

4.4: Oxygen and oxides (Part 2)

Molecular oxides

Ruthenium tetroxide, RuO_4 , (mp 25 °C and bp 40 °C) and osmium tetroxide, OsO_4 , (mp 40 °C and bp 130 °C) have low melting and boiling points and their structures are molecular. They are prepared by heating the metal powder in an oxygen atmosphere at about 800 °C. The structures are tetrahedral and they are soluble in organic solvents and also slightly soluble in water. OsO_4 is used in organic chemistry especially in the preparation of *cis*-diols by oxidation of C=C double bonds. For example, cyclohexane diol is prepared from cyclohexene. Since these oxides are very volatile and poisonous, they should be handled very carefully.

1-dimensional chain-like oxide

Mercury oxide, HgO , is a red crystalline compound that is formed when mercury nitrate is heated in air. HgO has an infinite zigzag structure. Chromium trioxide, CrO_3 , is a red crystalline compound with a low melting point (197 °C) and its structure is composed of CrO_4 tetrahedra connected in one dimension. The acidity and oxidizing power of chromium trioxide are very high. It is used as an oxidation reagent in organic chemistry.

Two dimensional stratified oxides

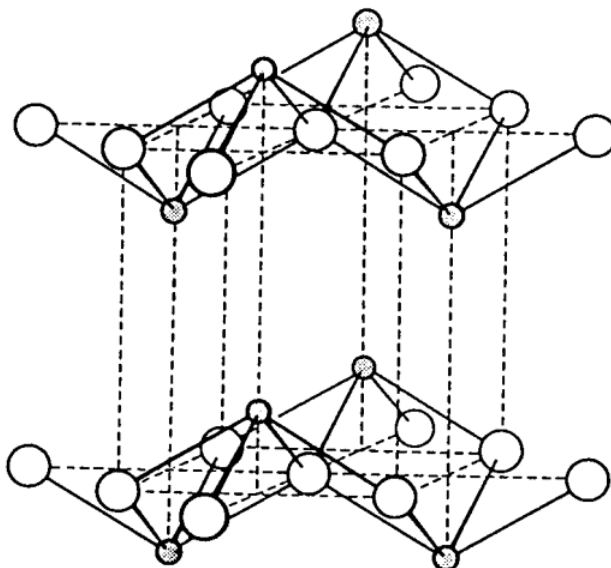


Figure 4.4.11: - Structure of PbO .

Tetragonal and blue black tin oxide, SnO , and red lead oxide, PbO , are layer compounds composed of square pyramids with the metal atom at the peak and four oxygen atoms at the bottom vertices. The structure contains metal atoms above and below the layer of oxygen atoms alternately and in parallel with the oxygen layers (Figure 4.4.11). Molybdenum trioxide, MoO_3 , is formed by burning the metal in oxygen and shows weak oxidizing power in aqueous alkaline solutions. It has a 2-dimensional lamellar structure in which the chains of edge-sharing octahedra MoO_6 are corner-linked.

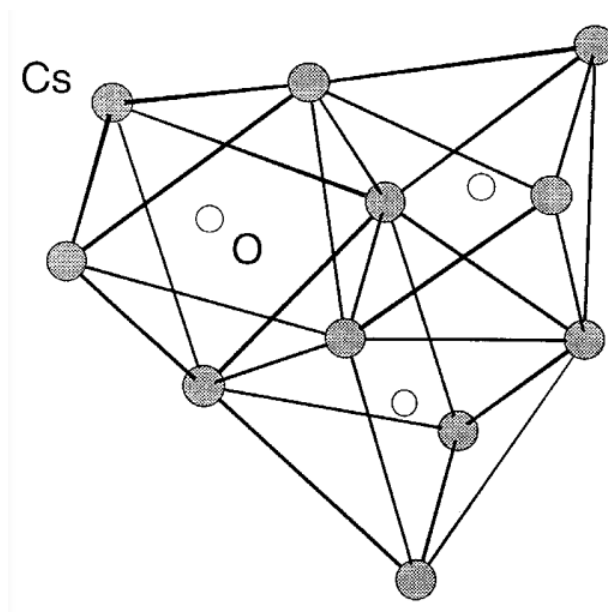


Figure 4.4.12: - Structure of Cs_{11}O_3 .

