4 Chemistry of Nonmetallic Elements

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There are about 20 nonmetallic elements which are generally found as either anions in ionic compounds or else as elementary substances. It is possible to learn the names, structures, and main properties of these various compounds following a relatively simple classification. Hydrides, oxides, sulfides, and halides are important, and essential for the study of pure and applied inorganic chemistry of the solid state compounds.

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4.1 Hydrogen and hydrides

(a) Hydrogen

Hydrogen is the simplest element consisting of a proton and an electron, and the most abundant element in the universe. It is next to oxygen and silicon, and about 1 wt% of all the elements on the Earth. Needless to say, most hydrogen exists as water on the Earth. Since its polarity may change freely between hydride (H^-), atom (H), and proton (H^+), hydrogen also forms various compounds with many elements including oxygen and carbon. Therefore, hydrogen is highly important in chemistry.

Of the three kinds of isotopes of hydrogen, deuterium, D, was discovered by H. C. Urey and others in 1932, and subsequently tritium, T, was prepared from deuterium in 1934. About 0.015% of hydrogen is present as deuterium, and this can be enriched by electrolysis of water. Tritium is a radioactive isotope emitting β-particles with a half-life of 12.33 years. Since the mass of deuterium and tritium is about twice and three times that of hydrogen, respectively, the physical properties of the isotopes, and compounds containing them, differ considerably. Some properties of the isotopes and water are listed in Table 4.1. When the E-H bond in a hydrogen compound is converted into the E-D by deuterium substitution, the E-H stretching frequency in an infrared spectrum is reduced to about $1/\sqrt{2}$, which is useful for determining the position of the hydrogen atom. It is sometimes possible to conclude that scission of the bond with a hydrogen is the rate-determining step when the deuterium substitution shows a marked effect on the rate of reaction of a hydrogen-containing compound.

Since the nuclear spin of hydrogen is 1/2 and given its abundance, it is the most important nuclide for NMR spectroscopy. NMR is widely used not only for identification of organic compounds, but also for medical diagnostic purposes using MRI (magnetic resonance imaging) of water in living bodies. Human organs can now be observed with this non-invasive method.

Table 4.1 Properties of isotopic hydrogen and water

Properties	H_2	D_2	T_2	H_2O	D_2O	T_2O
Melting point*	13.957	18.73	20.62	0.00	3.81	4.48
Boiling point	20.39	23.67	25.04	100.00	101.42	101.51
Density (g cm^{-3}, 25°C)				0.9970	1.1044	1.2138
Temp. of maximum density (°C)				3.98	11.23	13.4

* hydrogen (K), water (°C)

There are nuclear-spin isomers in diatomic molecules of the nuclides whose spin is not zero. Especially in the case of a hydrogen molecule, the difference of properties is significant. Spins of ***para*-hydrogen** are anti-parallel and the sum is 0 leading to a **singlet state**. Spins of ***ortho*-hydrogen** are parallel and the sum is 1 resulting in a **triplet state**. Since *para*-hydrogen is in a lower energy state, it is the stabler form at low temperatures. The theoretical ratio of *para*-hydrogen is 100% at 0 K, but it decreases to about 25% at room temperature, since the ratio of *ortho*-hydrogen increases at higher temperatures. Gas chromatography and rotational lines in the electronic band spectrum of H_2 can distinguish two hydrogen isomers.

(b) Hydride

Binary hydrides can be classified according to the position of the element in the periodic table, and by the bond characters. The hydrides of alkali and alkaline earth metals among *s*-block elements are ionic compounds structurally analogous to halides and are called **saline hydrides**. The Group 13-17 *p*-block elements form covalent molecular hydrides. No hydride of rare gas elements has been reported.

Some of the *d*-block and *f*-block transition metals form metal hydrides exhibiting metallic properties. Transition metals which do not give binary hydrides form many **molecular hydride complexes** coordinated by stabilization ligands, such as carbonyl (CO), tertiaryphosphines (PR_3), or cyclopentadienyl (C_5H_5) (refer to Section 6.1). Typical hydrides of each class are given below.

Saline hydrides

Lithium hydride, LiH, is a colorless crystalline compound (mp (melting point) 680 °C). Li^+ and H^- form a lattice with a rock salt type structure. Quantitative evolution of hydrogen gas at the anode during the electrolysis of the fused salt suggests the existence of H^-. Water reacts vigorously with lithium hydride evolving hydrogen gas. Since it dissolves in ethers slightly, the hydride is used as a reducing agent in organic chemistry.

Calcium hydride, CaH_2, is a colorless crystalline compound (mp 816 ^oC), and reacts mildly with water evolving hydrogen gas. This hydride is used as a hydrogen gas generator, or a dehydrating agent for organic solvents. It is used also as a reducing agent.

Lithium tetrahydridoaluminate, $LiAlH_4$, is a colorless crystalline compound (decomposes above 125^oC) usually called lithium aluminum hydride. The hydride dissolves in ethers, and reacts violently with water. It is used as a reducing and hydrogenating agent and for dehydrating organic solvents.

Sodium tetrahydroborate, $NaBH_4$, is a white crystalline compound (decomposes at 400 ^oC) usually called sodium borohydride. It is soluble in water and decomposes at high temperatures evolving hydrogen gas. It is used as a reducing agent for inorganic and organic compounds, for preparation of hydride complexes, *etc*.

Molecular hydrides

All hydrides other than those of carbon (methane) and oxygen (water) are poisonous gases with very high reactivity and should be handled very carefully. Although there are methods of generating the gases in laboratories, recently many are also available in cylinders.

Diborane, B_2H_6, is a colorless and poisonous gas (mp -164.9 ^oC and bp -92.6 ^oC) with a characteristic irritating odor. This hydride is a powerful reducing agent of inorganic and organic compounds. It is also useful in organic synthesis as a hydroboration agent that introduces functional groups to olefins, after addition of an olefin followed by reactions with suitable reagents.

Silane, SiH_4, is a colorless and deadly poisonous gas (mp -185 ^oC and bp -111.9 ^oC) with a pungent smell, and is called also monosilane.

Ammonia, NH_3, is a colorless and poisonous gas (mp -77.7 ^oC and bp -33.4 ^oC) with a characteristic irritating odor. Although it is used in many cases as aqueous ammonia since it dissolves well in water, liquid ammonia is also used as a nonaqueous solvent for special reactions. Since the Harber-Bosch process of ammonia synthesis was developed in 1913, it has been one of the most important compounds in chemical industries and is used as a starting chemical for many nitrogenous compounds. It is used also as a refrigerant.

Phosphine, PH_3, is a colorless and deadly poisonous gas (mp -133 ^oC and bp -87.7 ^oC) with a bad smell, and is called also phosphorus hydride. It burns spontaneously in air. It is used in vapor phase epitaxial growth, in transition metal coordination chemistry, *etc*.

Hydrogen sulfide, H_2S**,** is a colorless and deadly poisonous gas (mp -85.5 ^{o}C and bp -60.7 ^{o}C) with a rotten egg odor. Although often used with insufficient care, it is very dangerous and should be handled only in an environment with good ventilation. It is used in chemical analysis for the precipitation of metal ions, preparation of sulfur compounds, *etc*.

Hydrogen fluoride, HF, is a colorless, fuming, and low boiling point liquid (mp -83 ^{o}C and bp 19.5 ^{o}C), with an irritating odor. It is used for preparing inorganic and organic fluorine compounds. Because of its high permittivity, it can be used as a special nonaqueous solvent. The aqueous solution is called fluoric acid and is stored in polyethylene containers since the acid corrodes glass.

Metallic hydrides

The hydrides MH_x which show metallic properties are nonstoichiometric interstitial-type solids in which hydrogen occupies a part of the cavities of the metal lattice. Usually x is not an integer in these compounds. There are Group 3 (Sc, Y), Group 4 (Ti, Zr, Hf), Group 5 (V, Nb, Ta), Cr, Ni, Pd, and Cu metallic hydrides among the *d* block elements, but the hydrides of other metals in Group 6 to 11 are not known. Palladium Pd reacts with hydrogen gas at ambient temperatures, and forms hydrides that have the composition PdH_x ($x < 1$). Many metallic hydrides show metallic conductivity. $LaNi_5$ is an intermetallic compound of lanthanum and nickel. It occludes nearly 6 hydrogen atoms per unit lattice and is converted to $LaNi_5H_6$. It is one of the candidates for use as a hydrogen storage material with the development of hydrogen-fueled cars.

Exercise 4.1 Write the oxidation number of the hydrogen atom in H_2, NaH, NH_3, and HCl.

[Answer] H_2 (0), NaH (-1), NH_3 (+1), and HCl (+1).

Hydride complexes

Complexes coordinated by hydride ligands are called **hydride complexes**.
The Group 6 to 10 transition metals that do not form binary hydrides give many hydride complexes with auxiliary ligands such as carbonyl and tertiaryphosphines. Although it was only at the end of the 1950s that hydride was accepted as a ligand, thousands of hydride complexes are known at present. Furthermore, with the synthesis in the 1980's of molecular hydrogen complexes, the chemistry of transition metal hydrogen compounds took a new turn. Research on the homogeneous catalysis of hydrocarbons in which hydride or dihydrogen complexes participate is also progressing.

4.2 Main group elements of 2nd and 3rd periods and their compounds

(a) Boron

Refined elemental boron is a black solid with a metallic luster. The unit cell of crystalline boron contains 12, 50, or 105 boron atoms, and the B_{12} icosahedral structural units join together by 2 center 2 electron (2c-2e) bonds and 3 center 2 electron (3c-2e) bonds (electron deficient bonds) between boron atoms (Fig. 4.1). Boron is very hard and shows semiconductivity.

