome and reaction only proceeds at elevated temperatures (e.g. $C + H_2O \rightarrow CO + H_2$; p. 307).

The acid-base behaviour of aqueous solutions has already been discussed (p. 48). The ionic self-dissociation of water is well established (Table 14.8) and can be formally represented as

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
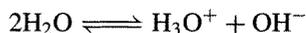
On the Brønsted theory (p. 51), solutions with concentrations of H_3O^+ greater than that in pure water are acids (proton donors), and solutions rich in OH^- are bases (proton acceptors). The same classifications follow from the solvent-system theory of acids and bases

Table 14.10   Standard reduction potentials of oxygen

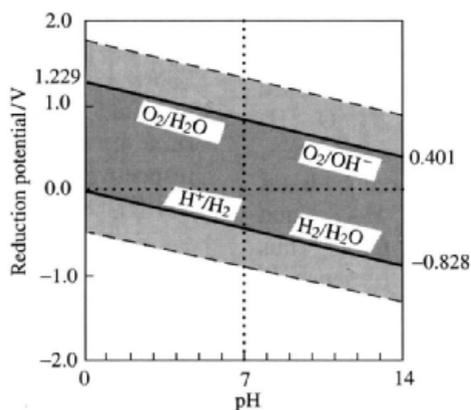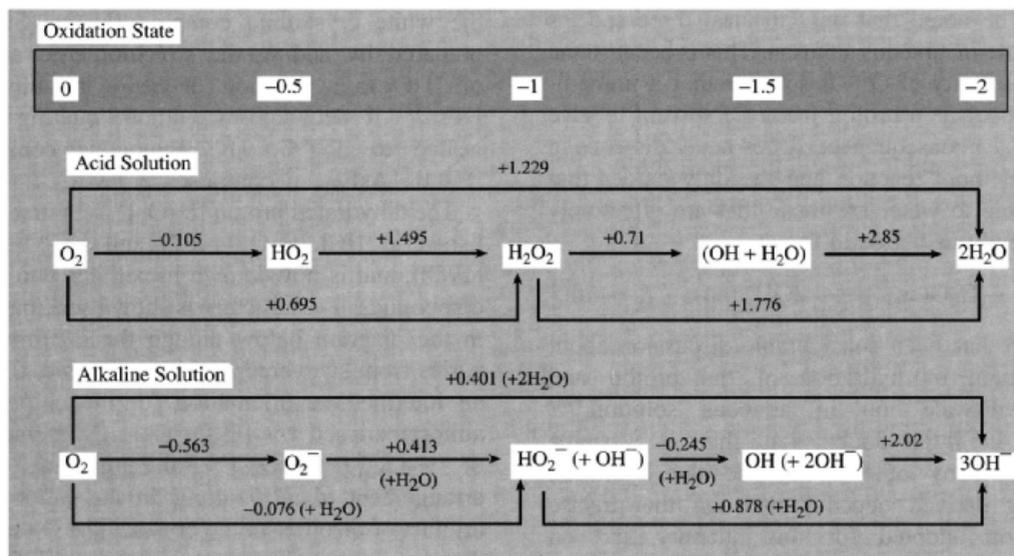| Acid solution (pH 0)	$E^°/V$	Alkaline solution (pH 14)	$E^°/V$
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.229	$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	0.401
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.695	$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$	-0.076
$O_2 + H^+ + e^- \rightleftharpoons HO_2$	-0.105	$O_2 + e^- \rightleftharpoons O_2^-$	-0.563
$HO_2 + H^+ + e^- \rightleftharpoons H_2O_2$	1.495	$O_2^- + H_2O + e^- \rightleftharpoons HO_2^- + OH^-$	0.413
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	1.776	$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^-$	0.878
$H_2O_2 + H^+ + e^- \rightleftharpoons OH + H_2O$	0.71	$HO_2^- + H_2O + e^- \rightleftharpoons OH + 2OH^-$	-0.245
$OH + H^+ + e^- \rightleftharpoons H_2O$	2.85	$OH + e^- \rightleftharpoons OH^-$	2.02

