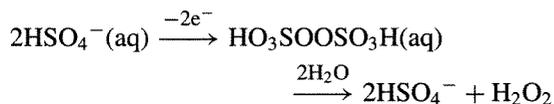


which traces the course of this controversy and analyses the reasons why it took so long to resolve.<sup>(111)</sup>

### 14.2.3 Hydrogen peroxide

Hydrogen peroxide was first made in 1818 by J. L. Thenard who acidified barium peroxide (p. 121) and then removed excess H<sub>2</sub>O by evaporation under reduced pressure. Later the compound was prepared by hydrolysis of peroxodisulfates obtained by electrolytic oxidation of acidified sulfate solutions at high current densities:



Such processes are now no longer used except in the laboratory preparation of D<sub>2</sub>O<sub>2</sub>, e.g.:



On an industrial scale H<sub>2</sub>O<sub>2</sub> is now almost exclusively prepared by the autoxidation of 2-alkylanthraquinols (see Panel on next page).

#### Physical properties

Hydrogen peroxide, when pure, is an almost colourless (very pale blue) liquid, less volatile than water and somewhat more dense and viscous. Its more important physical properties are in Table 14.11 (cf. H<sub>2</sub>O, p. 623). The compound is miscible with water in all proportions and forms a hydrate H<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O, mp  $-52^\circ$ . Addition of water increases the already high dielectric constant of H<sub>2</sub>O<sub>2</sub> (70.7) to a maximum value of 121 at ~35% H<sub>2</sub>O<sub>2</sub>, i.e. substantially higher than the value of water itself (78.4 at 25°).

In the gas phase the molecule adopts a skew configuration with a dihedral angle of 111.5° as

**Table 14.11** Some physical properties of hydrogen peroxide<sup>(a)</sup>

| Property   | Value                |
|--|----------------------|
| MP/°C  | -0.41                |
| BP/°C (extrap)   | 150.2                |
| Vapour pressure(25°)/mmHg                                  | 1.9                  |
| Density (solid at $-4.5^\circ$ )/g cm <sup>-3</sup>        | 1.6434               |
| Density (liquid at 25°)/g cm <sup>-3</sup>                 | 1.4425               |
| Viscosity(20°)/centipoise                                  | 1.245                |
| Dielectric constant $\epsilon(25^\circ)$                   | 70.7                 |
| Electric conductivity(25°)/ $\Omega^{-1}$ cm <sup>-1</sup> | $5.1 \times 10^{-8}$ |
| $\Delta H_f^\circ/\text{kJ mol}^{-1}$                      | -187.6               |
| $\Delta G_f^\circ/\text{kJ mol}^{-1}$                      | -118.0               |

<sup>(a)</sup>For D<sub>2</sub>O<sub>2</sub>: mp +1.5°;  $d_{20}$  1.5348 g cm<sup>-3</sup>;  $\eta_{20}$  1.358 centipoise.

shown in Fig. 14.16a. This is due to repulsive interaction of the O–H bonds with the lone-pairs of electrons on each O atom. Indeed, H<sub>2</sub>O<sub>2</sub> is the smallest molecule known to show hindered rotation about a single bond, the rotational barriers being 4.62 and 29.45 kJ mol<sup>-1</sup> for the *trans* and *cis* conformations respectively. The skew form persists in the liquid phase, no doubt modified by H bonding, and in the crystalline state at  $-163^\circ\text{C}$  a neutron diffraction study<sup>(112)</sup> gives the dimensions shown in Fig. 14.16b. The dihedral angle is particularly sensitive to H bonding, decreasing from 111.5° in the gas phase to 90.2° in crystalline H<sub>2</sub>O<sub>2</sub>; in fact, values spanning the complete range from 90° to 180° (i.e. *trans* planar) are known for various solid phases containing molecular H<sub>2</sub>O<sub>2</sub> (Table 14.12). The O–O distance in H<sub>2</sub>O<sub>2</sub> corresponds to the value expected for a single bond (p. 616).

#### Chemical properties

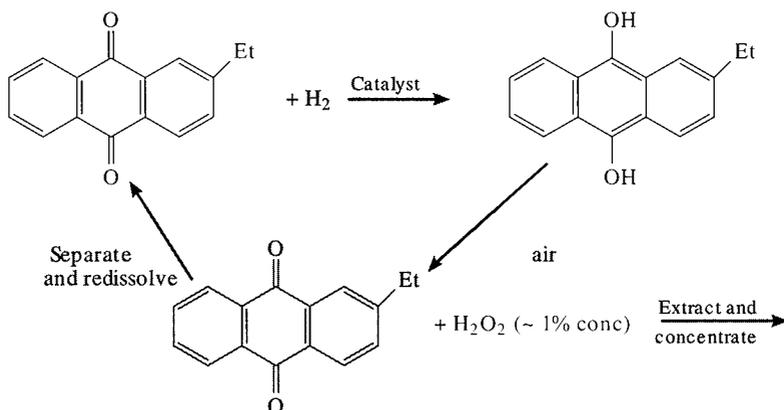
In H<sub>2</sub>O<sub>2</sub> the oxidation state of oxygen is  $-1$ , intermediate between the values for O<sub>2</sub> and H<sub>2</sub>O, and, as indicated by the reduction potentials on p. 628, aqueous solutions of H<sub>2</sub>O<sub>2</sub> should spontaneously disproportionate. For the pure

<sup>111</sup> F. PERCIVAL and A. H. JOHNSTONE, *Polywater — A Library Exercise for Chemistry Degree Students*, The Chemical Society, London, 1978, 24 pp. [See also B. F. POWELL, *J. Chem. Educ.* **48**, 663–7 (1971). H. FREIZER, *J. Chem. Educ.* **49**, 445 (1972). F. FRANKS, *Polywater*, MIT Press, Cambridge, Mass., 1981, 208 pp.]

<sup>112</sup> J.-M. SAVARIAULT and M. S. LEHMANN, *J. Am. Chem. Soc.* **102**, 1298–303 (1980).

### Preparation and Uses of Hydrogen Peroxide<sup>(113)</sup>

Hydrogen peroxide is a major industrial chemical manufactured on a multikilotonne scale by an ingenious cycle of reactions introduced by I. G. Farbenindustrie about 60 years ago. Since the value of the solvents and organic substrates used are several hundred times that of the  $\text{H}_2\text{O}_2$  produced, the economic viability of the process depends on keeping losses very small indeed. The basic process consists of dissolving 2-ethylantraquinone in a mixed ester/hydrocarbon or alcohol/hydrocarbon solvent and reducing it by a Raney nickel or supported palladium catalyst to the corresponding quinol. The catalyst is then separated and the quinol non-catalytically reoxidized in a stream of air:



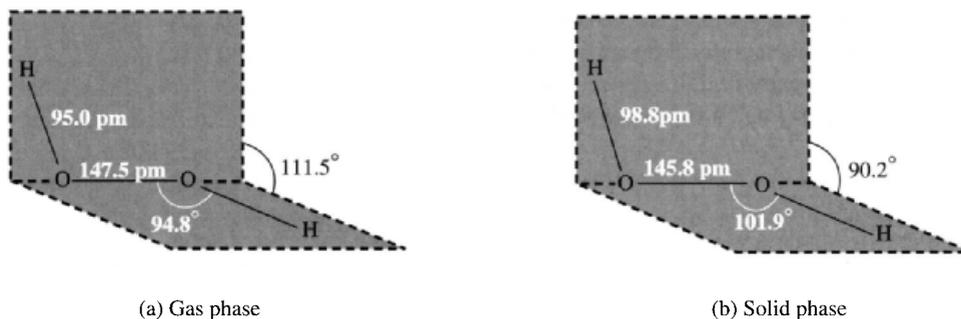
The  $\text{H}_2\text{O}_2$  is extracted by water and concentrated to ~30% (by weight) by distillation under reduced pressure. Further low-pressure distillation to concentrations up to 85% are not uncommon.