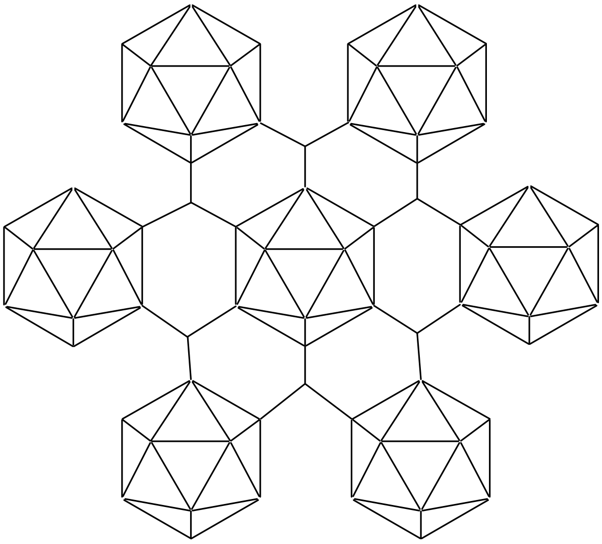


Fig. 4.1 The structure of the elemental boron with B_{12} icosahedra.

The chemistry of **boranes** (boron hydrides) started from the research of A. Stock reported during the period 1912-1936. Although boron is adjacent to carbon in the periodic table, its hydrides have completely different properties from those of hydrocarbons. The structures of boron hydrides in particular were unexpected and could be explained only by a new concept in chemical bonding. For his contribution to the very extensive new inorganic chemistry of boron hydrides, W. N. Lipscomb won the Nobel prize in 1976. Another Nobel prize (1979) was awarded to H. C. Brown for the discovery and development of a very useful reaction in organic synthesis called hydroboration.

Because of the many difficulties associated with the low boiling points of boranes, as well as their activity, toxicity, and air-sensitivity, Stock had to develop new experimental methods for handling the compounds *in vacuo*. Using these techniques, he prepared six boranes B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$ by the reactions of magnesium boride, MgB_2, with inorganic acids, and determined their compositions. However, additional research was necessary to determine their structures. At present, the original synthetic method of Stock using MgB_2 as a starting compound is used only for the preparation of B_6H_{10}. Since reagents such as lithium tetrahydroborate, $LiBH_4$, and sodium tetrahydroborate, $NaBH_4$, are now readily available, and **diborane**, B_2H_6, is prepared according to the following equation, higher boranes are synthesized by the pyrolysis of diborane.

$$3\ LiBH_4 + 4\ BF_3.OEt_2 \rightarrow 2\ B_2H_6 + 3\ LiBF_4 + 4\ Et_2O$$

A new theory of chemical bonding was introduced to account for the bonding structure of diborane, B_2H_6. Although an almost correct hydrogen-bridged structure for diborane was proposed in 1912, many chemists preferred an ethane-like structure, $H_3B\text{-}BH_3$, by analogy with hydrocarbons. However, H. C. Longuet-Higgins proposed the concept of the electron-deficient **3-center 2-electron bond** (3c-2e bond) and it was proven by electron diffraction in 1951 that the structure was correct (Fig. 4.2).

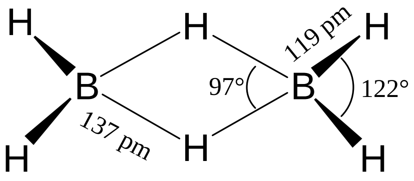
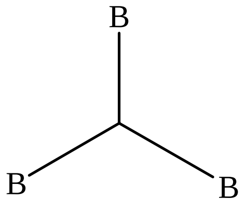


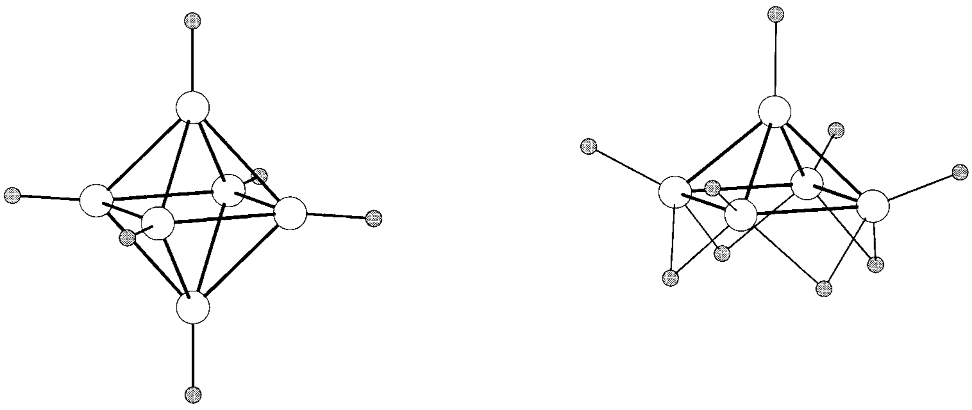
Fig. 4.2 Structure of diborane.

It has been elucidated by electron diffraction, single crystal X-ray structure analysis, infrared spectroscopy, *etc*. that boranes contain 3-center 2-electron bonds (3c-2e bond) B-H-B and



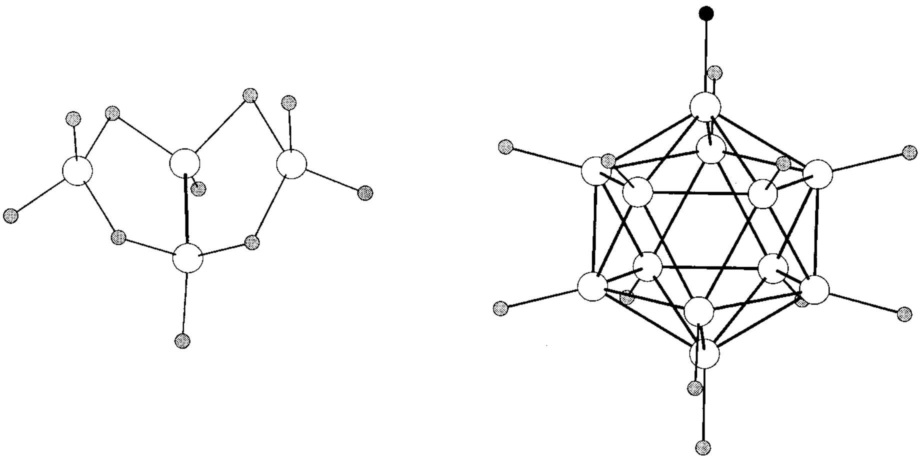
besides the usual 2 center 2 electron covalent bonds (2c-2e bond) B-H and B-B. Such structures can be treated satisfactorily by molecular orbital theory. Boranes are classified into *closo, nido, arachno, etc*. according to the skeletal structures of boron atoms.

Closo-borane $[B_nH_n]^{2-}$ has the structure of a closed polyhedron of n boron atoms bonded to n hydrogen atoms, as seen in the examples of a regular octahedron $[B_6H_6]^{2-}$ and an icosahedron $[B_{12}H_{12}]^{2-}$. The boranes of this series do not contain B-H-B bonds. Boranes B_nH_{n+4}, such as B_5H_9, form structures with B-B, B-B-B, and B-H-B bonds and lack the apex of the polyhedron of *closo* boranes, and are referred to as ***nido*** type boranes. Borane B_nH_{n+6}, such as B_4H_{10}, have a structures that lacks two apexes from the *closo* type and are more open. Skeletons are also built by B-B, B-B-B, and B-H-B bonds, and these are called ***arachno*** type boranes. The structures of typical boranes are shown in Fig. 4.3.



(a) *closo*-$[B_6H_6]^{2-}$

(b) *nido*-$[B_5H_9]$



(c) *arachino*-$[B_4H_{10}]$

(d) *closo*-$[B_{12}H_{12}]^{2-}$

Fig. 4.3 Structures of boranes.

Not only diborane but also higher boranes are **electron-deficient compounds** that are difficult to explain using Lewis' electronic structure based on simple 2-center 2-electron covalent bonds.

Exercise 4.2 Why is diborane called an electron deficient compound?

[Answer] It is because there are only 12 valence electrons of boron and hydrogen atoms, although 16 electrons are necessary to assign two electrons each to eight B-H bonds.

K. Wade summarized the relation of the number of valence electrons used for skeletal bonds and the structures of boranes and proposed an empirical rule called the **Wade rule**. According to this rule, when the number of boron atoms is n, the skeletal valence electrons are $2(n+1)$ for a *closo* type, $2(n+2)$ for a *nido* type, and $2(n+3)$ for an *arachno* type borane. The relationship between the skeletal structure of a cluster compound and the number of valence electrons is also an important problem in the cluster compounds of transition metals, and the Wade rule has played a significant role in furthering our understanding of the structures of these compounds.

(b) Carbon

Graphite, diamond, fullerene, and amorphous carbon are carbon allotropes.
Usually a carbon atom forms four bonds using four valence electrons.

Graphite Graphite is structured as layers of honeycomb-shaped 6 membered rings of carbon atoms that look like condensed benzene rings without any hydrogen atoms (Fig. 4.4). The carbon-carbon distance between in-layer carbon atoms is 142 pm and the bonds have double bond character analogous to aromatic compounds. Since the distance between layers is 335 pm and the layers are held together by comparatively weak van der Waals forces, they slide when subjected to an applied force. This is the origin of the lubricating properties of graphite. Various molecules, such as alkali metals, halogens, metal halides, and organic compounds intercalate between the layers and form intercalation compounds. Graphite has semi-metallic electrical conductivity (about 10^{-3} Ωcm parallel to layers and about 100 times more resistant in the perpendicular direction).

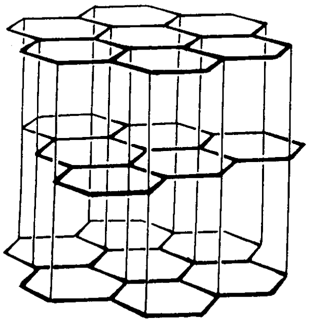


Fig. 4.4 Structure of graphite.