Figure 14.12 Variation of the reduction potentials of the couples O_2/H_2O and H^+/H_2 (or O_2/OH^- and H_2/H_2O) as a function of pH (full lines). The broken lines lie 0.5 V above and below these full lines and give the approximate practical limits of oxidants and reductants in aqueous solution beyond which the solvent itself is oxidized to $O_2(g)$ or reduced to $H_2(g)$.

since compounds enhancing the concentrations of the characteristic solvent cation (H_3O^+) and anion (OH^-) are solvo-acids and solvo-bases (p. 425). On the Lewis theory, H^+ is an electro-pair acceptor (acid) and OH^- an electron-pair donor (base, or ligand) (p. 198). The various definitions tend to diverge only in other systems (either nonaqueous or solvent-free), particularly when aprotic media are being considered (e.g. N_2O_4, p. 456; BrF_3, p. 831; etc.).

In considering the following isoelectronic sequence (8 valence electrons) and the corresponding gas-phase proton affinities ($A_{H^+}/$ kJ mol^{-1}):[97]

$$O^{2-} \xrightarrow[(-2860)]{H^+} OH^- \xrightarrow[(-1650)]{H^+} H_2O \xrightarrow[(-695)]{H^+} H_3O^+$$
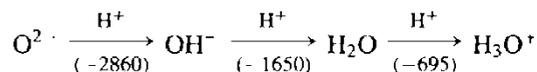
97 R. E. KARI and I. G. CSIZMADIA, *J. Am. Chem. Soc.* **99**, 4539–45 (1977).

it will be noted that only the last three species are stable in aqueous solution. This is because the proton affinity of O^{2-} is so huge that it immediately abstracts a proton from the solvent to give OH^-; as a consequence, oxides never dissolve in water without reaction and the only oxides that are stable to water are those that are effectively completely insoluble in it:

$$O^{2-}(s) + H_2O(aq) \longrightarrow 2OH^-(aq); \quad K > 10^{22}$$
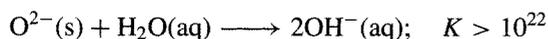
There has been considerable discussion about the extent of hydration of the proton and the hydroxide ion in aqueous solution.[98] There is little doubt that this is variable (as for many other ions) and the hydration number derived depends both on the precise definition adopted for this quantity and on the experimental method used to determine it. H_3O^+ has definitely been detected by vibration spectroscopy, and by ^{17}O nmr spectroscopy on a solution of $HF/SbF_5/H_2{}^{17}O$ in SO_2; a quartet was observed at $-15°$ which collapsed to a singlet on proton decoupling, $J(^{17}O-^1H)$ 106 Hz.[99] In crystalline hydrates there are a growing number of well-characterized hydrates of the series H_3O^+, $H_5O_2{}^+$, $H_7O_3{}^+$, $H_9O_4{}^+$ and $H_{13}O_6{}^+$, i.e. $[H(OH_2)_n]^+$ $n = 1–4$, 6.[100] Thus X-ray studies have established the presence of H_3O^+ in the monohydrates of HCl, HNO_3 and $HClO_4$, and in the mono- and di-hydrates of sulfuric acid, $[H_3O][HSO_4]$ and $[H_3O]_2[SO_4]$. As expected, H_3O^+ is pyramidal like the isoelectronic molecule NH_3, but the values of the angles $H–O–H$ vary considerably due to extensive H bonding throughout the crystal, e.g. 117° in the chloride, 112° in the nitrate, and 101°, 106° and 126° in $[H_3O][HSO_4]$.[92] Likewise the H-bonded distance $O–H\cdots O$ varies: it is 266 pm in the nitrate, 254–265 in $[H_3O]$-$[HSO_4]$ and 252–259 in $[H_3O]_2[SO_4]$. The most stable hydroxonium salt yet known is

the white crystalline complex $[H_3O]^+[SbF_6]^-$, prepared by adding the stoichiometric amount of H_2O to a solution of SbF_5 in anhydrous HF;[101] it decomposes without melting when heated to 357°C. The analogous compound $[H_3O]^+[AsF_6]^-$ decomposes at 193°C.