3-dimensional oxides

Alkali metal oxides, M_2O (M is Li, Na, K, and Rb), have the antifluorite structure (refer to [Section 2.2 \(e\)](#)), and Cs_2O is the anti- CdCl_2 lamellar structure (refer to [Section 4.5 \(d\)](#)). M_2O forms together with peroxide M_2O_2 when an alkali metal burns in air, but M_2O becomes the main product if the amount of oxygen is less than stoichiometric. Alternatively, M_2O is obtained by the pyrolysis of M_2O_2 after complete oxidation of the metal. Peroxide M_2O_2 (M is Li, Na, K, Rb, and Cs) can be regarded also as the salts of dibasic acid H_2O_2 . Na_2O_2 is used industrially as a bleaching agent. Superoxide MO_2 (M is K, Rb, and Cs) contains paramagnetic ion O_2^- , and is stabilized by the large alkali metal cation. If there is a deficit of oxygen during the oxidation reactions of alkali metals, suboxides like Rb_9O_2 or Cs_{11}O_3 form. These suboxides exhibit metallic properties and have interesting cluster structures (Figure 4.4.12). Many other oxides in which the ratio of an alkali metal and oxygen varies, such as M_2O_3 , have also been synthesized.

MO type metal oxides

Except for BeO (Wurtz type), the basic structure of Group 2 metal oxides MO is the rock salt structure. They are obtained by calcination of the metal carbonates. Their melting points are very high and all are refractory. Especially quicklime, CaO, is produced and used in large quantities. The basic structure of transition metal oxides MO (M is Ti, Zr, V, Mn, Fe, Co, Ni, Eu, Th, and U) is also the rock salt structure, but they have defect structures and the ratios of a metal and oxygen are non-stoichiometric. For example, FeO has the composition Fe_xO ($x = 0.89\text{--}0.96$) at 1000°C . The charge imbalance of the charge is compensated by the partial oxidation of Fe^{2+} into Fe^{3+} . NbO has a defective rock salt-type structure where only three NbO units are contained in a unit cell.

MO_2 type metal oxides

The dioxides of Sn, Pb, and other transition metals with small ionic radii take rutile-type structures (Figure 4.4.13), and the dioxides of lanthanide and actinide metals with large ionic radii take fluorite-type structures.

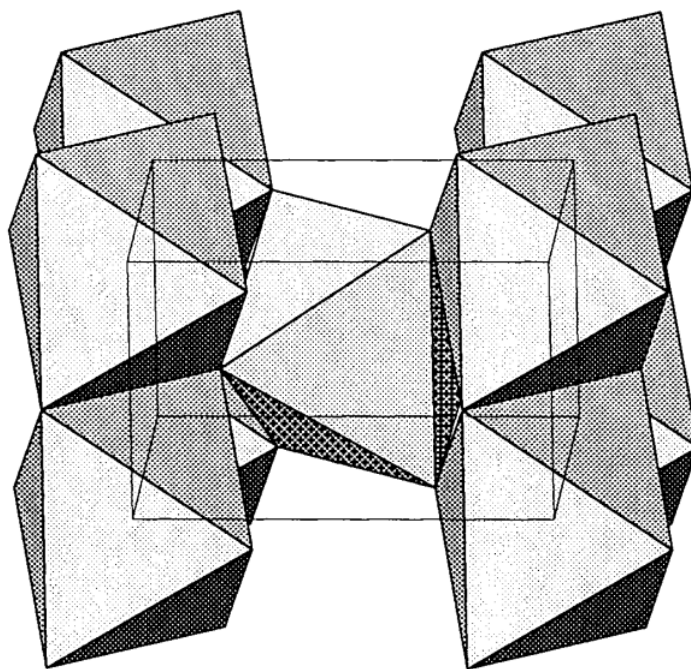
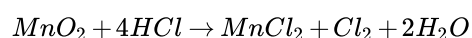


Figure 4.4.13: - Structure of rutile.

Rutile is one of the three structure types of TiO_2 , and is the most important compound used in the manufacture of the white pigments. Rutile has also been extensively studied as a water photolysis catalyst. As shown in Figure 4.4.13 the rutile-type structure has TiO_6 octahedra connected by the edges and sharing corners. It can be regarded as a deformed hcp array of oxygen atoms in which one half of the octahedral cavities are occupied by titanium atoms. In the normal rutile-type structure, the distance between adjacent M atoms in the edge-sharing octahedra is equal, but some rutile-type metal oxides that exhibit semiconductivity have unequal M-M-M distances. CrO_2 , RuO_2 , OsO_2 , and IrO_2 show equal M-M distances and exhibit metallic conductivity.