Diamond Its structure is called the diamond-type structure (Fig. 4.5). A unit cell of diamond contains eight carbon atoms and each carbon atom is 4-coordinate in a regular tetrahedron. Diamond is the hardest substance known, with a Mohs hardness 10. Diamond has very high heat conductivity although it is an electrical insulator. Although previously a precious mineral only formed naturally, industrial diamonds are now commercially prepared in large quantities at high temperatures (1200 °C or higher) and under high pressures (5 GPa or more) from graphite using metal catalysts. In recent years, diamond thin films have been made at low temperatures (about 900 °C) and under low pressures (about 102 Pa) by the pyrolysis of hydrocarbons, and are used for coating purposes, *etc*.

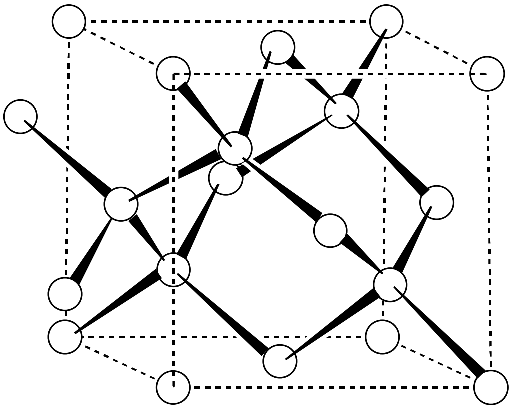


Fig. 4.5 Structure of diamond.

Fullerene Fullerene is the general name of the 3rd carbon allotrope, of which the soccer ball-shaped molecule C_{60} is a typical example (Fig.4.6). R. E. Smalley, H. W. Kroto and others detected C_{60} in the mass spectra of the laser heating product of graphite in 1985, and fullerene's isolation from this so-called "soot" was reported in 1991. It has the structure of a truncated (corner-cut)-icosahedron and there is double bond character between carbon atoms. It is soluble in organic solvents, with benzene solutions being purple. Usually, it is isolated and purified by chromatography of fullerene mixtures. Wide-ranging research on chemical reactivities and physical properties such as superconductivity, is progressing rapidly. Besides C_{60}, C_{70} and carbon nanotubes are attracting interest.

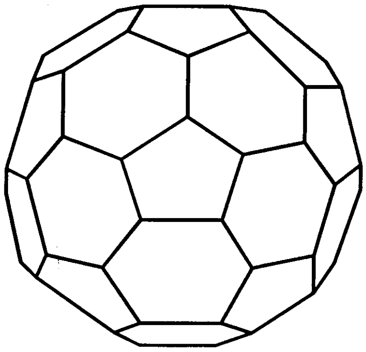


Fig. 4.6 Structure of C_{60}.

(c) Silicon

Silicon is the most abundant element in the earth's crust after oxygen. Most of this silicon exists as a component of silicate rocks and the element is not found as a simple substance. Therefore, silicon is produced by the reduction of quartz and sand with high-grade carbon using electric arc furnaces. Higher-grade silicon is obtained by hydrogen reduction of $SiHCl_3$, which is produced by the hydrochlorination of low purity silicon followed by rectification. The silicon used for semiconductor devices is further refined by the crystal Czochralski or zone melting methods. The crystal (mp 1410 ^{o}C) has a metallic luster and the diamond type structure.

There are three isotopes of silicon, ^{28}Si (92.23%), ^{29}Si (4.67%), and ^{30}Si (3.10%). Because of its nuclear spin of $I = 1/2$, ^{29}Si is used for NMR studies of organic silicon compounds or silicates (solid-state NMR).

Silicates and organosilicon compounds show a wide range of structures in silicon chemistry. Section 4.3 (c) describes the properties of silicates. Organosilicon chemistry is the most active research area in the inorganic chemistry of main group elements other than carbon. Silicon chemistry has progressed remarkably since the development of an industrial process to produce organosilicon compounds by the direct reaction of silicon with methyl chloride CH_3Cl in the presence of a copper catalyst. This historical process was discovered by E. G. Rochow in 1945. Silicone resin, silicone rubber, and silicone oil find wide application. In recent years, silicon compounds have also been widely used in selective organic syntheses.

Although silicon is a congener of carbon, their chemical properties differ considerably. A well-known example is the contrast of silicon dioxide SiO_2 with its 3-dimensional structure, and gaseous carbon dioxide, CO_2. The first compound $(Mes)_2Si{=}Si(Mes)_2$ (Mes is mesityl $C_6H_2(CH_3)_3$) with a silicon-silicon double bond was reported in 1981, in contrast with the ubiquitous carbon-carbon multiple bonds. Such compounds are used to stabilize unstable bonds with bulky substituents (kinetic stabilization).

Exercise 4.3 Why are the properties of CO_2 and SiO_2 different?

[Answer] Their properties are very different because CO_2 is a chain-like three-atom molecule and SiO_2 is a solid compound with the three dimensional bridges between silicon and oxygen atoms.

(d) Nitrogen

Nitrogen is a colorless and odorless gas that occupies 78.1% of the atmosphere (volume ratio). It is produced in large quantities together with oxygen (bp -183.0 ^oC) by liquefying air (bp -194.1 ^oC) and fractionating nitrogen (bp -195.8 ^oC). Nitrogen is an inert gas at room temperatures but converted into nitrogen compounds by biological nitrogen fixation and industrial ammonia synthesis. The cause of its inertness is the large bond energy of the $N{\equiv}N$ triple bond.

The two isotopes of nitrogen are ^{14}N (99.634%) and ^{15}N (0.366%). Both isotopes are NMR-active nuclides.

(e) Phosphorus

Simple phosphorus is manufactured by the reduction of calcium phosphate, $Ca_3(PO_4)_2$, with quartz rock and coke. Allotropes include white phosphorus, red phosphorus, and black phosphorus.

White phosphorus is a molecule of composition of P_4 (Fig. 4.7). It has a low melting-point (mp 44.1 ^oC) and is soluble in benzene or carbon disulfide. Because it is pyrophoric and deadly poisonous, it must be handling carefully.

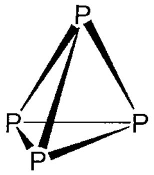


Fig. 4.7 Structure of white phosphorus.

Red phosphorus is amorphous, and its structure is unclear. The principal component is assumed to be a chain formed by the polymerization of P_4 molecules as the result of the opening of one of the P-P bonds. It is neither pyrophoric nor poisonous, and used in large quantities for the manufacturing of matches, *etc*.

Black phosphorus is the most stable allotrope and is obtained from white phosphorus under high pressure (about 8 GPa). It is a solid with a metallic luster and a lamellar structure. Although it is a semiconductor under normal pressures, it shows metallic conductivity under high pressures (10 GPa) .

Phosphorus compounds as ligands

Tertiary phosphines, PR_3, and phosphites, $P(OR)_3$, are very important ligands in transition metal complex chemistry. Especially triphenylphosphine, $P(C_6H_5)_3$, triethyl phosphine, $P(C_2H_5)_3$, and their derivatives are useful ligands in many complexes, because it is possible to control precisely their electronic and steric properties by modifying substituents (refer to Section 6.3 (c)). Although they are basically sigma donors, they can exhibit some pi accepting character by changing the substituents into electron accepting Ph (phenyl), OR, Cl, F, *etc*. The order of the electron-accepting character estimated from the C-O stretching vibrations and ^{13}C NMR chemical shifts of the phosphine- or phosphite-substituted metal carbonyl compounds is as follows (Ar is an aryl and R is an alkyl).

$$PF_3 > PCl_3 > P(OAr)_3 > P(OR)_3 > PAr_3 > PRAr_2 > PR_2Ar > PR_3$$

On the other hand, C. A. Tolman has proposed that the angle at the vertex of a cone that surrounds the substituents of a phosphorus ligand at the van der Waals contact distance can be a useful parameter to assess the steric bulkiness of phosphines and phosphites. This parameter, called the **cone angle,** is widely used (Fig. 4.8). When the cone angle is large, the coordination number decreases by steric hindrance, and the dissociation equilibrium constant and dissociation rate of a phosphorus ligand become large (Table 4.2). The numerical expression of the steric effect is very useful, and many studies have been conducted into this effect.

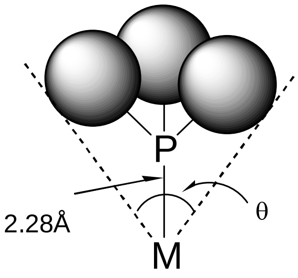


Fig. 4.8 Cone angle.

Table 4.2 Cone angles (θ °) of tertiary phosphines and phosphites

Ligands	Cone angles
$P(OEt)_3$	109
PMe_3	118
$P(OPh)_3$	121
PEt_3	132
PMe_2Ph	136
PPh_3	145
P^iPr_3	160
P^tBu_3	182

4.3 Oxygen and oxides

(a) Oxygen

Dioxygen, O_2, is a colorless and odorless gas (bp -183.0 ^oC) that occupies 21% of air (volume ratio). Since oxygen atoms are also the major components of water and rocks, oxygen is the most abundant element on the Earth’s surface. Despite its abundance, it was established as an element as late as the 18th century. Since an immense quantity of oxygen gas is consumed for steel production now, it is separated in large quantities from liquified air.

The isotopes of oxygen are ^{16}O (99.762% abundance), ^{17}O (0.038%), and ^{18}O (0.200%). ^{17}O has nuclear spin I = 5/2 and is an important nuclide for NMR measurements. ^{18}O is used as a tracer for tracking reagents or for the study of reaction mechanisms. It is also useful for the assignment of absorption lines in infrared or Raman spectra by means of isotope effects.

As already described in section 2.3 (e), dioxygen, O_2, in the ground state has two unpaired spins in its molecular orbitals, shows paramagnetism and is called **triplet dioxygen**. In the excited state, the spins are paired and dioxygen becomes diamagnetic, which is called singlet dioxygen. Singlet dioxygen is important in synthetic chemistry, because it has characteristic oxidation reactivity. **Singlet dioxygen** is generated in a solution by an energy transfer reaction from a photo-activated complex or by the pyrolysis of ozonides (O_3 compounds).