The dihydrated proton $[H_5O_2]^+$ was first established in $HCl.2H_2O$ (1967) and $HClO_4.2H_2O$ (1968), and is now known in perhaps two dozen compounds. The structure is shown schematically in the diagram below though the conformation varies from staggered in the perchlorate, through an intermediate orientation for the chloride to almost eclipsed for $[H_5O_2]Cl.H_2O$. In the case of $[H_5O_2]_3^+[PW_{12}O_{40}]^{3-}$, an apparently planar arrangement of all 7 atoms in the cation is an artefact of disorder in the crystal. The $O–H\cdots O$ distance is usually in the range 240–245 pm though in the deep-yellow crystalline compound $[NEt_4]_3[H_5O_2][Mo_2Cl_8H][MoCl_4O(OH_2)]$ it is only 234 pm, one of the shortest $O–H\cdots O$ bonds known.[102] The detailed crystal structures of the hydrated hexafluorosilicic acids, $H_2SiF_6.nH_2O$ ($n = 4$, 6, 9.5) have shown them to be, respectively, $[H_5O_2]_2SiF_6$, $[H_5O_2]_2SiF_6.2H_2O$ and $[H_5O_2][H_7O_3]SiF_6.4.5H_2O$.[103]
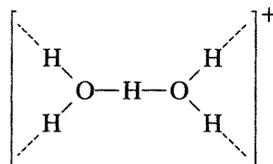
The ions $[H_7O_3]^+$ and $[H_9O_4]^+$ are both featured in the compound $HBr.4H_2O$ which has the unexpectedly complicated formulation $[H_9O_4]^+[H_7O_3]^+[Br]_2^-.H_2O$. The structures of the cations are shown schematically in Fig. 14.13

[98] P. A. GIGUÈRE, *J. Chem. Educ.* **56**, 571–5 (1979).

[99] G. D. METEESCU and G. M. BENEDIKT, *J. Am. Chem. Soc.* **101**, 3959–60 (1979). See also G. A. OLAH, G. K. S. PRAKASH, M. BARZAGHI, K. LAMMERTSMA, P. von R. SCHLEYER and J. A. POPLE, *J. Am. Chem. Soc.* **108**, 1032–5 (1986).

[100] E. KOCHANSKI, *J. Am. Chem. Soc.* **107**, 7869–73 (1985).

[101] K. O. CHRISTE, C. J. SCHACK and R. D. WILSON, *Inorg. Chem.* **14**, 2224–30 (1975). See also K. O. CHRISTE, P. CHARPIN, E. SOULIE, R. BOUGON, J. FAWCETT and D. R. RUSSELL, *Inorg. Chem.* **23**, 3756–66 (1984).

[102] A. BINO and F. A. COTTON, *J. Am. Chem. Soc.* **101**, 4150–4 (1979). See also G. J. KEARLEY, H. A. PRESSMAN and R. C. T. SLADE, *J. Chem. Soc., Chem. Commun.*, 1801–2 (1986).

[103] D. MOOTZ and E.-J. OELLERS, *Z. anorg. allg. Chem.* **559**, 27–39 (1988).
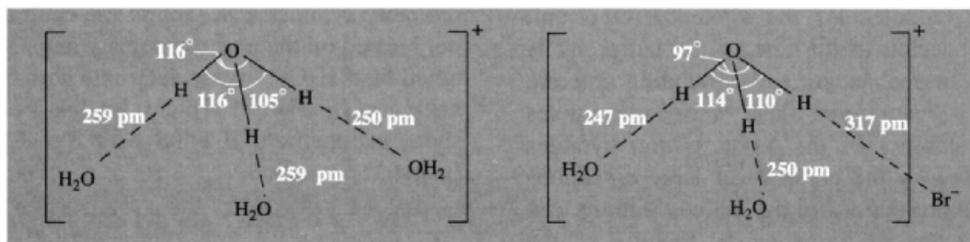
Figure 14.13   Schematic representation of the structures of the $[H_9O_4]^+$ and $[H_7O_3]^+ \cdots Br^-$ units in HBr.4H$_2$O, showing bond angles and O–H $\cdots$ O (O–H $\cdots$ Br) distances.

