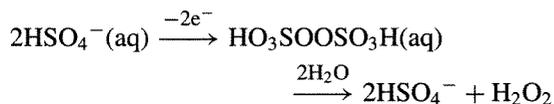


which traces the course of this controversy and analyses the reasons why it took so long to resolve.⁽¹¹¹⁾

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 H₂O 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 D₂O₂, e.g.:



On an industrial scale H₂O₂ 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. H₂O, p. 623). The compound is miscible with water in all proportions and forms a hydrate H₂O₂·H₂O, mp -52° . Addition of water increases the already high dielectric constant of H₂O₂ (70.7) to a maximum value of 121 at ~35% H₂O₂, 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^(a)

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

^(a)For D₂O₂: mp +1.5°; d_{20} 1.5348 g cm⁻³; η_{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, H₂O₂ is the smallest molecule known to show hindered rotation about a single bond, the rotational barriers being 4.62 and 29.45 kJ mol⁻¹ 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°C a neutron diffraction study⁽¹¹²⁾ 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 H₂O₂; in fact, values spanning the complete range from 90° to 180° (i.e. *trans* planar) are known for various solid phases containing molecular H₂O₂ (Table 14.12). The O–O distance in H₂O₂ corresponds to the value expected for a single bond (p. 616).

Chemical properties

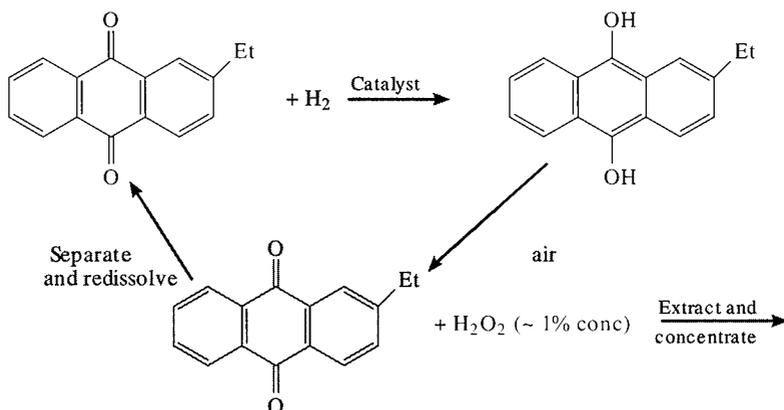
In H₂O₂ the oxidation state of oxygen is -1 , intermediate between the values for O₂ and H₂O, and, as indicated by the reduction potentials on p. 628, aqueous solutions of H₂O₂ should spontaneously disproportionate. For the pure

¹¹¹ 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.]

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

Preparation and Uses of Hydrogen Peroxide⁽¹¹³⁾

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 H_2O_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 H_2O_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% H_2O_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 H_2O_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, H_2O_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 H_2O_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 H_2O and O_2 on decomposition. An indication of the proportion of H_2O_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 H_2O_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."

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

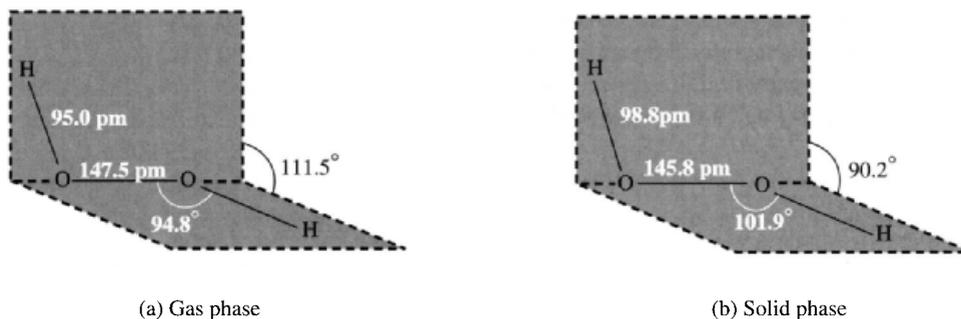


Figure 14.16 Structure of the H_2O_2 molecule (a) in the gas phase, and (b) in the crystalline state.