Superoxide ion, O_2^-, and **peroxide ion**, O_2^{2-}, are the anions of dioxygen (Table 4.3). They can be isolated as alkali metal salts. There is another state, O_2^+, called the **dioxygen (1+) cation**, and it can be isolated as a salt with suitable anions.

Table 4.3 Oxidation states of dioxygen

	Bond order	Compound	O-O distance (Å)	ν(O-O) (cm^{-1})
O_2^+	2.5	$O_2[AsF_6]$	1.123	1858
O_2	2.0		1.207	1554
O_2^-	1.5	$K[O_2]$	1.28	1145
O_2^{2-}	1.0	$Na_2[O_2]$	1.49	842

Ozone, O_3, is an allotrope of oxygen that is an unstable gas with an irritating odor. Ozone is a bent three-atom molecule (117^o) and has unique reactivities. In recent years it has been discovered that ozone plays an important role in intercepting the detrimental ultraviolet radiation from the sun in the upper atmospheric zone, and in protecting life on the Earth from photochemical damage. It is now clear that chlorofluorocarbons, frequently used as refrigerants or as cleaners of electronic components, destroy the ozone layer, and measures are being taken on a global scale to cope with this serious environmental problem.

(b) Oxides of hydrogen

Oxygen is highly reactive, and direct reactions with many elements form oxides. Water is an oxide of hydrogen and is crucially important for the global environment and life in general.

Water H_2O

Ninety-seven percent of water on the Earth is present as sea water, 2% as ice of the polar zone, and fresh water represents only the small remaining fraction. Fundamental chemical and physical properties of water are very significant to chemistry. The main physical properties are shown in Table 4.1. Most of the unusual properties of water are caused by its strong hydrogen bonds. Physical properties of water differ considerably with the presence of isotopes of hydrogen. At least nine polymorphs of ice are known and their crystal structures depend on the freezing conditions of the ice.

Water has a bond angle of 104.5 ° and a bond distance of 95.7 pm as a free molecule. It is described in Section 3.4 (b) that self-dissociation of water generates oxonium ion, H_3O^+. Further water molecules add to H_3O^+ to form $[H(OH_2)_n]^+$ ($H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$, and $H_{13}O_6^+$), and the structures of the various species have been determined.

Hydrogen peroxide H_2O_2

Hydrogen peroxide is an almost colorless liquid (mp -0.89 °C and bp (extrapolated) 151.4 °C) that is highly explosive and dangerous in high concentrations. Usually it is used as a dilute solution but occasionally 90% aqueous solutions are used. Since it is consumed in large quantities as a bleaching agent for fiber and paper, large-scale industrial synthetic process has been established. This process applies very subtle catalytic reactions to produce a dilute solution of hydrogen peroxide from air and hydrogen using a substituted anthraquinone. This dilute solution is then concentrated.

When deuterium peroxide is prepared in a laboratory, the following reaction is applied.

$$K_2S_2O_8 + 2\,D_2O \longrightarrow D_2O + 2\,KDSO_4$$

Hydrogen peroxide is decomposed into oxygen and water in the presence of catalysts such as manganese dioxide, MnO_2. Hydrogen peroxide may be either an oxidant or a reductant depending on its co-reactants. Its reduction potential in an acidic solution expressed in a Latimer diagram (refer to Section 3.3 (c)) is

$$O_2 \xrightarrow{+0.70} H_2O_2 \xrightarrow{+1.76} H_2O$$

(c) Silicon oxides

Silicon oxides are formed by taking SiO_4 tetrahedra as structural units and sharing the corner oxygen atoms. They are classified by the number of corner-sharing oxygen atoms in the SiO_4 tetrahedra, as this determines their composition and structure. When the SiO_4 tetrahedra connect by corner sharing, the structures of the polymeric compounds become a chain, a ring, a layer, or 3-dimensional depending on the connection modes of adjacent units. Fractional expression is adopted in order to show the bridging modes. Namely, the numerator in the fraction is the number of bridging oxygens and the denominator is 2, meaning that one oxygen atom is shared by two tetrahedra. The empirical formulae are as follows and each structure is illustrated in Fig. 4.9 in coordination-polyhedron form.

A bridge is constructed with one oxygen atom. $(SiO_3O_{1/2})^{3-} = Si_2O_7^{6-}$
Bridges are constructed with two oxygen atoms. $(SiO_2O_{2/2})_n^{2n-} = (SiO_3)_n^{2n-}$
Bridges are constructed with three oxygen atoms. $(SiOO_{3/2})_n^{n-} = (Si_2O_5)_n^{2n-}$
Amalgamation of bridging modes with three oxygen and two oxygen atoms.
$[(Si_2O_5)(SiO_2O_{2/2})_2]_n^{6-} = (Si_4O_{11})_n^{6-}$
Bridges are constructed with four oxygen atoms. $(SiO_{4/2})_n = (SiO_2)_n$

Silicates with various cross linkage structures are contained in natural rocks, sand, clay, soil, *etc*.

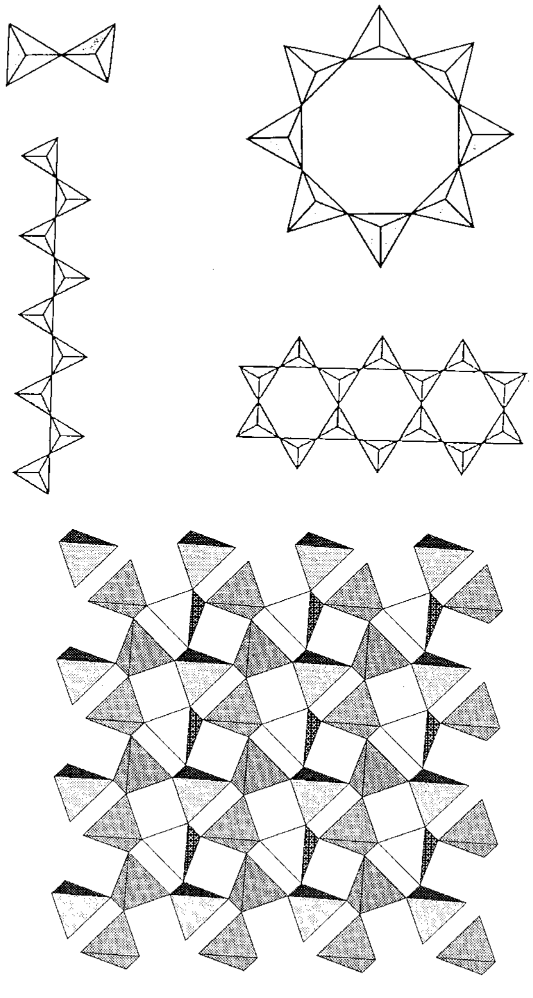


Fig. 4.9 Bridging modes of the SiO_4 tetrahedra.

Aluminosilicates

There are many minerals in which some silicon atoms of silicate minerals are replaced by aluminum atoms. They are called **aluminosilicates**. Aluminum atoms replace the silicon atoms in the tetrahedral sites or occupy the octahedral cavities of oxygen atoms, making the structures more complicated. The substitution of a tetravalent silicon by a trivalent aluminum causes a shortage of charge which is compensated by occlusion of extra cations such as H^+, Na^+, Ca^{2+}, *etc*. Feldspars are a typical aluminosilicate mineral , and $KAlSi_3O_8$ (orthoclase) and $NaAlSi_3O_8$ (albite) are also known well. Feldspars take 3-dimensional structures in which all the corners of the SiO_4 and AlO_4 tetrahedra are shared.

On the other hand, 2-dimensional layers are formed if $[AlSiO_5]^{3-}$ units are lined, and stratified minerals like mica are constructed if 6-coordinate ions are inserted between layers. If the number of oxygen atoms in the layers is not enough to form regular octahedra between layers, hydroxide groups bond to the interstitial Al^{3+} ions. Muscovite, $KAl_2(OH)_2Si_3AlO_{10}$, is a type of mica with such a structure and can be easily peeled into layers.

Zeolite

One of the important aluminosilicates is zeolite. Zeolites are present as natural minerals and also many kinds of zeolites are prepared synthetically in large quantities. The SiO_4 and AlO_4 tetrahedra are bonded by oxygen bridges, and form holes and tunnels of various sizes. The structures are composites of the basic structural units of tetrahedral MO_4. As shown in Fig. 4.10, the basic units are cubes with 8 condensed MO_4, hexagonal prisms with 12 condensed MO_4, and truncated octahedra with 24 condensed MO_4.

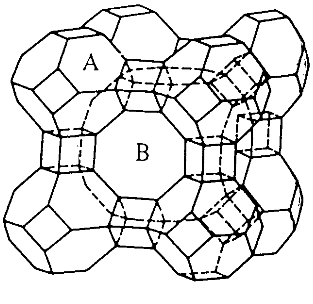


Fig. 4.10 Structure of zeolite A.

Silicon or aluminum atoms are located on the corners of the polyhedra and the bridging oxygen atoms on the middle of each edge (it should be noted that this expression is different from the polyhedron model of oxides).

When these polyhdra are bonded, various kinds of zeolite structures are formed. For example, the truncated octahedra called β cages are the basic frames of **synthetic zeolite A**, $Na_{12}(Al_{12}Si_{12}O_{48})].27H_2O$, and the quadrangle portions are connected through cubes. It can be seen that an octagonal tunnel B forms when eight truncated octahedra bind in this way. The structure in which the hexagon portions connect through hexagonal prisms is faujasite, $NaCa_{0.5}(Al_2Si_5O_{14})] .10H_2O$.

Alkali metal or alkaline earth metal cations exist in the holes, and the number of these cations increases with the content of aluminum to compensate for the charge deficiency. The structures of zeolites have many crevices in which cations and water are contained. Utilizing this cation-exchange property, zeolites are used in large quantities as softeners of hard water. As zeolites dehydrated by heating absorb water efficiently, they are also used as desiccants of solvents or gases. Zeolites are sometimes called **molecular sieves**, since the sizes of holes and tunnels change with the kinds of zeolites and it is possible to segregate organic molecules according to their sizes. Zeolites can fix the directions of more than two molecules in their cavities and can be used as catalysts for selective reactions.