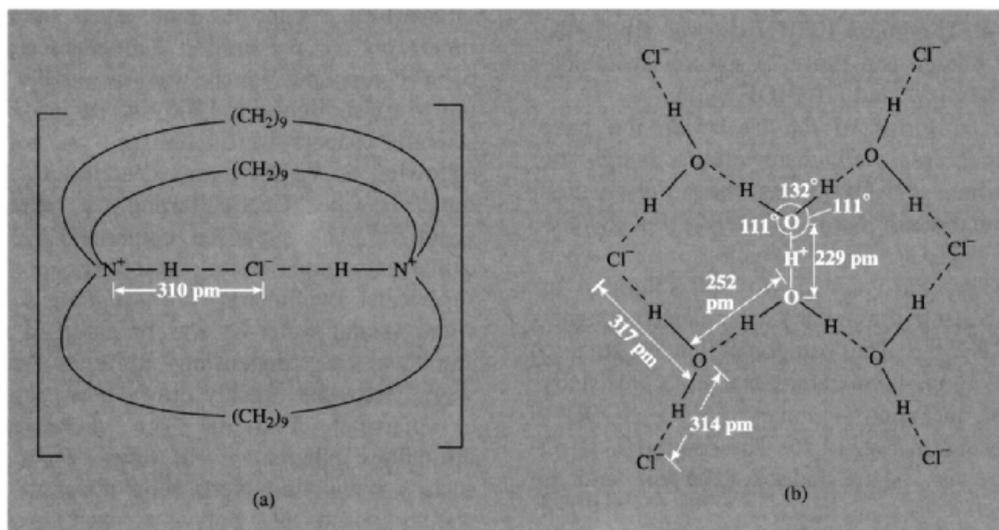**Figure 14.14**   (a) Schematic representation of the structure of the cage cation $[(C_9H_{18})_3(NH)_2Cl]^+$, and (b) detailed structure of the $[H_{13}O_6]^+$ ion showing its H bonding to surrounding Cl$^-$ anions. The ion has C_{2h} symmetry with the very short central O–H–O lying across the centre of symmetry.

which indicates that a bromide ion has essentially displaced the fourth water molecule of the second cation to give an effectively neutral H-bonded unit $[(H_3O)_2H^+Br^-]$. The discrete $[H_7O_3]^+$ ion is now known in about a dozen complexes of which a good example is the deep-green complex $[NEt_4]_2[H_7O_3]_2[Ru_3Cl_{12}]$ in which the 2 O–H $\cdots$ O distances are 245 and 255 pm and the O–O $\cdots$ O angle is 115.9°.[104] Similar dimensions were found in the hexafluorosilicate.[103]

The largest protonated cluster of water molecules yet definitively characterized is the discrete unit $[H_{13}O_6]^+$ formed serendipitously when the cage compound $[(C_9H_{18})_3(NH)_2Cl]^+Cl^-$ was crystallized from a 10% aqueous hydrochloric acid solution.[105] The structure of the cage cation is shown in Fig. 14.14 and the unit cell contains $4\{[C_9H_{18})_3(NH)_2Cl]Cl[H_{13}O_6]Cl\}$. The hydrated proton features a short symmetrical O–H–O bond at the centre of symmetry and 4 longer unsymmetrical O–H $\cdots$ O bonds to 4

[104] A. BINO and F. A. COTTON, *J. Am. Chem. Soc.* **102**, 608–11 (1980).