Table 14.12 Dihedral angle of H_2O_2 in some crystalline phases

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

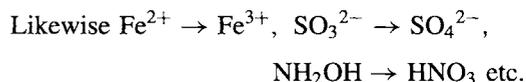
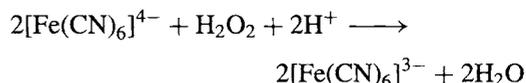
liquid: $\text{H}_2\text{O}_2(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g}); \Delta H^\circ = -98.2 \text{ kJ mol}^{-1}$, $\Delta G^\circ = -119.2 \text{ kJ mol}^{-1}$. In fact, in the absence of catalysts, the compound decomposes negligibly slowly but the reaction is strongly catalysed by metal surfaces (Pt, Ag), by MnO_2 or by traces of alkali (dissolved from glass), and for this reason H_2O_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 H_2O_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

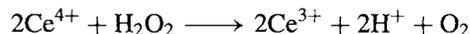
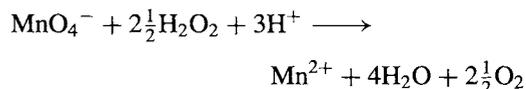
peroxonium salts $(\text{H}_2\text{OOH})^+$, hydroperoxides $(\text{OOH})^-$ and peroxides $(\text{O}_2)^{2-}$, and (iii) its reactions to give peroxometal complexes and peroxyacid anions.

The ability of H_2O_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:

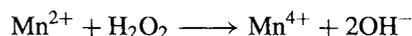
Oxidizing agent in acid solution:



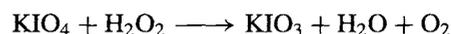
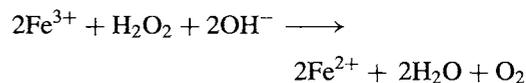
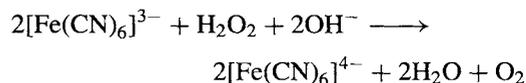
Reducing agent in acid solution:



Oxidizing agent in alkaline solution:



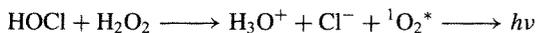
Reducing agent in alkaline solution:



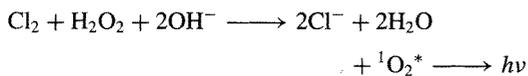
¹¹⁴ V. A. SARIN, V. YA. DUDAREV, T. A. DOBRYNINA and V. E. ZAVODNIK, *Soviet Phys. Crystallogr.* **24**, 472-3 (1979), and references therein.

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.:

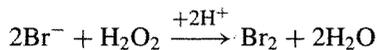
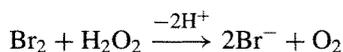
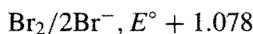
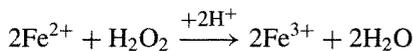
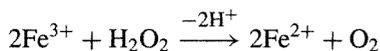
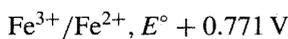
Acid solution:



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):



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

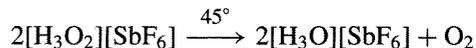
Conversely, H_2O_2 is a much weaker base than H_2O (perhaps by a factor of 10^6), and the following equilibrium lies far to the right:



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.:⁽¹¹⁵⁾



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° ; 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 .⁽¹¹⁶⁾ Double deprotonation yields the peroxide ion O_2^{2-} , and this is a standard route to transition metal peroxides.⁽⁵³⁾

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

¹¹⁶ O. KNOP and P. A. GIGUERE, *Canad. J. Chem.* **37**, 1794–7 (1959).