Manganese dioxide, MnO_2 , tends to have a non-stoichiometric metal-oxygen ratio when prepared by the reaction of manganese nitrate and air, although the reaction of manganese with oxygen gives almost stoichiometric MnO_2 with a rutile structure. The following reaction of manganese dioxide with hydrochloric acid is useful for generating chlorine in a laboratory.



Zirconium dioxide, ZrO_2 , has a very high melting-point (2700 °C), and is resistant to acids and bases. It is also a hard material and used for crucibles or firebricks. However, since pure zirconium dioxide undergoes phase transitions at 1100 °C and 2300 °C that result in it breaking up, solid solutions with CaO or MgO are used as fireproof materials. This is called **stabilized zirconia**.

M_2O_3 -type oxides

The most important structure of the oxides of this composition is the **corundum structure** (Al, Ga, Ti, V, Cr, Fe, and Rh). In the corundum structure, $2/3$ of the octahedral cavities in the hcp array of oxygen atoms are occupied by M^{3+} . Of the two forms of alumina, Al_2O_3 , α alumina and (γ) alumina, α alumina takes the corundum structure and is very hard. It is unreactive to water or acids. Alumina is the principal component of jewelry, such as ruby and sapphire. Moreover, various **fine ceramics** (functional porcelain materials) utilizing the properties of α -alumina have been developed. On the other hand, γ alumina has a defective spinel-type structure, and it adsorbs water and dissolves in acids, and is the basic component of activated alumina. It has many chemical uses including as a catalyst, a catalyst support, and in chromatography.

MO_3 type oxides

Rhenium and tungsten oxides are important compounds with this composition. **Rhenium trioxide**, ReO_3 , is a dark red compound prepared from rhenium and oxygen that has a metallic luster and conductivity. ReO_3 has a three-dimensional and very orderly array of ReO_6 regular, corner-sharing octahedra (Figure 4.4.14).

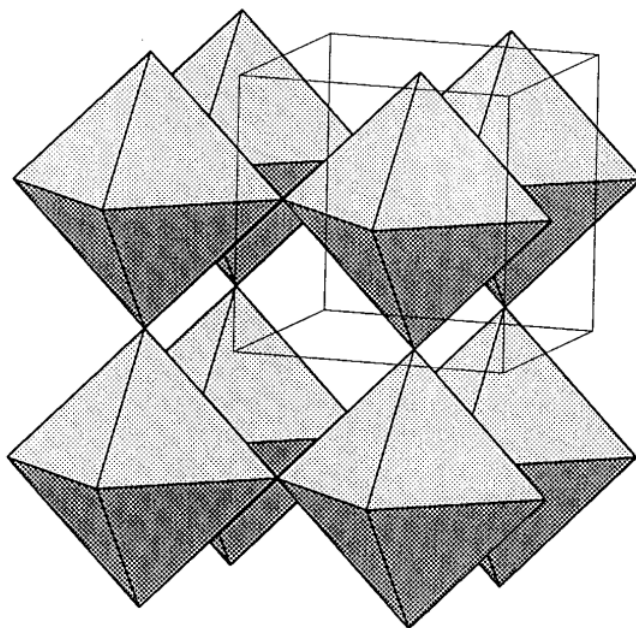


Figure 4.4.14: - Structure of ReO_3 .

Tungsten trioxide, WO_3 , is the only oxide that shows various phase transitions near room temperature and at least seven polymorphs are known. These polymorphs have the ReO_3 -type three-dimensional structure with corner-sharing WO octahedra. When these compounds are heated in a vacuum or with powdered tungsten, reduction takes place and many oxides with complicated compositions ($\text{W}_{18}\text{O}_{49}$, $\text{W}_{20}\text{O}_{58}$, etc.) are formed. Similar molybdenum oxides are known and they had been regarded as non-stoichiometric compounds before A. Magneli found that they were in fact stoichiometric compounds.

Mixed metal oxides

Spinel, MgAl_2O_4 , has a structure in which Mg^{2+} occupy 1/8 of the tetrahedral cavities and Al^{3+} 1/2 of the octahedral cavities of a ccp array of oxygen atoms (Figure 4.4.15).