For example, synthetic zeolite ZSM-5 is useful as a catalyst to convert methanol to gasoline. This zeolite is prepared hydrothermally in an autoclave (high-pressure reaction vessel) at *ca*. 100 ^oC using meta-sodium aluminate, $NaAlO_2$, as the source of aluminum oxide and silica sol as the source of silicon oxide and with tetrapropylammonium bromide, Pr_4NBr, present in the reaction. The role of this ammonium salt is a kind of mold to form zeolite holes of a fixed size. When the ammonium salt is removed by calcination at 500 ^oC, the zeolite structure remains.

(d) Nitrogen oxides

A variety of nitrogen oxides will be described sequentially from lower to higher oxidation numbers (Table 4.4).

Table 4.4 Typical oxides of main group elements

	1	2	12	13	14	15	16	17	18
2	Li_2O	BeO		B_2O_3	CO CO_2	N_2O NO NO_2			
3	Na_2O Na_2O_2 NaO_2	MgO		Al_2O_3	SiO_2	P_4O_6 P_4O_{10}	SO_2 SO_3	Cl_2O ClO_2	
4	K_2O K_2O_2 KO_2	CaO	ZnO	Ga_2O_3	GeO_2	As_4O_6 As_4O_{10}	SeO_2 SeO_3		
5	Rb_2O Rb_2O_2 Rb_9O_2	SrO	CdO	In_2O_3	SnO_2	Sb_4O_6 Sb_4O_{10}	TeO_2 TeO_3	I_2O_5	XeO_3 XeO_4
6	Cs_2O $Cs_{11}O_3$	BaO	HgO	Tl_2O Tl_2O_3	PbO PbO_2	Bi_2O_3			

Dinitrogen monoxide, N_2O. Oxide of monovalent nitrogen. Pyrolysis of ammonium nitrate generates this oxide as follows.

$$NH_4NO_3 \xrightarrow[250\ ^{o}C]{} N_2O + 2\ H_2O$$

Although the oxidation number is a formality, it is an interesting and symbolic aspect of the versatility of the oxidation number of nitrogen that NH_4NO_3 forms a monovalent nitrogen oxide (+1 is a half of the average of -3 and +5 for NH_4 and NO_3, respectively). The N-N-O bond distances of the straight N_2O are 112 pm (N-N) and 118 pm (N-O), corresponding to 2.5th and 1.5th bond order, respectively. N_2O (16e) is isoelectronic with carbon dioxide CO_2 (16e). This compound is also called laughing gas and is widely used for analgesia.

Nitric oxide, NO. An oxide of divalent nitrogen. This is obtained by reduction of nitrite as follows.

$$KNO_2 + KI + H_2SO_4 \rightarrow NO + K_2SO_4 + H_2O + \frac{1}{2} I_2$$

Having an odd number of valence electrons (11 electrons), it is paramagnetic. The N-O distance is 115 pm and the bond has double bond character. The unpaired electron in the highest antibonding π^* orbital is easily removed, and NO becomes NO^+ (nitrosonium), which is isoelectronic with CO. Since an electron is lost from the antibonding orbital, the N-O bond becomes stronger. The compounds $NOBF_4$ and $NOHSO_4$ containing this cation are used as 1 electron oxidants.

Although NO is paramagnetic as a monomer in the gas phase, dimerization in the condensed phase leads to diamagnetism. It is unique as a ligand of transition metal complexes and forms complexes like $[Fe(CO)_2(NO)_2]$, in which NO is a neutral 3-electron ligand. Although M-N-O is straight in these kind of complexes, the M-N-O angle bends to 120^{o} ~ 140^{o} in $[Co(NH_3)_5NO]\ Br_2$, in which NO^- coordinates as a 4-electron ligand. It has become clear recently that nitric oxide has various biological control functions, such as blood-pressure depressing action, and it attracts attention as the second inorganic material after Ca^{2+} to play a role in signal transduction.

Dinitrogen trioxide, N_2O_3. The oxidation number of nitrogen is +3, and this is an unstable compound decomposing into NO and NO_2 at room temperature. It is generated when equivalent quantities of NO and NO_2 are condensed at low temperatures. It is light blue in the solid state and dark blue in the liquid state but the color fades at higher temperatures.

Nitrogen dioxide, NO_2. A nitrogen compound with oxidation number +4. It is an odd electron compound with an unpaired electron, and is dark reddish brown in color. It is in equilibrium with the colorless dimer dinitrogen tetroxide, N_2O_4. The proportion of NO_2 is 0.01% at -11 ^{o}C, and it increases gradually to 15.9% at its boiling point (21.2 ^{o}C), and becomes 100% at 140 ^{o}C.

N_2O_4 can be generated by the pyrolysis of lead nitrate as follows.

$$2\ Pb(NO_3)_2 \xrightarrow[400\ ^{o}C]{} 4\ NO_2 + 2\ PbO + O_2$$

When NO_2 is dissolved in water, nitric acid and nitrous acid are formed.

$$2\ NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

By one electron oxidation, NO^{2+} (nitroyl) forms and the O-N-O angle changes from 134^{o} to 180^{o} in the neutral NO_2. On the other hand, by one electron reduction, NO^{2-} (nitrito) forms and the angle bends to 115^{o}.

Dinitrogen pentoxide, N_2O_5, is obtained when concentrated nitric acid is carefully dehydrated with phosphorus pentoxide at low temperatures. It sublimes at 32.4 ^{o}C. As it forms nitric acid by dissolving in water, it may also be called a nitric anhydride.

$$N_2O_5 + H_2O \longrightarrow 2\,HNO_3$$

Although it assumes an ion-pair structure NO_2NO_3 and straight NO_2^+ and planar NO_3^- ions are located alternately in the solid phase, it is molecular in the gas phase.

Oxoacids

Oxyacids of nitrogen include nitric acid, HNO_3, nitrous acid, HNO_2, and hyponitrous acid, $H_2N_2O_2$. Nitric acid, HNO_3, is one of the most important acids in the chemical industry, along with sulfuric acid and hydrochloric acid. Nitric acid is produced industrially by the **Ostwald process**, which is the oxidation reaction of ammonia in which the oxidation number of nitrogen increases from -3 to +5. Because the Gibbs energy of the direct conversion of dinitrogen to the intermediate NO_2 is positive, and therefore the reaction is unfavorable thermodynamically, dinitrogen is firstly reduced to ammonia, and this is then oxidized to NO_2.

$$\begin{array}{ccccccc} N_2 & \longrightarrow & NH_3 & \longrightarrow & NO_2 & \longrightarrow & HNO_3 \\ 0 & & -3 & & +4 & & +5 \end{array}$$

Nitric acid, HNO_3. Commercial nitric acid is a *ca.*70% aqueous solution and vacuum distillation of it in the presence of phosphorus pentoxide gives pure nitric acid. As it is a strong oxidizing agent while also being a strong acid, it can dissolve metals (copper, silver, lead, *etc.*) which do not dissolve in other acids. Gold and platinum can even be dissolved in a mixture of nitric acid and hydrochloric acid (*aqua regia*). The nitrate ion, NO_3^-, and nitrite ion, NO_2^-, take various coordination forms when they coordinate as ligands in transition metal complexes.

Nitrous acid, HNO_2. Although not isolated as a pure compound, aqueous solutions are weak acids ($pKa = 3.15$ at 25 °C) and important reagents. Since $NaNO_2$ is used industrially for hydroxylamine (NH_2OH) production and also used for diazotidation of aromatic amines, it is important for the manufacture of azo dyes and drugs. Among the various coordination forms of NO_2^- isomers now known, monodentate nitro (N-coordination) and nitrito (O-coordination) ligands had already been discovered in the 19th century.

(e) Phosphorus oxides.

The structures of the phosphorus oxides P_4O_{10}, P_4O_9, P_4O_7, and P_4O_6 have been determined.

Phosphorus pentoxide, P_4O_{10}, is a white crystalline and sublimable solid that is formed when phosphorus is oxidized completely. Four phosphorus atoms form a tetrahedron and they are bridged by oxygen atoms (refer to Fig. 2.12). Since a terminal oxygen atom is bonded to each phosphorus atom, the coordination polyhedron of oxygen is also a tetrahedron. When the molecular P_4O_{10} is heated, a vitrified isomer is formed. This is a polymer composed of similar tetrahedra of phosphorus oxide with the same composition that are connected to one another in sheets. Since it is very reactive with water , phosphorus pentoxide is a powerful dehydrating agent. It is used not only as a desiccant, but also it has remarkable dehydration properties, and N_2O_5 or SO_3 can be formed by dehydration of HNO_3 or H_2SO_4, respectively. Phosphorus pentoxide forms orthophosphoric acid, H_3PO_4, when reacted with sufficient water, but if insufficient water is used, various kinds of condensed phosphoric acids are produced depending on the quantity of reacting water.

Phosphorus trioxide, P_4O_6, is a molecular oxide, and its tetrahedral structure results from the removal of only the terminal oxygen atoms from phosphorus pentoxide.
Each phosphorus is tri-coordinate. This compound is formed when white phosphorus is oxidized at low temperatures in insufficient oxygen. The oxides with compositions intermediate between phosphorus pentoxide and trioxide have 3 to 1 terminal oxygen atoms and their structures have been analyzed.

Although arsenic and antimony give molecular oxides As_4O_6 and Sb_4O_6 that have similar structures to P_4O_6, bismuth forms a polymeric oxide of composition Bi_2O_3.

Phosphoric acid

Orthophosphoric acid, H_3PO_4. It is one of the major acids used in chemical industry, and is produced by the hydration reaction of phosphorus pentoxide, P_4O_{10}. Commercial phosphoric acid is usually of 75-85% purity. The pure acid is a crystalline compound (mp 42.35 ^{o}C). One terminal oxygen atom and three OH groups are bonded to the phosphorus atom in the center of a tetrahedron. The three OH groups release protons making the acid tribasic ($pK_1 = 2.15$). When two orthophosphoric acid molecules condense by the removal of an H_2O molecule, pyrophosphoric acid, $H_4P_2O_7$, is formed.