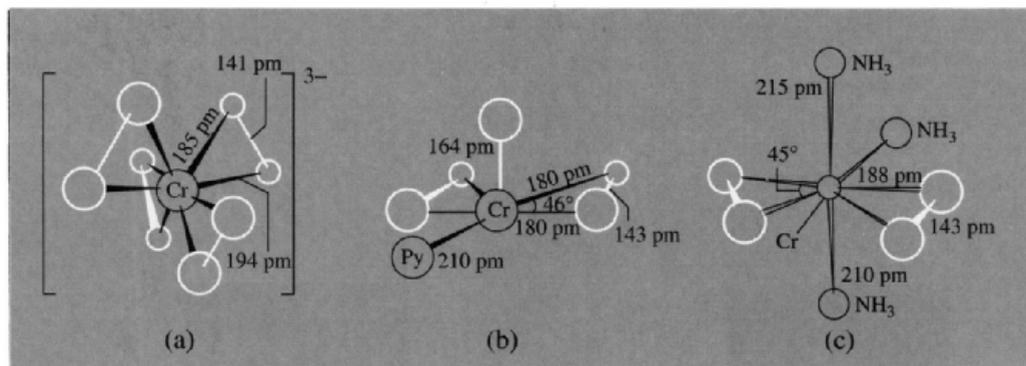


Figure 14.17 Structures of (a) the tetraperoxochromate(V) ion $[\text{Cr}^{\text{V}}(\text{O}_2)_4]^{3-}$, (b) the pyridine oxodiperoxochromium(VI) complex $[\text{Cr}^{\text{VI}}\text{O}(\text{O}_2)_2\text{py}]$, and (c) the triamminodiperoxochromium(IV) complex $[\text{Cr}^{\text{IV}}(\text{NH}_3)_3(\text{O}_2)_2]$ 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,⁽¹¹⁷⁾ and is a salutary example of the factual and interpretative errors that can arise even in X-ray diffraction studies.⁽¹¹⁸⁾)

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 H_2O_2 yields the stable red paramagnetic tetraperoxochromate(V) compounds $[\text{Cr}^{\text{V}}(\text{O}_2)_4]^{3-}$ (μ 1.80 BM), whereas treatment of chromate(VI) with H_2O_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 $[\text{Cr}^{\text{IV}}(\text{NH}_3)_3(\text{O}_2)_2]$ (μ 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 H_2O_2 . Besides deprotonation of H_2O_2 , other routes to metal

peroxides include the direct reduction of O_2 by combustion of the electropositive alkali and alkaline earth metals in oxygen (pp. 84, 119) or by reaction of O_2 with transition metal complexes in solution (p. 616).⁽¹¹⁹⁾ Very recently K_2O_2 has been obtained as a colourless crystalline biproduct of the synthesis of the orthonitrate K_3NO_4 (p. 472) by prolonged heating of KNO_3 and K_2O in a silver crucible at temperatures up to 400°C .⁽¹²⁰⁾ The O–O distance was found to be 154.1(6) pm, significantly longer than the values of ~ 150 pm previously obtained for alkali metal peroxides (Table 14.4, p. 616).

Another recent development is the production of HOOOH (the ozone analogue of H_2O_2) in 40% yield by the simple expedient of replacing O_2 by O_3 in the standard synthesis via 2-ethylanthraquinone at -78° (cf. p. 634); H_2O_3 begins to decompose appreciably around -40° to give single oxygen, $\Delta^1\text{O}_2$, but is much more stable (up to $+20^\circ$) in MeOBU^t and similar solvents.⁽¹²¹⁾

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

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

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

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

¹¹⁸ R. STROMBERG, *Arkiv Kemi* **22**, 49–64 (1974).