World production expressed as 100%  $\text{H}_2\text{O}_2$  approached 1.9 million tonnes in 1994 of which half was in Europe and one-fifth in the USA. The earliest and still the largest industrial use for  $\text{H}_2\text{O}_2$  is as a bleach for textiles, paper pulp, straw, leather, oils and fats, etc. Domestic use as a hair bleach and a mild disinfectant has diminished somewhat. Hydrogen peroxide is also extensively used to manufacture chemicals, notably sodium perborate (p. 206) and percarbonate, which are major constituents of most domestic detergents at least in the UK and Europe. Normal formulations include 15–25% of such peroxyacid salts, though the practice is much less widespread in the USA, and the concentrations, when included at all, are usually less than 10%.

In the organic chemicals industry,  $\text{H}_2\text{O}_2$  is used in the production of epoxides, propylene oxide, and caprolactones for PVC stabilizers and polyurethanes, in the manufacture of organic peroxy compounds for use as polymerization initiators and curing agents, and in the synthesis of fine chemicals such as hydroquinone, pharmaceuticals (e.g. cephalosporin) and food products (e.g. tartaric acid).

One of the rapidly growing uses of  $\text{H}_2\text{O}_2$  is in environmental applications such as control of pollution by treatment of domestic and industrial effluents, e.g. oxidation of cyanides and obnoxious malodorous sulfides, and the restoration of aerobic conditions to sewage waters. Its production in the USA for these and related purposes has trebled during the past decade (from 126 kt in 1984 to 360 kt in 1994) and it has substantially replaced chlorine as an industrial bleach because it yields only  $\text{H}_2\text{O}$  and  $\text{O}_2$  on decomposition. An indication of the proportion of  $\text{H}_2\text{O}_2$  production used for various applications in North America (1991) is: pulp and paper treatment 49%, chemicals manufacture 15%, environmental uses 15%, textiles 8%, all other uses 13%. The price per kg for technical grade aqueous  $\text{H}_2\text{O}_2$  in tank-car lots (1994) is \$0.54 (30%), \$0.75 (50%) and \$1.05 (70%), i.e. essentially a constant price of \$1.50 per kg on a "100% basis."

<sup>113</sup>W. T. HESS, Hydrogen Peroxide in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Edn., Wiley, New York, Vol. 13, 961–95 (1995).



**Figure 14.16** Structure of the  $\text{H}_2\text{O}_2$  molecule (a) in the gas phase, and (b) in the crystalline state.

**Table 14.12** Dihedral angle of  $\text{H}_2\text{O}_2$  in some crystalline phases

| Compound   | Dihedral angle | Compound   | Dihedral angle |
|--|----------------|--|----------------|
| $\text{H}_2\text{O}_2(\text{s})$                             | $90.2^\circ$   | $\text{Li}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ | $180^\circ$    |
| $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  | $101.6^\circ$  | $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ | $180^\circ$    |
| $\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ | $103.4^\circ$  | $\text{NH}_4\text{F} \cdot \text{H}_2\text{O}_2^{(114)}$     | $180^\circ$    |
| $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$             | $129^\circ$    |  |                |

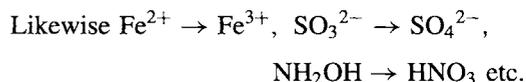
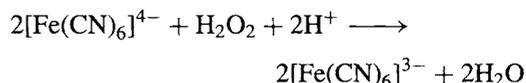
liquid:  $\text{H}_2\text{O}_2(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g}); \Delta H^\circ = -98.2 \text{ kJ mol}^{-1}$ ,  $\Delta G^\circ = -119.2 \text{ kJ mol}^{-1}$ . In fact, in the absence of catalysts, the compound decomposes negligibly slowly but the reaction is strongly catalysed by metal surfaces (Pt, Ag), by  $\text{MnO}_2$  or by traces of alkali (dissolved from glass), and for this reason  $\text{H}_2\text{O}_2$  is generally stored in wax-coated or plastic vessels with stabilizers such as urea; even a speck of dust can initiate explosive decomposition and all handling of the anhydrous compound or its concentrated solutions must be carried out in dust-free conditions and in the absence of metal ions. A useful "carrier" for  $\text{H}_2\text{O}_2$  in some reactions is the adduct  $(\text{Ph}_3\text{PO})_2 \cdot \text{H}_2\text{O}_2$ .

Hydrogen peroxide has a rich and varied chemistry which arises from (i) its ability to act either as an oxidizing or a reducing agent in both acid and alkaline solution, (ii) its ability to undergo proton acid/base reactions to form

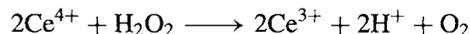
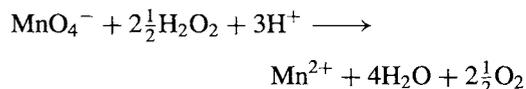
peroxonium salts  $(\text{H}_2\text{OOH})^+$ , hydroperoxides  $(\text{OOH})^-$  and peroxides  $(\text{O}_2)^{2-}$ , and (iii) its reactions to give peroxometal complexes and peroxyacid anions.

The ability of  $\text{H}_2\text{O}_2$  to act both as an oxidizing and a reducing agent is well known in analytical chemistry. Typical examples (not necessarily of analytical utility) are:

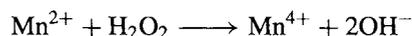
*Oxidizing agent in acid solution:*



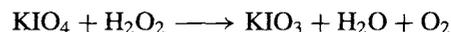
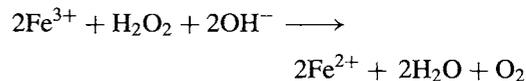
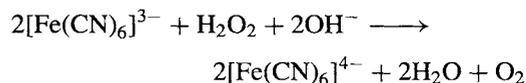
*Reducing agent in acid solution:*



*Oxidizing agent in alkaline solution:*



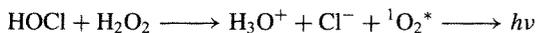
*Reducing agent in alkaline solution:*



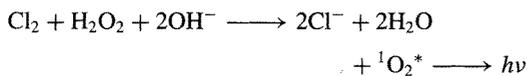
<sup>114</sup> V. A. SARIN, V. YA. DUDAREV, T. A. DOBRYNINA and V. E. ZAVODNIK, *Soviet Phys. Crystallogr.* **24**, 472-3 (1979), and references therein.