Phosphonic acid, H_3PO_3. This acid is also called phosphorous acid and has H in place of one of the OH groups of orthophosphoric acid. Since there are only two OH groups, it is a dibasic acid.

Phosphinic acid, H_3PO_2. It is also called hypophosphorous acid, and two of the OH groups in orthophosphoric acid are replaced by H atoms. The remaining one OH group shows monobasic acidity. If the PO_4 tetrahedra in the above phosphorus acids bind by O bridges, many **condensed phosphoric acids** form. **Adenosine triphosphate (**ATP**)**, **deoxyribonucleic acid (**DNA**)**, *etc*., in which the triphosphorus acid moieties are combined with adenosine are phosphorus compounds that are fundamentally important for living organisms.

(f) Sulfur oxides

Sulfur dioxide, SO_2. This is formed by the combustion of sulfur or sulfur compounds. This is a colorless and poisonous gas (bp -10.0 ^oC) and as an industrial emission is one of the greatest causes of environmental problems. However, it is very important industrially as a source material of sulfur. Sulfur dioxide is an angular molecule, and recently it has been demonstrated that it takes various coordination modes as a ligand to transition metals. It is a nonaqueous solvent similar to liquid ammonia, and is used for special reactions or as a solvent for special NMR measurements.

Sulfur trioxide, SO_3. It is produced by catalytic oxidation of sulfur dioxide and used for manufacturing sulfuric acid. The usual commercial reagent is a liquid (bp 44.6 ^oC). The gaseous phase monomer is a planar molecule. It is in equilibrium with a ring trimer (γ-SO_3 = S_3O_9) in the gaseous or liquid phase. In the presence of a minute amount of water SO_3 changes to β-SO_3, which is a crystalline high polymer with a helical structure. α-SO_3 is also known as a solid of still more complicated lamellar structure. All react violently with water to form sulfuric acid.

Sulfur acids.

Although there are many oxy acids of sulfur, most of them are unstable and cannot be isolated. They are composed of a combination of S=O, S-OH, S-O-S, and S-S bonds with a central sulfur atom. As the oxidation number of sulfur atoms varies widely, various redox equilibria are involved.

Sulfuric acid, H_2SO_4. It is an important basic compound produced in the largest quantity of all inorganic compounds. Pure sulfuric acid is a viscous liquid (mp 10.37 ^oC), and dissolves in water with the generation of a large amount of heat to give strongly acidic solutions.

Thiosulfuric acid, $H_2S_2O_3$. Although it is generated if thiosulfate is acidified, the free acid is unstable. The $S_2O_3^{2-}$ ion is derived from the replacement of one of the oxygen atoms of SO_4^{2-} by sulfur, and is mildly reducing.

Sulfurous acid, H_2SO_3. The salt is very stable although the free acid has not been isolated. The SO_3^{2-} ion that has pyramidal C_{3v} symmetry is a reducing agent. In dithionic acid, $H_2S_2O_6$, and the dithionite ion, $S_2O_6^{2-}$, the oxidation number of sulfur is +5, and one S-S bond is formed. This is a very strong reducing agent.

(g) Metal oxides

Oxides of all the metallic elements are known and they show a wide range of properties in terms of structures, acidity and basicity, and conductivity. Namely, an oxide can exhibit molecular, 1-dimensional chain, 2-dimensional layer, or 3-dimensional structures. There are basic, amphoteric, and acidic oxides depending on the identity of the metallic element. Moreover, the range of physical properties displayed is also broad, from insulators, to semiconductors, metallic conductors, and superconductors. The compositions of metallic oxide can be simply stoichiometric, stoichiometric but not simple, or sometimes non-stoichiometric. Therefore, it is better to classify oxides according to each property. However, since structures give the most useful information to understand physical and chemical properties, typical oxides are classified first according to the dimensionality of their structures (Table 4.4, Table 4.5).

Table 4.5 Typical binary oxides of transition metals

Oxidation number	3	4	5	6	7	8	9	10	11
+1		Ti_2O^l							Cu_2O Ag_2O
+2		TiO	VO NbO		MnO	FeO	CoO	NiO	CuO Ag_2O_2
+3	Sc_2O_3 Y_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3		Fe_2O_3	 Rh_2O_3		
+4		TiO_2 ZrO_2 HfO_2	VO_2 NbO_2 TaO_2	CrO_2 MoO_2 WO_2	MnO_2 TcO_2 ReO_2	 RuO_2 OsO_2	 RhO_2 IrO_2	 PtO_2	
+5			$V_2O_5{}^i$ Nb_2O_5 Ta_2O_5						
+6				$CrO_3{}^c$ $MoO_3{}^l$ WO_3	 ReO_3				
+7					$Re_2O_7{}^l$				
+8						$RuO_4{}^m$ $OsO_4{}^m$			

^{m} molecular, ^{c} chain, ^{l} layer, others 3-demensional.

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 crystallline 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

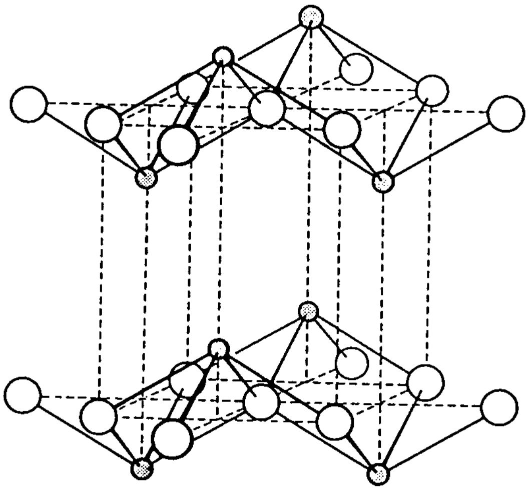


Fig. 4.11 Structure of PbO.

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 (Fig. 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.

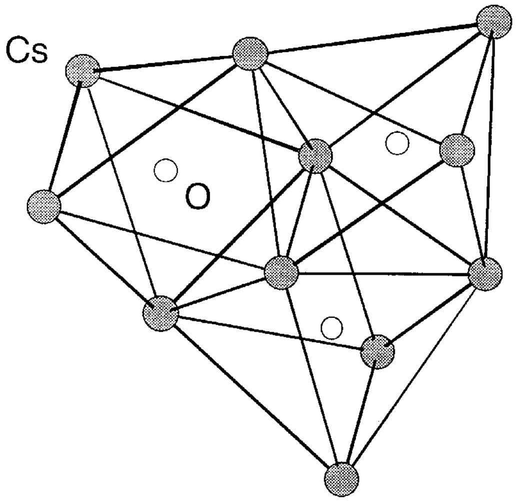


Fig. 4.12 Structure of $Cs_{11}O_3$.

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 (Fig. 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 ($x = 0.89$-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 (Fig. 4.13), and the dioxides of lanthanide and actinide metals with large ionic radii take fluorite-type structures.

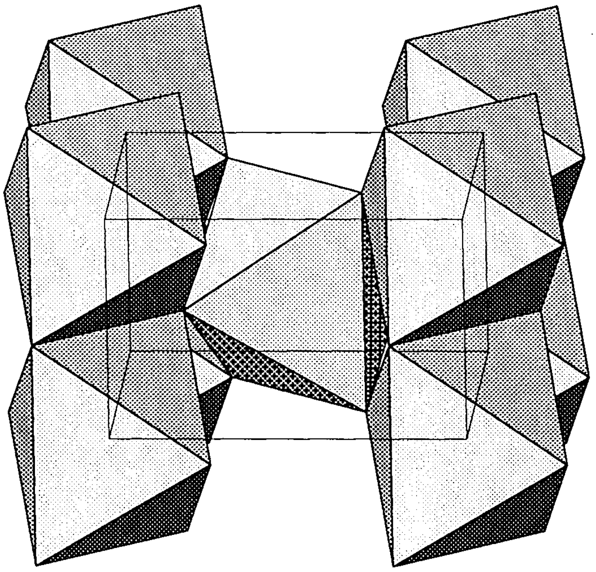


Fig. 4.13 Structure of rutile.

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 Fig. 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.

$$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + Cl_2 + 2\,H_2O$$

Zirconium dioxide, ZrO_2, has a very high melting-point (2700 ^{o}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 ^{o}C and 2300 ^{o}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 (Fig. 4.14).

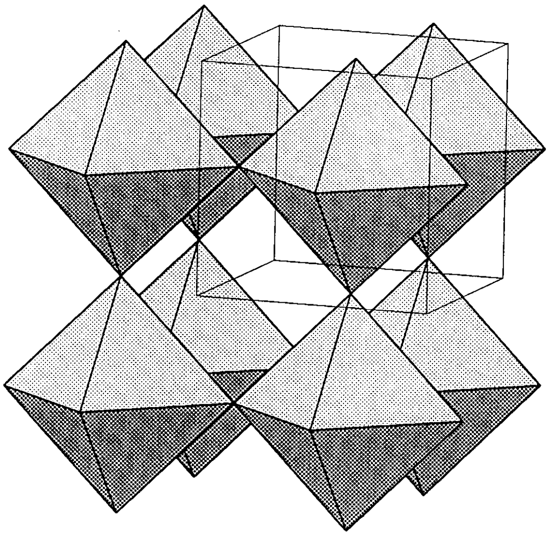


Fig. 4.14 Structure of ReO_3.

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_6 octahedra. When these compounds are heated in a vacuum or with powdered tungsten, reduction takes place and many oxides with complicated compositions ($W_{18}O_{49}$, $W_{20}O_{58}$, *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 (Fig. 4.15)
Among the oxides of composition $A^{2+}B_2{}^{3+}O_4$ (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.