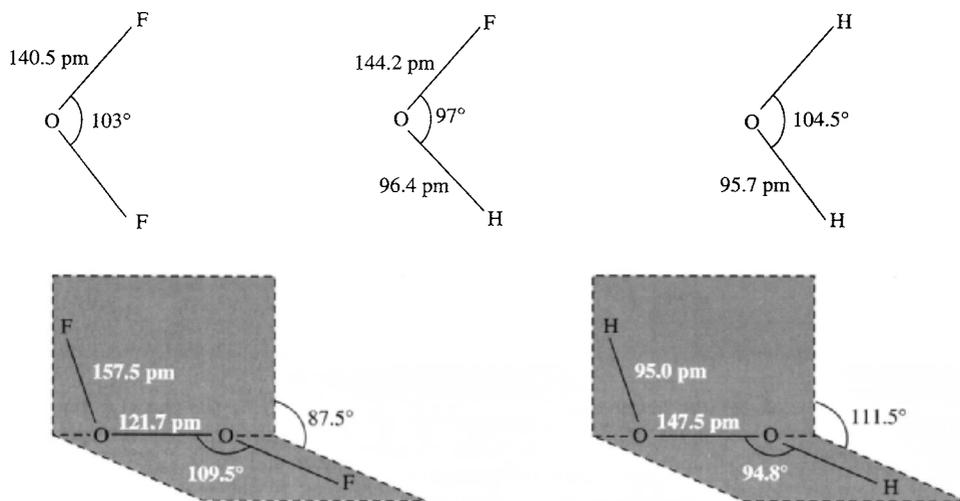
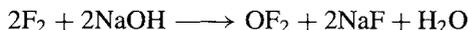


Figure 14.18 Comparison of the molecular dimensions of various gaseous molecules having O-F and O-H bonds.

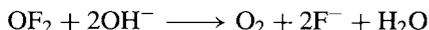
Peroxoanions are described under the appropriate element, e.g. peroxoborates (p. 206), peroxonitrates (p. 459), peroxophosphates (p. 512), peroxosulfates (p. 712), and peroxodisulfates (p. 713).

14.2.4 Oxygen fluorides⁽¹²²⁾

Oxygen forms several binary fluorides of which the most stable is OF_2 . This was first made in 1929 by the electrolysis of slightly moist molten KF/HF but is now generally made by reacting F_2 gas with 2% aqueous 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

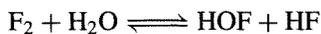
-223.8° , bp -145.3°C). When pure it is stable to 200° in glass vessels but above this temperature it decomposes by a radical mechanism to the elements. Molecular dimensions (microwave) are in Fig. 14.18, where they are compared with those of related molecules. The heat of formation has been given as ΔH_f° 24.5 kJ mol^{-1} , leading to an average O-F bond energy of 187 kJ mol^{-1} . Though less reactive than elementary fluorine, OF_2 is a powerful oxidizing and fluorinating agent. Many metals give oxides and fluorides, phosphorus yields PF_5 plus POF_3 , sulfur SO_2 plus SF_4 , and xenon gives XeF_4 and oxofluorides (p. 900). H_2S explodes on being mixed with OF_2 at room temperature. OF_2 is formally the anhydride of hypofluorous acid, HOF , but there is no evidence that it reacts with water to form this compound. Indeed, HOF had been sought for many decades but has only relatively recently been prepared and fully characterized.⁽¹²³⁾

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

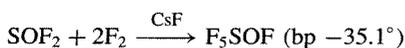
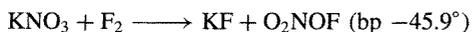
¹²² E. A. V. EBSWORTH, J. A. CONNOR and J. J. TURNER, in J. C. BAILAR, H. J. EMELÉUS, R. S. NYHOLM and A. F. TROTMAN-DICKENSON (eds.), *Comprehensive Inorganic Chemistry*, Vol. 2, Chap. 22, Section 5, pp. 747–71. Pergamon Press, Oxford, 1973.