It will be noted that  $O_2$  is always evolved when  $H_2O_2$  acts as a reducing agent, and sometimes this gives rise to a red chemiluminescence if the dioxygen molecule is produced in a singlet state (p. 605), e.g.:

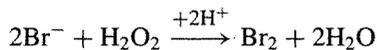
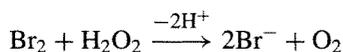
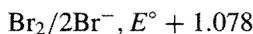
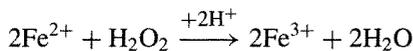
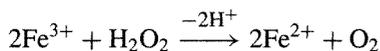
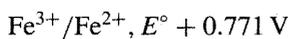
*Acid solution:*



*Alkaline solution:*



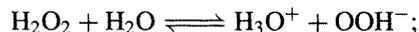
The catalytic decomposition of aqueous solutions  $H_2O_2$  alluded to on p. 635 can also be viewed as an oxidation–reduction process and, indeed, most homogeneous catalysts for this reaction are oxidation–reduction couples of which the oxidizing agent can oxidize (be reduced by)  $H_2O_2$  and the reducing agent can reduce (be oxidized by)  $H_2O_2$ . Thus, using the data on p. 628, any complex with a reduction potential between +0.695 and +1.776 V in acid solution should catalyse the reaction. For example:



In many such reactions, experiments using  $^{18}O$  show negligible exchange between  $H_2O_2$  and  $H_2O$ , and all the  $O_2$  formed when  $H_2O_2$  is used as a reducing agent comes from the  $H_2O_2$ , implying that oxidizing agents do not break the O–O bond but simply remove electrons. Not all reactions are heterolytic, however, and free radicals are sometimes involved, e.g.  $Ti^{3+}/H_2O_2$  and Fenton's

reagent ( $Fe^{2+}/H_2O_2$ ). The most important free radicals are OH and  $O_2H$ .

Hydrogen peroxide is a somewhat stronger acid than water, and in dilute aqueous solutions has  $pK_a(25^\circ) = 11.65 \pm 0.02$ , i.e. comparable with the third dissociation constant of  $H_3PO_4$  (p. 519):



$$K_a = \frac{[H_3O^+][OOH^-]}{[H_2O_2]} = 2.24 \times 10^{-12} \text{ mol l}^{-1}$$

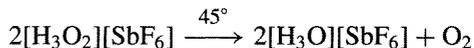
Conversely,  $H_2O_2$  is a much weaker base than  $H_2O$  (perhaps by a factor of  $10^6$ ), and the following equilibrium lies far to the right:



As a consequence, salts of  $H_3O_2^+$  cannot be prepared from aqueous solutions but they have been obtained as white solids from the strongly acid solvent systems anhydrous  $HF/SbF_5$  and  $HF/AsF_5$ , e.g.:<sup>(115)</sup>



The salts decompose quantitatively at or slightly above room temperature, e.g.:

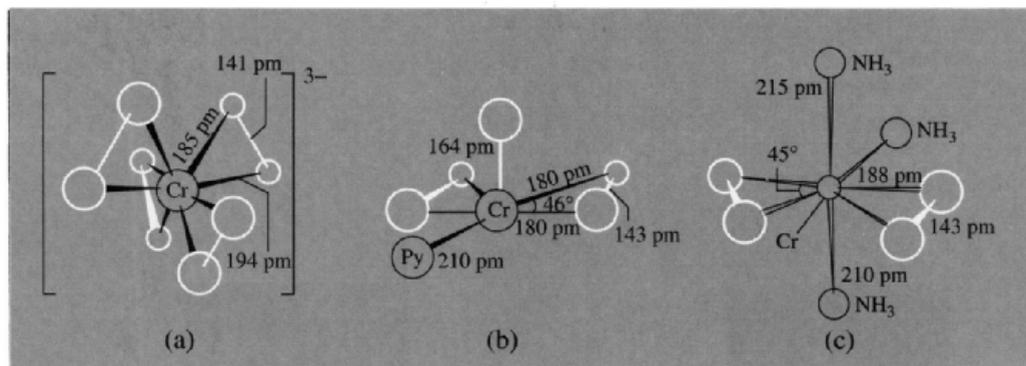


The ion  $[H_2OOH]^+$  is isoelectronic with  $H_2NOH$  and vibrational spectroscopy shows it to have the same ( $C_s$ ) symmetry.

Deprotonation of  $H_2O_2$  yields  $OOH^-$ , and hydroperoxides of the alkali metals are known in solution. Liquid ammonia can also effect deprotonation and  $NH_4OOH$  is a white solid, mp  $25^\circ$ ; infrared spectroscopy shows the presence of  $NH_4^+$  and  $OOH^-$  ions in the solid phase but the melt appears to contain only the H-bonded species  $NH_3$  and  $H_2O_2$ .<sup>(116)</sup> Double deprotonation yields the peroxide ion  $O_2^{2-}$ , and this is a standard route to transition metal peroxides.<sup>(53)</sup>

<sup>115</sup> K. O. CHRISTE, W. W. WILSON and E. C. CURTIS, *Inorg. Chem.* **18**, 2578–86 (1979).

<sup>116</sup> O. KNOP and P. A. GIGUÈRE, *Canad. J. Chem.* **37**, 1794–7 (1959).



**Figure 14.17** Structures of (a) the tetraperoxochromate(V) ion  $[\text{Cr}^{\text{V}}(\text{O}_2)_4]^{3-}$ , (b) the pyridine oxodiperoxochromium(VI) complex  $[\text{Cr}^{\text{VI}}\text{O}(\text{O}_2)_2\text{py}]$ , and (c) the triamminodiperoxochromium(IV) complex  $[\text{Cr}^{\text{IV}}(\text{NH}_3)_3(\text{O}_2)_2]$  showing important interatomic distances and angles. (This last compound was originally described as a chromium(II) superoxo complex  $[\text{Cr}^{\text{II}}(\text{NH}_3)_3(\text{O}_2)_2]$  on the basis of an apparent O–O distance of 131 pm,<sup>(117)</sup> and is a salutary example of the factual and interpretative errors that can arise even in X-ray diffraction studies.<sup>(118)</sup>)