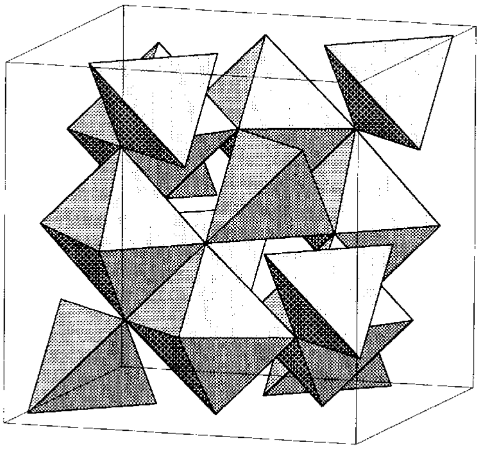


Fig. 4.15 Spinel structure.

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 (Fig. 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).

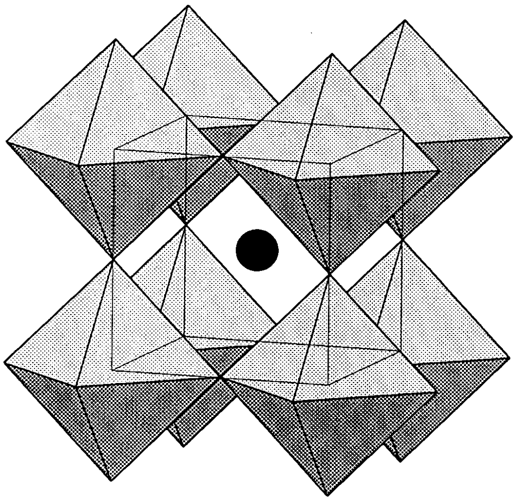


Fig. 4.16 Perovskite structure.

(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 $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ (M = Mo, W, and X = B, Al, Si, Ge, P, As, Ti, Mn, Fe, Co, 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 Fig. 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.

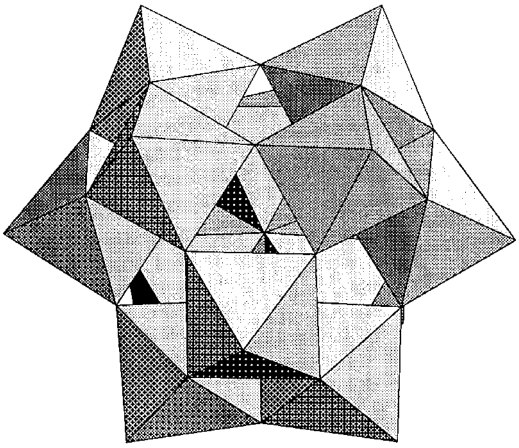


Fig. 4.17 Keggin structure.

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.

$$12\,[MoO_4]^{2-} + HPO_4^{2-} \xrightarrow{H^+} [PMo_{12}O_{40}]^{3-} + 12\,H_2O$$

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 M(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. 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.

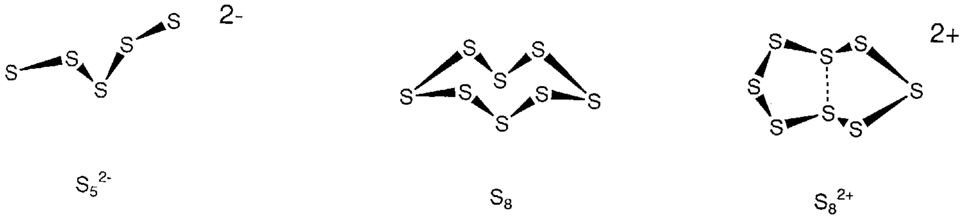
4.4 Chalcogen and chalcogenides

(a) Simple substances

Sulfur, selenium, and tellurium are called chalcogens. Simple substances and compounds of oxygen and of the elements of this group in the later periods have considerably different properties. As a result of having much smaller electronegativities than oxygen, they show decreased ionicity and increased bond covalency, resulting in a smaller degree of hydrogen bonding. Because they have available *d* orbitals , chalcogens have increased flexibility of valence and can easily bond to more than two other atoms. **Catenation** is the bonding between the same chalcogen atoms, and both simple substances and ions of chalcogens take a variety of structures.

The major isotopes of sulfur are ^{32}S (95.02% abundance), ^{33}S (0.75%), ^{34}S (4.21%), and ^{36}S (0.02%), and there are also six radioactive isotopes. Among these, ^{33}S ($I = 3/2$) can be used for NMR. Since the isotope ratio of sulfurs from different locations differs, the accuracy of the atomic weight is limited to 32.07+0.01. Because the electronegativity of sulfur ($\chi = 2.58$) is much smaller than that of oxygen ($\chi = 3.44$) and sulfur is a soft element, the ionicity in the bonds of sulfur compounds is low and hydrogen bonding is not important. Elemental sulfur has many allotropes, such as S_2, S_3, S_6, S_7, S_8, S_9, S_{10}, S_{11}, S_{12}, S_{18}, S_{20}, and S_∞, reflecting the catenation ability of sulfur atoms.

Elemental sulfur is usually a yellow solid with a melting point of 112.8 ^{o}C called orthorhombic sulfur (α sulfur). Phase-transition of this polymorph produces monoclinic sulfur (β sulfur) at 95.5 ^{o}C. It was established in 1935 that these are crown-like cyclic molecules (Fig. 4.18). Being molecular, they dissolve well in organic solvents, such as CS_2. Not only 8-membered rings but also S_{6-20} rings are known, and the helix polymer of sulfur is an infinitely annular sulfur. Diatomic molecular S_2 and triatomic molecular S_3 exist in the gaseous phase. When sulfur is heated, it liquifies and becomes a rubber-like macromolecule on cooling. The diversity of structures of catenated sulfur is also seen in the structures of the polysulfur cations or anions resulting from the redox reactions of the catenated species.



S_5^{2-} S_8 S_8^{2+}

Fig. 4.18 Structures of S_5^{2-}, S_8, and S_8^{2+}.

Selenium is believed to have six isotopes. ^{80}Se (49.7%) is the most abundant and ^{77}Se, with nuclear spin $I = 1/2$ is useful in NMR. The accuracy of atomic weight of selenium, 78.96+0.03, is limited to two decimal places because of composition change of its isotopes. Among many allotropes of selenium, so-called red selenium is an Se_8 molecule with a crown-like structure and is soluble in CS_2. Gray metallic selenium is a polymer with a helical structure. Black selenium, which is a complicated polymer, is also abundant.

Tellurium also has eight stable isotopes and an atomic weight of 127.60+0.03. ^{130}Te (33.8%) and ^{128}Te (31.7%) are the most abundant isotopes, and ^{125}Te and ^{123}Te with $I = 1/2$ can be used in NMR. There is only one crystalline form of tellurium, which is a spiral chain polymer that shows electric conductivity.

(b) Polyatomic chalcogen cations and anions

Although it has long been recognized that solutions of chalcogen elements in sulfuric acid showed beautiful blue, red, and yellow colors, the polycationic species that give rise to these colors, S_4^{2+}, S_6^{2+}, S_6^{4+}, S_8^{2+}, S_{10}^{2+}, S_{19}^{2+}, or those of other chalcogen atoms, have been isolated by the reaction with AsF_5, *etc*. and their structures determined. For example, unlike neutral S_8, S_8^{2+} takes a cyclic structure that has a weak coupling interaction between two transannular sulfur atoms (Fig. 4.18).

On the other hand, alkali metal salts Na_2S_2, K_2S_5, and alkaline earth metal salt BaS_3, a transition-metal salt $[Mo_2(S_2)_6]^{2-}$, a complex $Cp_2W(S_4)$, *etc*. of polysulfide anions S_x^{2-} (x = 1-6), in which the sulfur atoms are bonded mutually have been synthesized and their structures determined. As is evident from the fact that elemental sulfur itself forms S_8 molecules, sulfur, unlike oxygen, tends to catenate. Therefore, formation of polysulfide ions, in which many sulfur atoms are bonded, is feasible, and a series of polysulfanes H_2S_x (x = 2-8) has actually been synthesized.

(c) Metal sulfides

Stratified disulfides, MS_2, are important in transition metal sulfides. They show two types of structures. One has a metal in a triangular prismatic coordination environment, and the other has a metal in an octahedral coordination environment.

MoS_2 is the most stable black compound among the molybdenum sulfides. L. Pauling determined the structure of MoS_2 in 1923. The structure is constructed by laminating two sulfur layers between which a molybdenum layer is intercalated (Fig. 4.19). Alternatively, two sulfur layers are stacked and a molybdenum layer is inserted between them. Therefore, the coordination environment of each molybdenum is a triangular prism of sulfur atoms. Since there is no bonding interaction between sulfur layers, they can easily slide, resulting in graphite-like lubricity. MoS_2 is used as a solid lubricant added to gasoline, and also as a catalyst for hydrogenation reactions.

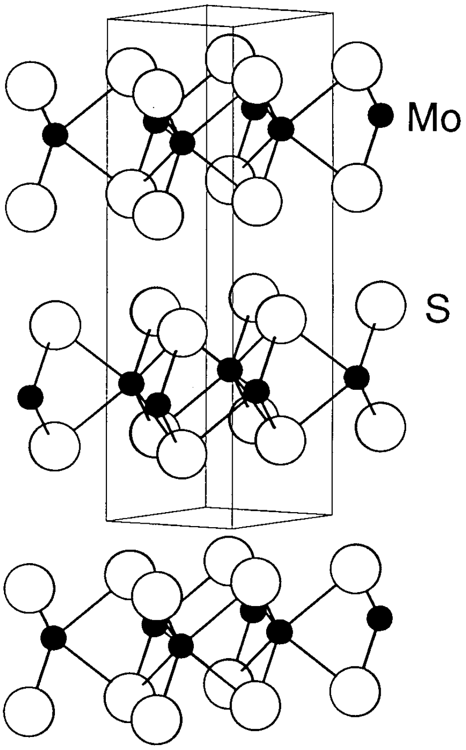


Fig. 4.19 Structure of MoS_2.

ZrS_2, TaS_2, *etc.* take the CdI_2type structure containing metal atoms in an octahedral coordination environment constructed by sulfur atoms.