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

N₂ 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 F₂ rapidly through a Kel-F U-tube filled with Räschtig 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 H₂O 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 O₂ 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 F₂ or metal surfaces. HOF reacts rapidly with water to produce HF, H₂O₂ and O₂; with acid solutions H₂O is oxidized primarily to H₂O₂, whereas in alkaline solutions O₂ is the principal oxygen-containing product. Ag^I is oxidized to Ag^{II} and, in alkaline solution, BrO₃[–] yields the elusive perbromate ion BrO₄[–] (p. 871). All these reactions parallel closely those of F₂ in water, and it may well be that HOF is the reactive species produced when F₂ 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.:



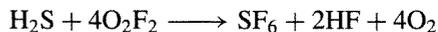
Dioxygen difluoride, O₂F₂, is best prepared by passing a silent electric discharge through a low-pressure mixture of F₂ and O₂: the products obtained depend markedly on conditions, and the

yield of O₂F₂ 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 O₂F₂ can be synthesized by subjecting a mixture of liquid O₂ and F₂ in a stainless steel reactor at –196° to 3 MeV bremsstrahlung radiation for 1–4 h. O₂F₂ is a yellow solid and liquid, mp –154°, bp –57° (extrapolated). It is much less stable than OF₂ 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 O₂F₂ (Fig. 14.18) resembles that of H₂O₂ but the remarkably short O–O distance is a notable difference in detail (cf. O₂ gas 120.7 pm). Conversely, the O–F distance is unusually long when compared to those in OF₂ and HOF (Fig. 14.18). These features are paralleled by the bond dissociation energies:

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

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

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 O₄F₂, which is a dark red-brown solid, mp –191°C. Impure O₄F₂ can also be prepared by silent electric discharge but the material previously thought to be O₃F₂ is probably a mixture of O₄F₂ and O₂F₂. Dioxygen difluoride, as expected, is a very vigorous and powerful oxidizing and fluorinating agent even at very low temperatures (–150°). It converts ClF to ClF₃, BrF₃ to BrF₅, and SF₄ to SF₆. Similar products are obtained from HCl, HBr and H₂S, e.g.:

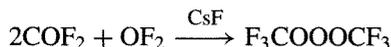
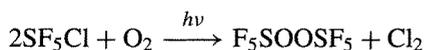
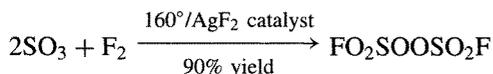


Interest in the production of high-energy oxidizers for use in rocket motors has stimulated the study of peroxy compounds bound to highly electronegative groups during the past few decades. Although such applications have not yet materialized, numerous new compounds of this type

Table 14.13 Properties of some fluorinated peroxides

Compound	MP/°C	BP/°C	Compound	MP/°C	BP/°C
FO ₂ SOOSO ₂ F	-55.4	67.1	F ₃ COONO ₂	—	0.7
FO ₂ SOOF	—	0	F ₃ COOP(O)F ₂	-88.6	15.5
FO ₂ SOOSF ₅	—	54.1	F ₃ COOCl	-132	-22
F ₅ SOOSF ₅	-95.4	49.4	(F ₃ C) ₃ COOC(CF ₃) ₃	12	98.6
F ₅ SOOCF ₃	-136	7.7	F ₃ COOOCF ₃	-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.⁽¹²⁴⁾

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 ZrO₂ (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. ReO₃). 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⁽¹²⁵⁾ 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 (CO₂, NO₂, P₄O₁₀, SO₃, etc.);

basic: e.g. oxides of electropositive elements (Na₂O, CaO, Ti₂O, La₂O₃, etc.);

amphoteric: oxides of less electropositive elements (BeO, Al₂O₃, Bi₂O₃, 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. Na₂O, MgO, Al₂O₃, SiO₂, P₄O₁₀, SO₃, ClO₂). Acidity also increases with increasing oxidation state (e.g. MnO < Mn₂O₃ < MnO₂ < Mn₂O₇). A similar trend is

¹²⁴ 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).