Many such compounds are discussed under the individual transition elements and it is only necessary here to note that the chemical identity of the products obtained is often very sensitive to the conditions employed because of the combination of acid-base and redox reactions in the system. For example, treatment of alkaline aqueous solutions of chromate(VI) with  $\text{H}_2\text{O}_2$  yields the stable red paramagnetic tetraperoxochromate(V) compounds  $[\text{Cr}^{\text{V}}(\text{O}_2)_4]^{3-}$  ( $\mu$  1.80 BM), whereas treatment of chromate(VI) with  $\text{H}_2\text{O}_2$  in acid solution followed by extraction with ether and coordination with pyridine yields the neutral peroxochromate(VI) complex  $[\text{CrO}(\text{O}_2)_2\text{py}]$  which has a small temperature-independent paramagnetism of about 0.5 BM. The structure of these two species is in Fig. 14.17 which also includes the structure of the brown diperoxochromium(IV) complex  $[\text{Cr}^{\text{IV}}(\text{NH}_3)_3(\text{O}_2)_2]$  ( $\mu$  2.8 BM) prepared by treating either of the other two complexes with an excess of aqueous ammonia or more directly by treating an aqueous ammoniacal solution of  $[\text{NH}_4]_2[\text{Cr}_2\text{O}_7]$  with  $\text{H}_2\text{O}_2$ . Besides deprotonation of  $\text{H}_2\text{O}_2$ , other routes to metal

peroxides include the direct reduction of  $\text{O}_2$  by combustion of the electropositive alkali and alkaline earth metals in oxygen (pp. 84, 119) or by reaction of  $\text{O}_2$  with transition metal complexes in solution (p. 616).<sup>(119)</sup> Very recently  $\text{K}_2\text{O}_2$  has been obtained as a colourless crystalline biproduct of the synthesis of the orthonitrate  $\text{K}_3\text{NO}_4$  (p. 472) by prolonged heating of  $\text{KNO}_3$  and  $\text{K}_2\text{O}$  in a silver crucible at temperatures up to  $400^\circ\text{C}$ .<sup>(120)</sup> The O–O distance was found to be 154.1(6) pm, significantly longer than the values of  $\sim 150$  pm previously obtained for alkali metal peroxides (Table 14.4, p. 616).

Another recent development is the production of  $\text{HOOH}$  (the ozone analogue of  $\text{H}_2\text{O}_2$ ) in 40% yield by the simple expedient of replacing  $\text{O}_2$  by  $\text{O}_3$  in the standard synthesis via 2-ethylanthraquinone at  $-78^\circ$  (cf. p. 634);  $\text{H}_2\text{O}_3$  begins to decompose appreciably around  $-40^\circ$  to give single oxygen,  $\Delta^1\text{O}_2$ , but is much more stable (up to  $+20^\circ$ ) in  $\text{MeOBU}^t$  and similar solvents.<sup>(121)</sup>

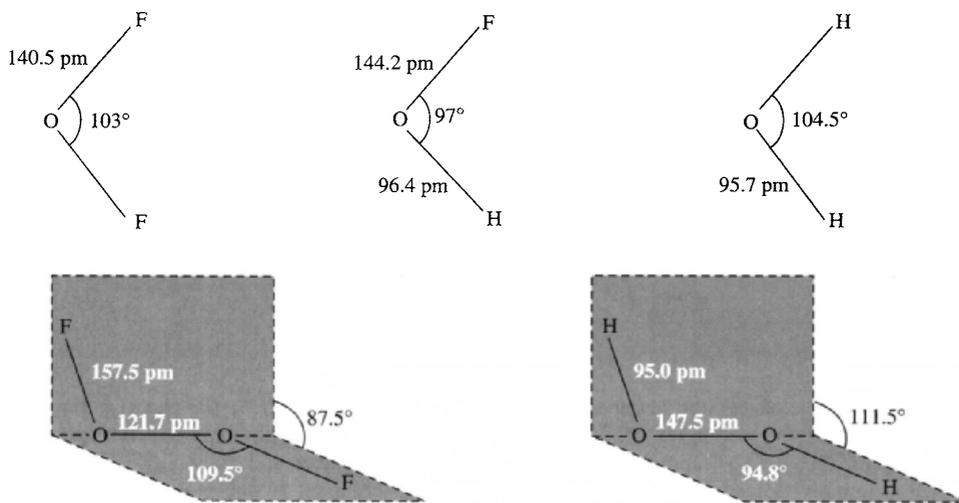
<sup>119</sup> N.-G. VANNERBERG, *Prog. Inorg. Chem.* **4**, 125–97 (1962).

<sup>120</sup> T. BREMM and M. JANSEN, *Z. anorg. allg. Chem.* **610**, 64–6 (1992).

<sup>121</sup> J. CERKOVNIK and B. PLESNIČAR, *J. Am. Chem. Soc.* **115**, 12169–70 (1993).

<sup>117</sup> E. H. McLAREN and L. HELMHOLZ, *J. Chem. Phys.* **63**, 1279–83 (1959).

<sup>118</sup> R. STROMBERG, *Arkiv Kemi* **22**, 49–64 (1974).

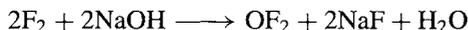


**Figure 14.18** Comparison of the molecular dimensions of various gaseous molecules having O-F and O-H bonds.

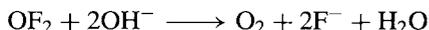
Peroxoanions are described under the appropriate element, e.g. peroxoborates (p. 206), peroxonitrates (p. 459), peroxophosphates (p. 512), peroxosulfates (p. 712), and peroxodisulfates (p. 713).

#### 14.2.4 Oxygen fluorides<sup>(122)</sup>

Oxygen forms several binary fluorides of which the most stable is  $\text{OF}_2$ . This was first made in 1929 by the electrolysis of slightly moist molten  $\text{KF}/\text{HF}$  but is now generally made by reacting  $\text{F}_2$  gas with 2% aqueous  $\text{NaOH}$  solution:



Conditions must be controlled so as to minimize loss of the product by the secondary reaction:



Oxygen fluoride is a colourless, very poisonous gas that condenses to a pale-yellow liquid (mp

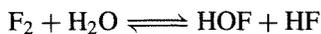
$-223.8^\circ$ , bp  $-145.3^\circ\text{C}$ ). When pure it is stable to  $200^\circ$  in glass vessels but above this temperature it decomposes by a radical mechanism to the elements. Molecular dimensions (microwave) are in Fig. 14.18, where they are compared with those of related molecules. The heat of formation has been given as  $\Delta H_f^\circ$   $24.5 \text{ kJ mol}^{-1}$ , leading to an average O-F bond energy of  $187 \text{ kJ mol}^{-1}$ . Though less reactive than elementary fluorine,  $\text{OF}_2$  is a powerful oxidizing and fluorinating agent. Many metals give oxides and fluorides, phosphorus yields  $\text{PF}_5$  plus  $\text{POF}_3$ , sulfur  $\text{SO}_2$  plus  $\text{SF}_4$ , and xenon gives  $\text{XeF}_4$  and oxofluorides (p. 900).  $\text{H}_2\text{S}$  explodes on being mixed with  $\text{OF}_2$  at room temperature.  $\text{OF}_2$  is formally the anhydride of hypofluorous acid,  $\text{HOF}$ , but there is no evidence that it reacts with water to form this compound. Indeed,  $\text{HOF}$  had been sought for many decades but has only relatively recently been prepared and fully characterized.<sup>(123)</sup>

$\text{HOF}$  was first identified by P. N. Noble and G. C. Pimentel in 1968 using matrix isolation techniques:  $\text{F}_2/\text{H}_2\text{O}$  mixtures were frozen in solid

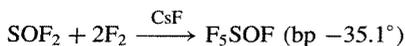
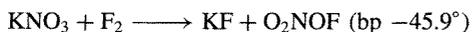
<sup>122</sup> E. A. V. EBSWORTH, J. A. CONNOR and J. J. TURNER, in J. C. BAILAR, H. J. EMELÉUS, R. S. NYHOLM and A. F. TROTMAN-DICKENSON (eds.), *Comprehensive Inorganic Chemistry*, Vol. 2, Chap. 22, Section 5, pp. 747–71. Pergamon Press, Oxford, 1973.