Among the oxides of composition $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4$ (A^{2+} are Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn, and B^{3+} are Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Ni, and Rh), those in which the tetrahedral holes are occupied by A^{2+} or B^{3+} are called **normal spinels** or **inverse spinels**, respectively. Spinel itself has a normal spinel-type structure, and MgFe_2O_4 and Fe_3O_4 have inverse spinel-type structures. Crystal field stabilization energies (refer to [Section 6.2 \(a\)](#)) differ depending on whether the crystal field of the oxygen atoms is a regular tetrahedron or octahedron. Therefore, when the metal component is a transition metal, the energy difference is one of the factors to determine which of A^{2+} or B^{3+} is favorable to fill the tetrahedral cavities.

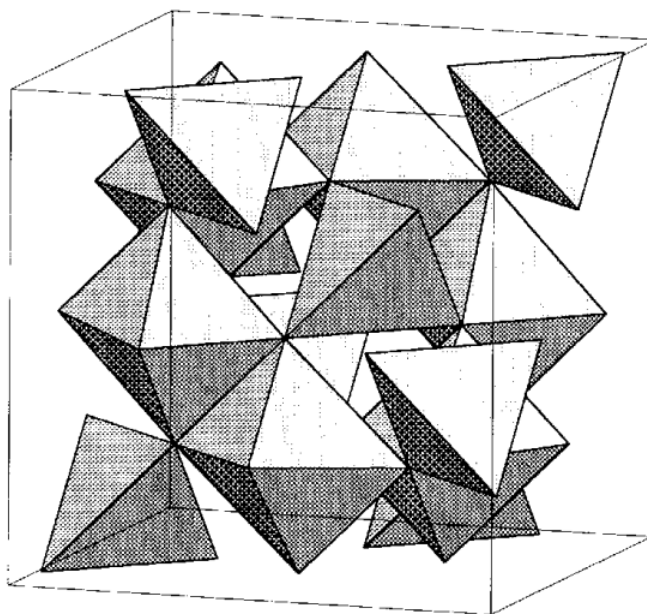


Figure 4.4.15: - Spinel structure.

Perovskite, CaTiO_3 , is an ABO_3 oxide (the net charge of A and B becomes $6+$), and it has a structure with calcium atom at the center of TiO_3 in the ReO_3 structure (Figure 4.4.16). Among this kind of compounds, BaTiO_3 , commonly called barium titanate, is especially important. This ferroelectric functional material is used in nonlinear resistance devices (varistor).

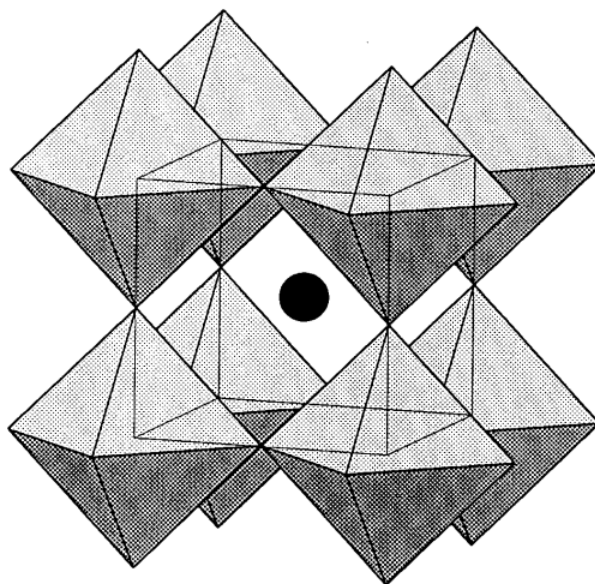


Figure 4.4.16: - Perovskite structure.

(h) Oxides of Group 14 elements

Although GeO_2 has a rutile-type structure, there is also a β quartz-type polymorphism. There are germanium oxides with various kinds of structures analogous to silicates and aluminosilicates. SnO_2 takes a rutile-type structure. SnO_2 is used in transparent electrodes, catalysts, and many other applications. Surface treatment with tin oxide enhances heat reflectivity of glasses. PbO_2 usually has a rutile-type structure. Lead oxide is strongly oxidizing and used for the manufacture of chemicals, and PbO_2 forms in a lead batteries.