¹²⁵ 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. CaO with SiO_2), (b) oxides with oxysalts (eg. CaO with CaSiO_3), and (c) oxysalts with each other (eg. Ca_2SiO_4 and $\text{Ca}_3(\text{PO}_4)_2$), and to predict the products of such reactions.⁽¹²⁶⁾

The thermodynamic and other physical properties of binary oxides (e.g. ΔH_f° , ΔG_f° , 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⁽¹²⁷⁾ can be a revealing and rewarding exercise.⁽¹²⁸⁾

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_π double bonds to oxygen. In structures which are conventionally described as “ionic”, the 6-coordinate radius of O^{2-} (140 pm) is larger than all 6-coordinate cation radii except for Rb^I , Cs^I , Fr^I , Ra^{II} , and Tl^I though it is approached by K^I (138 pm) and Ba^{II} (135 pm).⁽¹²⁹⁾ 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 π 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 MO , a coordination number of 1 (molecular) is found for CO and NO , though the latter tends towards a coordination number of 2 (dimers, p. 446). With the somewhat larger Be^{II} and 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 M^{IV}O_2 in Group 14 of the periodic table. The small C atom, with its propensity to form p_π – p_π 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 SiO_2 (p. 342) and the coordination geometry is thus 4:2. Similarly, GeO_2 adopts the quartz structure; in addition a rutile form (p. 961) is known in which the coordination is 6:3. SnO_2 and PbO_2 also have rutile structures as has 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 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	$\text{CO}, \text{CO}_2, \text{OsO}_4, \text{Tc}_2\text{O}_7,$ $\text{Sb}_2\text{O}_6, \text{P}_4\text{O}_{10}$
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

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

¹²⁷ 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.

¹²⁸ 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).

¹²⁹ 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.⁽¹³⁰⁾

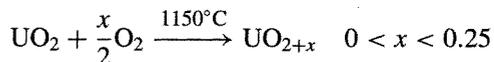
Nonstoichiometry

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.⁽¹³¹⁻¹³⁴⁾

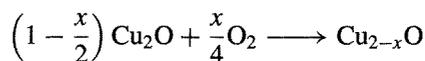
Any crystal in contact with the vapour of one of its constituents is potentially a nonstoichiometric compound since, for true thermodynamic equilibrium, the composition of the solid phase must depend on the concentration (pressure) of this constituent in the vapour phase. If the solid and vapour are 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)⁽¹³¹⁾ and Mössbauer (γ -ray resonance) spectroscopy.⁽¹³⁵⁾

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.:

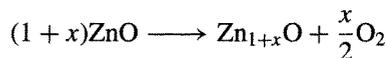


The electrons required to reduce $\frac{1}{2}O_2$ to O^{2-} come from individual cations which are thereby oxidized to a higher oxidation state. Alternatively, if suitable interstitial sites are not available, the excess O^{2-} ions can build on to normal lattice sites thereby creating cation vacancies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

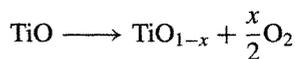


In this case the requisite electrons are provided by $2Cu^I$ becoming oxidized to $2Cu^{II}$.

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,

¹³⁰ 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.

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

¹³² 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.

¹³³ T. SØRENSEN, *Nonstoichiometric Oxides*, Academic Press, New York, 1981, 441 pp.