<sup>123</sup> E. H. APPELMAN, Nonexistent compounds: two case histories, *Acc. Chem. Res.* **6**, 113–7 (1973).

N<sub>2</sub> and photolysed at 14–20 K:



A more convenient larger-scale preparation was devised in 1971 by M. H. Studier and E. H. Appleman, who circulated F<sub>2</sub> rapidly through a Kel-F U-tube filled with Räschig rings of polytetrafluoroethylene (Teflon) which had been moistened with water and cooled to –40°. An essential further condition was the presence of traps at –50° and –79° to remove H<sub>2</sub>O and HF (both of which react with HOF), and the product was retained in a trap at –183°. HOF is a white solid, melting at –117° to a pale yellow liquid which boils below room temperature. Molecular dimensions are in Fig. 14.18; the small bond angle is particularly notable, being the smallest yet recorded for 2-coordinate O in an open chain. HOF is stable with respect to its elements:  $\Delta H_f^\circ(298) = -98.2$ ,  $\Delta G_f^\circ(298) = -85.7 \text{ kJ mol}^{-1}$ . However, HOF decomposes fairly rapidly to HF and O<sub>2</sub> at room temperature ( $t_{1/2} \sim 30 \text{ min}$  at 100 mmHg in Kel-F or Teflon). Decomposition is accelerated by light and by the presence of F<sub>2</sub> or metal surfaces. HOF reacts rapidly with water to produce HF, H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>; with acid solutions H<sub>2</sub>O is oxidized primarily to H<sub>2</sub>O<sub>2</sub>, whereas in alkaline solutions O<sub>2</sub> is the principal oxygen-containing product. Ag<sup>I</sup> is oxidized to Ag<sup>II</sup> and, in alkaline solution, BrO<sub>3</sub><sup>–</sup> yields the elusive perbromate ion BrO<sub>4</sub><sup>–</sup> (p. 871). All these reactions parallel closely those of F<sub>2</sub> in water, and it may well be that HOF is the reactive species produced when F<sub>2</sub> reacts with water (p. 856). No ionic salts of hypofluorous acid have been isolated but covalent hypofluorites have been known for several decades as highly reactive (sometimes explosive) gases, e.g.:



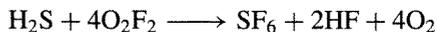
Dioxygen difluoride, O<sub>2</sub>F<sub>2</sub>, is best prepared by passing a silent electric discharge through a low-pressure mixture of F<sub>2</sub> and O<sub>2</sub>: the products obtained depend markedly on conditions, and the

yield of O<sub>2</sub>F<sub>2</sub> is optimized by using a 1:1 mixture at 7–17 mmHg and a discharge of 25–30 mA at 2.1–2.4 kV. Alternatively, pure O<sub>2</sub>F<sub>2</sub> can be synthesized by subjecting a mixture of liquid O<sub>2</sub> and F<sub>2</sub> in a stainless steel reactor at –196° to 3 MeV bremsstrahlung radiation for 1–4 h. O<sub>2</sub>F<sub>2</sub> is a yellow solid and liquid, mp –154°, bp –57° (extrapolated). It is much less stable than OF<sub>2</sub> and even at –160° decomposes at a rate of some 4% per day. Decomposition by a radical mechanism is rapid above –100°. The structure of O<sub>2</sub>F<sub>2</sub> (Fig. 14.18) resembles that of H<sub>2</sub>O<sub>2</sub> but the remarkably short O–O distance is a notable difference in detail (cf. O<sub>2</sub> gas 120.7 pm). Conversely, the O–F distance is unusually long when compared to those in OF<sub>2</sub> and HOF (Fig. 14.18). These features are paralleled by the bond dissociation energies:

$$D(\text{FO}–\text{OF}) 430 \text{ kJ mol}^{-1},$$

$$D(\text{F}–\text{OOF}) \sim 75 \text{ kJ mol}^{-1}.$$

Consistent with this, mass spectrometric, infrared and electron spin resonance studies confirm dissociation into F and OOF radicals, and low-temperature studies have also established the presence of the dimer O<sub>4</sub>F<sub>2</sub>, which is a dark red-brown solid, mp –191°C. Impure O<sub>4</sub>F<sub>2</sub> can also be prepared by silent electric discharge but the material previously thought to be O<sub>3</sub>F<sub>2</sub> is probably a mixture of O<sub>4</sub>F<sub>2</sub> and O<sub>2</sub>F<sub>2</sub>. Dioxygen difluoride, as expected, is a very vigorous and powerful oxidizing and fluorinating agent even at very low temperatures (–150°). It converts ClF to ClF<sub>3</sub>, BrF<sub>3</sub> to BrF<sub>5</sub>, and SF<sub>4</sub> to SF<sub>6</sub>. Similar products are obtained from HCl, HBr and H<sub>2</sub>S, e.g.:

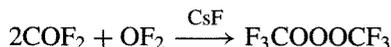
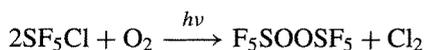
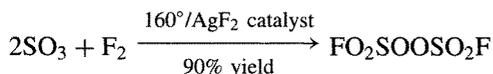


Interest in the production of high-energy oxidizers for use in rocket motors has stimulated the study of peroxy compounds bound to highly electronegative groups during the past few decades. Although such applications have not yet materialized, numerous new compounds of this type

Table 14.13 Properties of some fluorinated peroxides

| Compound                             | MP/°C | BP/°C | Compound  | MP/°C | BP/°C |
|--------------------------------------|-------|-------|---|-------|-------|
| FO <sub>2</sub> SOOSO <sub>2</sub> F | -55.4 | 67.1  | F <sub>3</sub> COONO <sub>2</sub>                                   | —     | 0.7   |
| FO <sub>2</sub> SOOF                 | —     | 0     | F <sub>3</sub> COOP(O)F <sub>2</sub>                                | -88.6 | 15.5  |
| FO <sub>2</sub> SOOSF <sub>5</sub>   | —     | 54.1  | F <sub>3</sub> COOCl  | -132  | -22   |
| F <sub>5</sub> SOOSF <sub>5</sub>    | -95.4 | 49.4  | (F <sub>3</sub> C) <sub>3</sub> COOC(CF <sub>3</sub> ) <sub>3</sub> | 12    | 98.6  |
| F <sub>5</sub> SOOCF <sub>3</sub>    | -136  | 7.7   | F <sub>3</sub> COOOCF <sub>3</sub>                                  | -138  | -16   |

have been synthesized and characterized, e.g.:



Such compounds are volatile liquids or gases (Table 14.13) and their extensive reaction chemistry has been very fully reviewed.<sup>(124)</sup>

## 14.2.5 Oxides

### Various methods of classification

Oxides are known for all elements of the periodic table except the lighter noble gases and, indeed, most elements form more than one binary compound with oxygen. Their properties span the full range of volatility from difficultly condensable gases such as CO (bp -191.5°C) to refractory oxides such as ZrO<sub>2</sub> (mp 3265°C, bp ~4850°C). Likewise, their electrical properties vary from being excellent insulators (e.g. MgO), through semi-conductors (e.g. NiO), to good metallic conductors (e.g. ReO<sub>3</sub>). They may be precisely stoichiometric or show stoichiometric variability over a narrow or a wide range of composition. They may be thermodynamically stable or unstable with respect to their elements, thermally stable or unstable, highly reactive to common reagents or almost completely inert even at very high temperatures. With such a vast array

of compounds and such a broad spectrum of properties any classification of oxides is likely to be either too simplified to be reliable or too complicated to be useful. One classification that is both convenient and helpful at an elementary level stresses the acid-base properties of oxides; this can be complemented and supplemented by classifications which stress the structural relationships between oxides. General classifications based on redox properties or on presumed bonding models have proved to be less helpful, though they are sometimes of use when a more restricted group of compounds is being considered.