[105] R. A. BELL, G. G. CHRISTOPH, F. R. FRONCZEK and R. E. MARSH, *Science* **190**, 151–2 (1975).

further H_2O molecules, the whole $[H_{13}O_6]^+$ unit being connected to the rest of the lattice by H bonds of normal length to surrounding chloride ions. It is clear from these various examples that the stability of the larger proton hydrates is enhanced by the presence of large co-cations and/or counter-anions in the lattice. Stability can also be enhanced by structural features of the cluster cation itself, as beautifully exemplified by the species $[H_{41}O_{20}]^+$ and $[H_{43}O_{21}]^+$:[106] these stable groupings comprise a central {H} or {H_3O} bonded to an encapsulating pentagonal dodecahedron of H-bonded {$(H_2O)_{20}$} over which the positive charge can move by proton switching, i.e $[H(OH_2)_{20}]^+$ and $[H_3O(OH_2)_{20}]^+$.

Hydrated forms of the hydroxide ion have been much less well characterized though the monohydrate $[H_3O_2]^-$ has been discovered in the mixed salt $Na_2[NEt_3Me][Cr\{PhC(S)=N-(O)\}_3].\frac{1}{2}NaH_3O_2.18H_2O$ which formed when $[NEt_3Me]I$ was added to a solution of tris(thiobenzohydroximato)chromate(III) in aqueous NaOH.[107] The compound tended to lose water at room temperature but an X-ray study identified the centro-symmetric $[HO-H-OH]^-$ anion shown in Fig. 14.15. The central O--H--O bond is very short indeed (229 pm) and is probably symmetrical, though the central H was not located on the electron density map. It will be noted that $[H_3O_2]^-$ is isoelectronic with the bifluoride ion $[F-H-F]^-$ which also features a very short, symmetrical H bond with $F \cdots F$ 227 pm (p. 60).

Polywater

The saga of polywater forms a fascinating and informative case history of the massive amount of work that can be done, even in modern times, on the preparation and characterization of a compound which was eventually found not to exist. Between 1966 and 1973 over 500 scientific papers were published on polywater following B. V. Deryagin's description of work done in the USSR during the preceding years.[108] The supposed compound, variously called anomalous water, orthowater, polywater, superwater, cyclimetric water, superdense water, water II and water-X, was prepared in minute amounts by condensing purified "ordinary water" into fine, freshly drawn glass capillaries of diameter $1-3 \mu m$. The thermodynamic difficulties inherent in the very existence of such a compound were soon apparent and it was proposed that polywater was, in fact, a dispersion of a silica gel leached from the glass capillaries,[109] despite the specific rejection of this possibility by several groups of earlier workers. The full panoply of physicochemical techniques was brought to bear on the problem, and it was finally conceded that the anomalous properties were caused by a mixture of colloidal silicic acid and dissolved compounds of Na, K, Ca, B, Si, N (nitrate), O (sulfate) and Cl leached from the glass by the aggressive action of freshly condensed water.[110] A very informative annotated bibliography is available

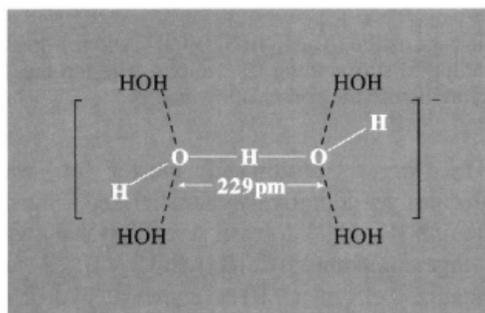**Figure 14.15** Structure of the centrosymmetric $[H_3O_2]^-$ ion showing the disposition of longer H bonds to neighbouring water molecules.

106 S. WEI, Z. SHI and A. W. CASTLEMAN, *J. Chem. Phys.* **94**, 3268–70 (1991).

107 J. ABU-DARI, K. N. RAYMOND and D. P. FREYBERG, *J. Am. Chem. Soc.* **101**, 3688–9 (1979).

108 B. V. DERYAGIN, *Discussions Faraday Soc.* **42**, 109–19 (1966).

109 A. CHERKIN, *Nature* **224**, 1293 (1969). (See also *Nature* **222**, 159–61 (1969)).

110 B. V. DERYAGIN and N. V. CHURAEV, *Nature* **244**, 430–1 (1973); B. V. DERYAGIN, *Recent Advances in Adhesion*, 1973, 23–31.