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

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

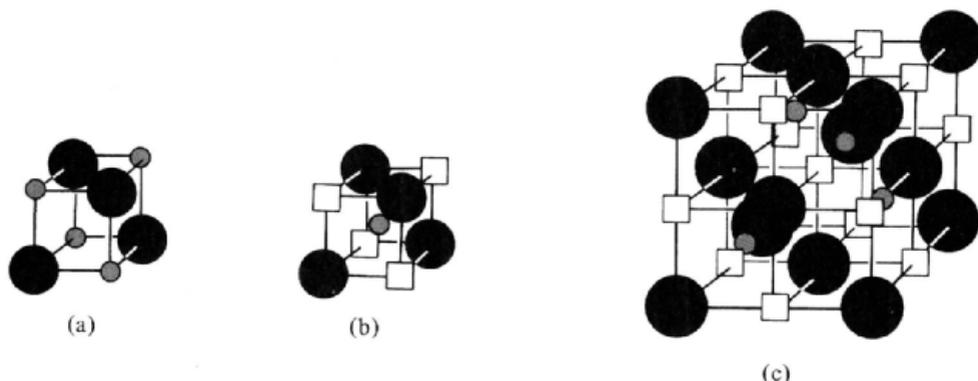


Figure 14.19 Schematic representation of defect clusters in Fe_{1-x}O . The normal NaCl-type structure (a) has Fe^{II} (small open circles) and O^{2-} (large dark circles) at alternate corners of the cube. In the 4:1 cluster (b), four octahedral Fe^{II} sites are left vacant and an Fe^{III} ion (grey) occupies the cube centre, thus being tetrahedrally coordinated by the 4O^{2-} . In (c) a more extended 13:4 cluster is shown in which, again, all anion sites are occupied but the 13 octahedral Fe^{II} sites are vacant and four Fe^{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 FeO at room temperature but exists as Fe_{1-x}O ($0.05 < x < 0.12$): the NaCl-type lattice has a substantial number of vacant Fe^{II} sites and these tend to cluster so that Fe^{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, PrO_{2-x} forms a disordered nonstoichiometric phase ($0 < x < 0.25$) at 1000°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 ∞ 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.⁽¹³⁶⁾

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

n	Formula $\text{Pr}_n\text{O}_{2n-2}$	y in PrO_y	Nonstoichiometric limits of x at $T^\circ\text{C}$	$T^\circ\text{C}$
4	Pr_2O_3	1.500	1.500–1.503	1000
7	Pr_7O_{12}	1.714	1.713–1.719	700
9	Pr_9O_{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
∞	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

¹³⁶ 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).

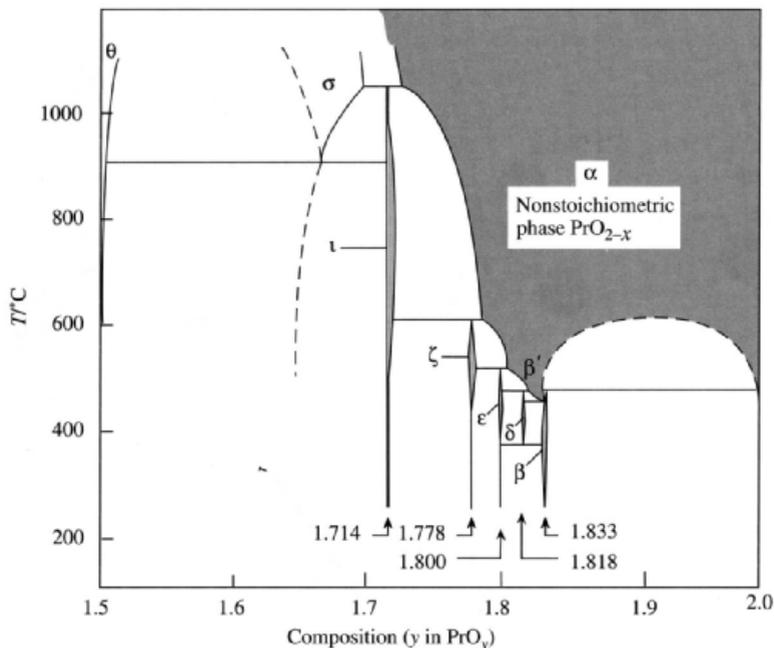


Figure 14.20 Part of the Pr–O phase diagram showing the extended nonstoichiometric α phase PrO_{2-x} at high temperatures (shaded) and the succession of phases $\text{Pr}_n\text{O}_{2n-2}$ at lower temperatures.

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 TiO_2 and the 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 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.^(131–134)