(i) Isopolyacids, heteropolyacids, and their salts

There are many polyoxo acids and their salts of Mo(VI) and W(VI). V(V), V(IV), Nb(V), and Ta(V) form similar polyoxo acids although their number is limited. **Polyoxoacids** are polynuclear anions formed by polymerization of the MO_6 coordination

polyhedra that share corners or edges. Those consisting only of metal, oxygen, and hydrogen atoms are called **isopolyacids** and those containing various other elements (P, Si, transition metals, etc.) are called **heteropolyacids**. The salts of polyacids have counter-cations such as sodium or ammonium instead of protons. The history of polyoxoacids is said to have started with J. Berzelius discovering the first polyoxoacid in 1826, with the formation of yellow precipitates when he acidified an aqueous solution containing Mo (VI) and P (V). The structures of polyoxoacids are now readily analyzed with single crystal X-ray structural analysis, ^{17}O NMR, etc. Because of their usefulness as industrial catalysts or for other purposes, polyoxoacids are again being studied in detail.

Keggin-structure

The **heteropolyoxo** anions expressed with the general formula $[\text{X}^{\text{n}+}\text{M}_{12}\text{O}_{40}]^{(8-\text{n})-}$ ($\text{M} = \text{Mo}, \text{W}$, and $\text{X} = \text{B}, \text{Al}, \text{Si}, \text{Ge}, \text{P}, \text{As}, \text{Ti}, \text{Mn}, \text{Fe}, \text{Co}, \text{Cu}$, etc.) have the **Keggin structure**, elucidated by J. F. Keggin in 1934 using X-ray powder diffraction. For example, the structure of the tungstate ion containing silicon, in which 12 WO_6 octahedra enclose the central SiO_4 tetrahedron and four groups of three edge-shared octahedra connect to each other by corner sharing, is shown in Figure 4.4.17. The four oxygen atoms that coordinate to the silicon atom of the SiO_4 tetrahedra also share three WO_6 octahedra. Therefore, the whole structure shows T_d symmetry. Although the Keggin structure is somewhat complicated, it is very symmetrical and beautiful and is the most typical structure of heteropolyoxo anions. Many other types of heteropolyoxo anions are known.

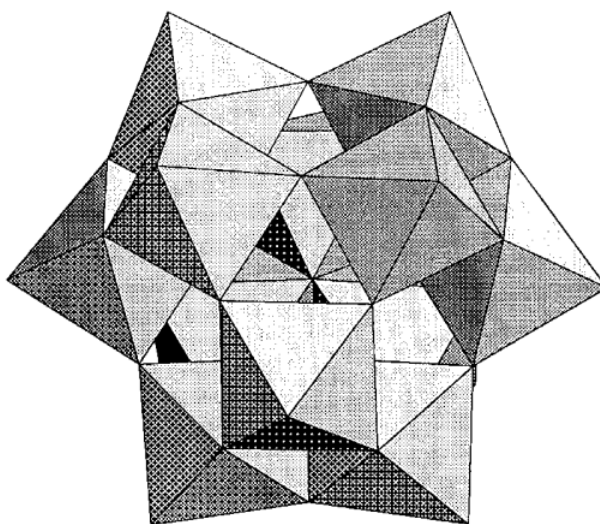
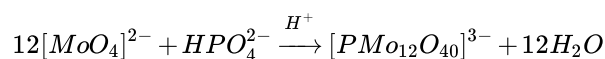


Figure 4.4.17: - Keggin structure.

Polyoxo anions are generated by the condensation of MO_6 units by removal of H_2O when MoO_4^{2-} reacts with a proton H^+ , as is shown in the following equation.



Therefore, the size and form of heteropolyoxo anions in the crystal precipitation are decided by the choice of acid, concentration, temperature, or the counter cation for crystallization. A number of studies on the solution chemistry of dissolved anions have been performed.

Heteropolyoxo anions display notable oxidizing properties. As heteropolyoxo anions contain metal ions of the highest oxidation number, they are reduced even by very weak reducing agents and show mixed valence. When Keggin-type anions are reduced by one electron, they show a very deep-blue color. It has been proved that the Keggin structure is preserved at this stage and polyoxo anions absorb more electrons and several $\text{M}(\text{V})$ sites are generated. Thus, a heteropolyoxo anion can serve as an electron sink for many electrons, and heteropolyoxo anions exhibit photo-redox reactions.

? Exercise 4.4.4

What is the major difference in the structures of a polyacid and a solid acid?

Answer

Although polyacids are molecules with definite molecular weights, the usual solid oxides have an infinite number of metal-oxygen bonds.

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