The acid-base classification<sup>(125)</sup> turns essentially on the thermodynamic properties of hydroxides in aqueous solution, since oxides themselves are not soluble as such (p. 630). Oxides may be:

*acidic*: e.g. most oxides of non-metallic elements (CO<sub>2</sub>, NO<sub>2</sub>, P<sub>4</sub>O<sub>10</sub>, SO<sub>3</sub>, etc.);

*basic*: e.g. oxides of electropositive elements (Na<sub>2</sub>O, CaO, Ti<sub>2</sub>O, La<sub>2</sub>O<sub>3</sub>, etc.);

*amphoteric*: oxides of less electropositive elements (BeO, Al<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, ZnO, etc.);

*neutral*: oxides that do not interact with water or aqueous acids or bases (CO, NO, etc.).

Periodic trends in these properties are well documented (p. 27). Thus, in a given period, oxides progress from strongly basic, through weakly basic, amphoteric, and weakly acidic, to strongly acidic (e.g. Na<sub>2</sub>O, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, P<sub>4</sub>O<sub>10</sub>, SO<sub>3</sub>, ClO<sub>2</sub>). Acidity also increases with increasing oxidation state (e.g. MnO < Mn<sub>2</sub>O<sub>3</sub> < MnO<sub>2</sub> < Mn<sub>2</sub>O<sub>7</sub>). A similar trend is

<sup>124</sup> R. A. DE MARCO and J. M. SHREEVE, *Adv. Inorg. Chem. Radiochem.*, **16**, 109-76 (1974); J. M. SHREEVE, *Endeavour* xxxv, No. 125, 79-82 (1976).

<sup>125</sup> C. S. G. PHILLIPS and R. J. P. WILLIAMS, *Inorganic Chemistry*, Vol. 1, Oxford University Press, Oxford, 1965; Section 14.1, see also pp. 722-9 of ref. 122.

the decrease in basicity of the lanthanide oxides with increase in atomic number from La to Lu. In the main groups, basicity of the oxides increases with increase in atomic number down a group (e.g.  $\text{BeO} < \text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$ ), though the reverse tends to occur in the later transition element groups. Acid–base interactions can also be used to classify reaction types of (a) oxides with each other (eg.  $\text{CaO}$  with  $\text{SiO}_2$ ), (b) oxides with oxysalts (eg.  $\text{CaO}$  with  $\text{CaSiO}_3$ ), and (c) oxysalts with each other (eg.  $\text{Ca}_2\text{SiO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$ ), and to predict the products of such reactions.<sup>(126)</sup>

The thermodynamic and other physical properties of binary oxides (e.g.  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$ , mp, etc.) show characteristic trends and variations when plotted as a function of atomic number, and the preparation of such plots using readily available compilations of data<sup>(127)</sup> can be a revealing and rewarding exercise.<sup>(128)</sup>

Structural classifications of oxides recognize discrete molecular species and structures which are polymeric in one or more dimensions leading to chains, layers, and ultimately, to three-dimensional networks. Some typical examples are in Table 14.14; structural details are given elsewhere under each individual element. The type of structure adopted in any particular case depends (obviously) not only on the

stoichiometry but also on the relative sizes of the atoms involved and the propensity to form  $p_\pi$  double bonds to oxygen. In structures which are conventionally described as “ionic”, the 6-coordinate radius of  $\text{O}^{2-}$  (140 pm) is larger than all 6-coordinate cation radii except for  $\text{Rb}^I$ ,  $\text{Cs}^I$ ,  $\text{Fr}^I$ ,  $\text{Ra}^{II}$ , and  $\text{Tl}^I$  though it is approached by  $\text{K}^I$  (138 pm) and  $\text{Ba}^{II}$  (135 pm).<sup>(129)</sup> Accordingly, many oxides are found to adopt structures in which there is a close-packed oxygen lattice with cations in the interstices (frequently octahedral). For “cations”, which have very small effective ionic radii (say  $< 50$  pm), particularly if they carry a high formal charge, the structure type and bonding are usually better described in covalent terms, particularly when  $\pi$  interactions enhance the stability of terminal  $\text{M}=\text{O}$  bonds ( $\text{M} = \text{C}, \text{N}, \text{P}^V, \text{S}^{VI}$ , etc.). Thus, for oxides of formula  $\text{MO}$ , a coordination number of 1 (molecular) is found for  $\text{CO}$  and  $\text{NO}$ , though the latter tends towards a coordination number of 2 (dimers, p. 446). With the somewhat larger  $\text{Be}^{II}$  and  $\text{Zn}^{II}$  the wurtzite (4:4) structure is adopted, whereas monoxides of still larger divalent cations tend to adopt the sodium chloride (6:6) structure (e.g.  $\text{M}^{II} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Co}, \text{Ni}, \text{Cd}, \text{Eu}$ , etc.).

A similar trend is observed for oxides of  $\text{M}^{IV}\text{O}_2$  in Group 14 of the periodic table. The small C atom, with its propensity to form  $p_\pi$ – $p_\pi$  bonds to oxygen, adopts a linear, molecular structure  $\text{O}=\text{C}=\text{O}$ . Silicon, being somewhat larger and less prone to double bonding (p. 361), is surrounded by 4 essentially single-bonded O in most forms of  $\text{SiO}_2$  (p. 342) and the coordination geometry is thus 4:2. Similarly,  $\text{GeO}_2$  adopts the quartz structure; in addition a rutile form (p. 961) is known in which the coordination is 6:3.  $\text{SnO}_2$  and  $\text{PbO}_2$  also have rutile structures as has  $\text{TiO}_2$ , but the largest Group 4 cations Zr and Hf adopt the fluorite (8:4) structure (p. 118) in their dioxides. Other large cations with a fluorite structure for  $\text{MO}_2$  are Po; Ce, Pr, Tb; Th, U, Np, Pu, Am and Cm. Conversely, the antifluorite structure is found for

**Table 14.14** Structure types for binary oxides in the solid state

| Structure type               | Examples   |
|------------------------------|--|
| Molecular structures         | $\text{CO}, \text{CO}_2, \text{OsO}_4, \text{Tc}_2\text{O}_7,$<br>$\text{Sb}_2\text{O}_6, \text{P}_4\text{O}_{10}$ |
| Chain structures             | $\text{HgO}, \text{SeO}_2, \text{CrO}_3, \text{Sb}_2\text{O}_3$  |
| Layer structures             | $\text{SnO}, \text{MoO}_3, \text{As}_2\text{O}_3, \text{Re}_2\text{O}_7$   |
| Three-dimensional structures | See text   |

<sup>126</sup> L. S. DENT-GLASSER and J. A. DUFFER, *J. Chem. Soc., Dalton Trans.*, 2323–8 (1987).

<sup>127</sup> M. C. BALL and A. H. NORBURY, *Physical Data for Inorganic Chemists*, Longmans, London, 1974, 175 pp. G. H. AYLWARD and T. J. V. FINDLAY, *SI Chemical Data*, 2nd edn., Wiley, Sydney, 1975, 136 pp.

<sup>128</sup> R. V. PARISH, *The Metallic Elements*, Longmans, London 1977, 254 pp. (see particularly pp. 25–8, 40–44, 66–74, 128–33, 148–50, 168–77, 188–98).

<sup>129</sup> R. D. SHANNON, *Acta Cryst.* **A32**, 751–67 (1976).

the alkali metal monoxides  $M_2O$  (p. 84). Such simple ideas are capable of considerable further elaboration.<sup>(130)</sup>

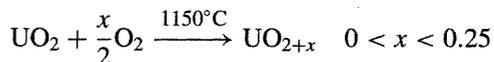
### Nonstoichiometry

Transition elements, for which variable valency is energetically feasible, frequently show nonstoichiometric behaviour (variable composition) in their oxides, sulfides and related binary compounds. For small deviations from stoichiometry a thermodynamic approach is instructive, but for larger deviations structural considerations super-vene, and the possibility of thermodynamically unstable but kinetically isolable phases must be considered. These ideas will be expanded in the following paragraphs but more detailed treatment must be sought elsewhere.<sup>(131-134)</sup>

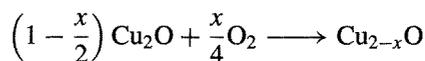
Any crystal in contact with the vapour of one of its constituents is potentially a nonstoichiometric compound since, for true thermodynamic equilibrium, the composition of the solid phase must depend on the concentration (pressure) of this constituent in the vapour phase. If the solid and vapour are in equilibrium with each other ( $\Delta G = 0$ ) at a given temperature and pressure, then a change in this pressure will lead to a change (however minute) in the composition of the solid, provided that the activation energy for the reaction is not too high at the temperature being used. Such deviations from ideal stoichiometry imply a change in valency of at least some of the ions in the crystal and

are readily detected for many oxides using a range of techniques such as pressure-composition isotherms, X-ray diffraction, neutron diffraction, electrical conductivity (semi-conductivity), visible and ultraviolet absorption spectroscopy (colour centres)<sup>(131)</sup> and Mössbauer ( $\gamma$ -ray resonance) spectroscopy.<sup>(135)</sup>

If the pressure of  $O_2$  above a crystalline oxide is increased, the oxide-ion activity in the solid can be increased by placing the supernumerary  $O^{2-}$  ions in the interstitial positions, e.g.:

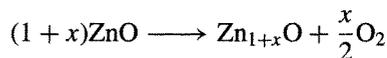


The electrons required to reduce  $\frac{1}{2}O_2$  to  $O^{2-}$  come from individual cations which are thereby oxidized to a higher oxidation state. Alternatively, if suitable interstitial sites are not available, the excess  $O^{2-}$  ions can build on to normal lattice sites thereby creating cation vacancies which diffuse into the crystal, e.g.:

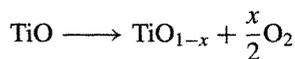


In this case the requisite electrons are provided by  $2Cu^I$  becoming oxidized to  $2Cu^{II}$ .

Conversely, if the pressure of  $O_2$  above a crystalline oxide is decreased below the equilibrium value appropriate for the stoichiometric composition, oxygen "boils out" of the lattice leaving supernumerary metal atoms or lower-valent ions in interstitial positions, e.g.:



The absorption spectrum of this nonstoichiometric phase forms the basis for the formerly much-used qualitative test for zinc oxide: "yellow when hot, white when cold". Alternatively, anion sites can be left vacant, e.g.:



In both cases the average oxidation state of the metal is reduced. It is important to appreciate that,

<sup>130</sup> A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., Oxford University Press, Oxford, 1984; Chap. 12, Binary metal oxides, pp. 531-74; Chap. 13, Complex oxides, pp. 575-625.

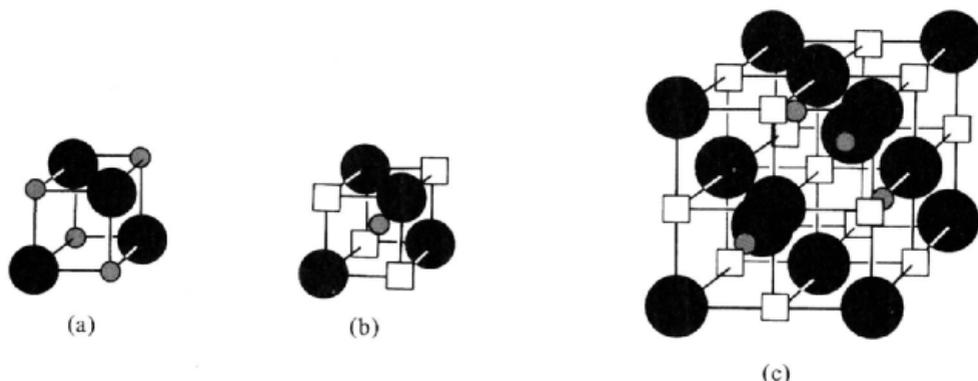
<sup>131</sup> N. N. GREENWOOD, *Ionic Crystals, Lattice Defects, and Nonstoichiometry*, Chaps. 6 and 7, pp. 111-81, Butterworths, London, 1968.

<sup>132</sup> D. J. M. BEVAN, Chap. 49 in J. C. BAILAR, H. J. EMELÉUS, R. S. NYHOLM and A. F. TROTMAN-DICKENSON (eds.), *Comprehensive Inorganic Chemistry*, Vol. 4, pp. 453-40, Pergamon Press, Oxford, 1973.

<sup>133</sup> T. SØRENSEN, *Nonstoichiometric Oxides*, Academic Press, New York, 1981, 441 pp.

<sup>134</sup> S. TRASATTI, *Electrodes of Conductive Metallic Oxides*, Elsevier, Amsterdam, Part A, 1980, 366 pp.; Part B, 1981, 336 pp.

<sup>135</sup> N. N. GREENWOOD and T. C. GIBB, *Mössbauer Spectroscopy*, Chapman & Hall, London, 1971, 659 pp.



**Figure 14.19** Schematic representation of defect clusters in  $\text{Fe}_{1-x}\text{O}$ . The normal NaCl-type structure (a) has  $\text{Fe}^{\text{II}}$  (small open circles) and  $\text{O}^{2-}$  (large dark circles) at alternate corners of the cube. In the 4:1 cluster (b), four octahedral  $\text{Fe}^{\text{II}}$  sites are left vacant and an  $\text{Fe}^{\text{III}}$  ion (grey) occupies the cube centre, thus being tetrahedrally coordinated by the  $4\text{O}^{2-}$ . In (c) a more extended 13:4 cluster is shown in which, again, all anion sites are occupied but the 13 octahedral  $\text{Fe}^{\text{II}}$  sites are vacant and four  $\text{Fe}^{\text{III}}$  occupy a tetrahedral array of cube centres.

in all such examples, the resulting nonstoichiometric compound is a homogeneous phase which is thermodynamically stable under the prevailing ambient conditions.

Sometimes the lattice defects form clusters amongst themselves rather than being randomly distributed throughout the lattice. A classic example is “ferrous oxide”, which is unstable as  $\text{FeO}$  at room temperature but exists as  $\text{Fe}_{1-x}\text{O}$  ( $0.05 < x < 0.12$ ): the NaCl-type lattice has a substantial number of vacant  $\text{Fe}^{\text{II}}$  sites and these tend to cluster so that  $\text{Fe}^{\text{III}}$  can occupy tetrahedral sites within the lattice as shown schematically in Fig. 14.19. Such clustering can sometimes nucleate a new phase in which “vacant sites” are eliminated by being ordered in a new structure type. For example,  $\text{PrO}_{2-x}$  forms a disordered nonstoichiometric phase ( $0 < x < 0.25$ ) at  $1000^\circ\text{C}$  but at lower temperatures ( $400\text{--}700^\circ\text{C}$ ) this is replaced by a succession of intermediate phases with only very narrow (and non-overlapping) composition ranges of general formula  $\text{Pr}_n\text{O}_{2n-2}$  with  $n = 4, 7, 9, 10, 11, 12$  and  $\infty$  as shown in Fig. 14.20 and Table 14.15. There is now compelling evidence that oxide-ion vacancies,  $\square$ , in these and other such fluorite-related lattices do not exist in

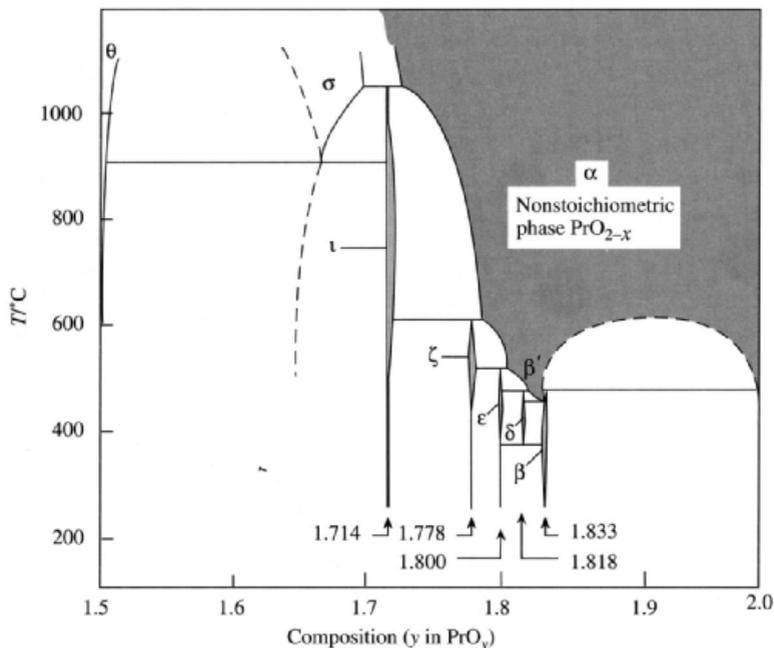
isolation but occur as octahedral ‘coordination defects’ of composition  $\{\text{M}_2^{\text{III}}\text{M}_{1.5}^{\text{IV}}\square\text{O}_6\}$ . The structure-forming topology of these coordination defects and their role in generating more extensive defects has recently been brilliantly expounded.<sup>(136)</sup>

**Table 14.15** Intermediate phases formed by ordering of defects in the praseodymium–oxygen system

| $n$      | Formula<br>$\text{Pr}_n\text{O}_{2n-2}$ | $y$ in $\text{PrO}_y$ | Nonstoichiometric<br>limits of $x$ at $T^\circ\text{C}$ | $T^\circ\text{C}$ |
|----------|---|-----------------------|---|-------------------|
| 4        | $\text{Pr}_2\text{O}_3$                 | 1.500                 | 1.500–1.503   | 1000              |
| 7        | $\text{Pr}_7\text{O}_{12}$              | 1.714                 | 1.713–1.719   | 700               |
| 9        | $\text{Pr}_9\text{O}_{16}$              | 1.778                 | 1.776–1.778   | 500               |
| 10       | $\text{Pr}_{10}\text{O}_{18}$           | 1.800                 | 1.799–1.801   | 450               |
| 11       | $\text{Pr}_{11}\text{O}_{20}$           | 1.818                 | 1.817–1.820   | 430               |
| 12       | $\text{Pr}_{12}\text{O}_{22}$           | 1.833                 | 1.831–1.836   | 400               |
| $\infty$ | $\text{PrO}_2$                          | 2.000                 | 1.999–2.000   | 400               |
|          |   |                       | 1.75–2.00   | 1000              |

Oxygen (oxide ions) in crystal lattices can be progressively removed by systematically

<sup>136</sup> B. F. HOSKINS and R. L. MARTIN, *Aust. J. Chem.* **48**, 709–39 (1995). R. L. MARTIN, *J. Chem. Soc., Dalton Trans.*, 3659–70 (1997).



**Figure 14.20** Part of the Pr–O phase diagram showing the extended nonstoichiometric  $\alpha$  phase  $\text{PrO}_{2-x}$  at high temperatures (shaded) and the succession of phases  $\text{Pr}_n\text{O}_{2n-2}$  at lower temperatures.

replacing corner-shared  $\{\text{MO}_6\}$  octahedra with edge-shared octahedra. The geometrical principles involved in the conceptual generation of such successions of phases (chemical-shear structures) are now well understood, but many mechanistic details of their formation remain unresolved. Typical examples are the rutile series  $\text{Ti}_n\text{O}_{2n-1}$  ( $n = 4, 5, 6, 7, 8, 9, 10, \infty$ ) between  $\text{TiO}_{1.75}$  and  $\text{TiO}_2$  and the  $\text{ReO}_3$  series  $\text{M}_n\text{O}_{3n-1}$  which leads to a succession of 6 phases with  $n = 8, 9, 10, 11, 12$  and 14 in the narrow composition range  $\text{MO}_{2.875}$  to  $\text{MO}_{2.929}$  ( $M = \text{Mo}$  or  $\text{W}$ ).

Nonstoichiometric oxide phases are of great importance in semiconductor devices, in heterogeneous catalysis and in understanding photoelectric, thermoelectric, magnetic and diffusional properties of solids. They have been used in thermistors, photoelectric cells, rectifiers, transistors, phosphors, luminescent materials and computer components (ferrites, etc.). They are crucially implicated in reactions at electrode surfaces, the performance of batteries, the tarnishing and corrosion of metals, and many other reactions of significance in catalysis.<sup>(131–134)</sup>