Chevrel phase compounds. There are superconducting compounds called **Chevrel phases** which are important examples of the chalcogenide compounds of molybdenum. The general formula is described by $M_xMo_6X_8$ (M = Pb, Sn, and Cu; X = S, Se, and Te), and six molybdenum atoms form a regular octahedral cluster, and eight chalcogenide atoms cap the eight triangular faces of the cluster. The cluster units are connected 3-dimensionally (Fig. 4.20). Since the cluster structure of molybdenum atoms is similar to that of molybdenum dichloride, $MoCl_2$, (= $(Mo_6Cl_8)Cl_2Cl_{4/2}$), the structural chemistry of these compounds has attracted as much attention as their physical properties.

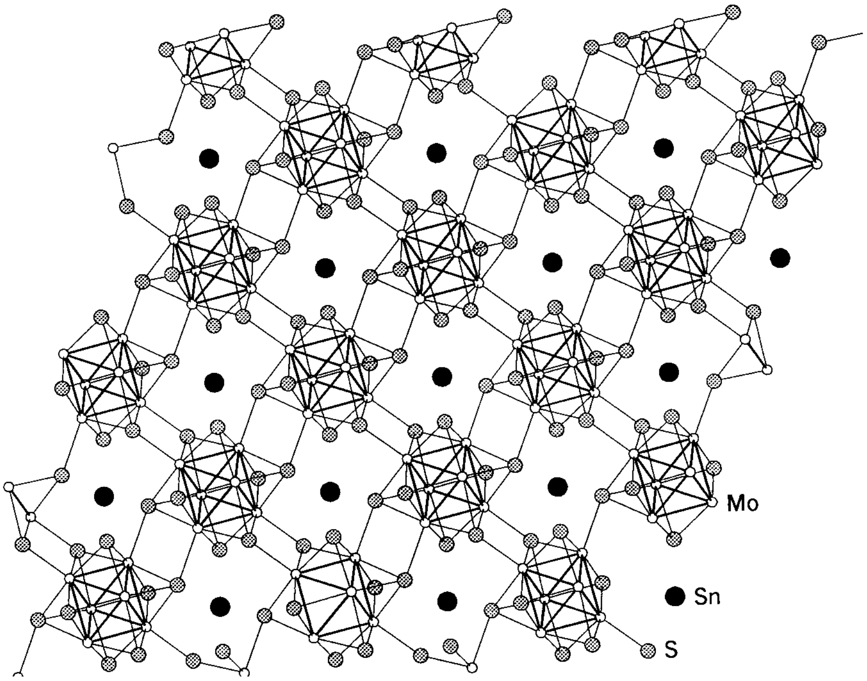


Fig. 4.20 Structure of $SnMo_6S_8$.

4.5 Halogens and halides

The origin of **halogen** is the Greek word meaning the production of salt by direct reaction with a metal. Since their reactivity is very high, halogens are found in nature only as compounds . The basic properties of halogens are shown in Table 4.6 and Table 4.7. The electron configuration of each halogen atom is ns^2np^5, and they lack one electron from the closed-shell structure of a rare gas. Thus a halogen atom emits energy when it gains an electron. Namely, the enthalpy change of the reaction $X(g) + e^- \rightarrow X^-(g)$ is negative. Although electron affinity is defined as the energy change of gaining an electron, a positive sign is customarily used. In order to be consistent with the enthalpy change, a negative sign would be appropriate.

Table 4.6 Properties of halogens

	Ionization energy (kJ mol^{-1})	Electronegativity χ_P	Ionic radius r(X$^-$) (pm)
F	1680.6	3.98	133
Cl	1255.7	3.16	181
Br	1142.7	2.96	196
I	1008.7	2.66	220

Table 4.7 Properties of halogen molecules

	Interatomic distance r(X-X) (pm)	mp °C	bp °C	Color
F_2	143	-218.6	-188.1	Colorless gas
Cl_2	199	-101.0	-34.0	Yellow green gas
Br_2	228	-7.75	59.5	Dark red liquid
I_2	266	113.6	185.2	Dark violet solid

The electron affinity of chlorine (348.5 kJmol^{-1}) is the largest and fluorine (332.6 kJmol^{-1}) comes between chlorine and bromine (324.7 kJmol^{-1}). The electronegativity of fluorine is the highest of all the halogens.

Since halogens are produced as metal salts, simple substances are manufactured by electrolysis. Fluorine only takes the oxidation number -1 in its compounds, although the oxidation number of other halogens can range from -1 to +7. Astatine, At, has no stable nuclide and little is known about its chemical properties .

(a) Manufacture of halogen

Fluorine has the highest reduction potential (E^0 = +2.87 V) and the strongest oxidizing power among the halogen molecules. It is also the most reactive nonmetallic element. Since water is oxidized by F_2 at much lower electrode potential (+1.23 V), fluorine gas cannot be manufactured by the electrolysis of aqueous solutions of fluorine compounds. Therefore, it was a long time before elemental fluorine was isolated , and F. F. H. Moisson finally succeeded in isolating it by the electrolysis of KF in liquid HF. Fluorine is still manufactured by this reaction.

Chlorine, which is especially important in inorganic industrial chemistry, is manufactured together with sodium hydroxide. The basic reaction for the production of chlorine is electrolysis of an aqueous solution of NaCl using an ion exchange process. In this process, chlorine gas is generated in an anodic cell containing brine and Na^+ moves through an ion exchange membrane to the cathodic cell where it pairs with OH^- to become an aqueous solution of NaOH

Exercise 4.5 Why can chlorine be manufactured by electrolysis of an aqueous solution of sodium chloride?

[Answer] Despite the higher reduction potential of chlorine (+1.36 V) than that of oxygen (+1.23 V), the reduction potential of oxygen can be raised (overvoltage) depending on the choice of electrode used for the electrolysis process

Bromine is obtained by the oxidation of Br^- with chlorine gas in saline water. Iodine is similarly produced by passing chlorine gas through saline water containing I^- ions. Since natural gas is found in Japan together with underground saline water containing I^-, Japan is one of the main countries producing iodine.

Anomalies of fluorine Molecular fluorine compounds have very low boiling points. This is due to the difficulty of polarization as a result of the electrons being strongly drawn to the nuclei of fluorine atoms. Since the electronegativity of fluorine is highest ($\chi = 3.98$) and electrons shift to F, resulting in the high acidity of atoms bonded to F. Because of the small ionic radius of F^-, high oxidation states are stabilized, and hence low oxidation compounds like CuF are unknown, in contrast with the compounds such as IF_7 and PtF_6.

Pseudohalogens Since the cyanide ion CN^-, the azide ion N^{3-}, and the thiocyanate ion SCN^-, *etc*. form compounds similar to those of halide ions, they are called **pseudohalide ions**. They form psudohalogen molecules such as cyanogene $(CN)_2$, hydrogen cyanide HCN, sodium thiocyanate NaSCN, *etc*. Fine-tuning electronic and steric effects that are impossible with only halide ions make pseudohalogens useful also in transition metal complex chemistry.

Polyhalogens Besides the usual halogen molecules, mixed halogen and polyhalogen molecules such as BrCl, IBr, ICl, ClF_3, BrF_5,IF_7 *etc* also exist. Polyhalogen anions and cations such as I_3^-, I_5^-, I_3^+, and I_5^+, are also known.

(b) Oxygen compounds

Although many binary oxides of halogens (consisting only of halogen and oxygen) are known, most are unstable. Oxygen difluoride OF_2 is the most stable such compound. This is a very powerful fluorinating agent and can generate plutonium hexafluoride PuF_6 from plutonium metal. While oxygen chloride, Cl_2O, is used for bleaching pulp and water treatment, it is generated *in situ* from ClO_3^-, since it is unstable.

Hypochlorous acid, HClO, chlorous acid, $HClO_2$, chloric acid, $HClO_3$, and perchloric acid, $HClO_4$ are oxoacids of chlorine and especially perchloric acid is a strong oxidizing agent as well as being a strong acid. Although analogous acids and ions of other halogens had been known for many years, BrO_4^- was synthesized as late as 1968. Once it was prepared it turned out to be no less stable than ClO_4^- or IO_4^-, causing some to wonder why it had not been synthesized before. Although ClO_4^- is often used for crystallizing transition metal complexes, it is explosive and should be handled very carefully.

(c) Halides of nonmetals

Halides of almost all nonmetals are known, including fluorides of even the inert gases krypton, Kr, and xenon, Xe. Although fluorides are interesting for their own unique characters, halides are generally very important as starting compounds for various compounds of nonmetals by replacing halogens in inorganic syntheses (Table 4.8).

Table 4.8 Typical chlorides and fluorides of main group elements

	1	2	12	13	14	15	16	17	18
2	LiCl	$BeCl_2$		BF_3	CCl_4	NF_3	OF_2		
3	NaCl	$MgCl_2$		$AlCl_3$	$SiCl_4$	PCl_3	S_2Cl_2	ClF_3	
						PCl_5	SF_6	ClF_5	
4	KCl	$CaCl_2$	$ZnCl_2$	$GaCl_3$	GeF_2	$AsCl_3$	Se_2Cl_2	BrF_3	KrF_2
					$GeCl_4$	AsF_5	SeF_5	BrF_5	
5	RbCl	$SrCl_2$	$CdCl_2$	InCl	$SnCl_2$	$SbCl_3$	Te_4Cl_{16}	IF_5	XeF_2
				$InCl_3$	$SnCl_4$	SbF_5	TeF_6	IF_7	XeF_6
6	CsCl	$BaCl_2$	Hg_2Cl_2	TlCl	$PbCl_2$	$BiCl_3$			
			$HgCl_2$	$TlCl_3$	$PbCl_4$	BiF_5			

Boron trifluoride, BF_3, is a colorless gas (mp -127 ^oC and bp -100 ^oC) that has an irritating odor and is poisonous. It is widely used as an industrial catalyst for Friedel-Crafts type reactions. It is also used as a catalyst for cationic polymerization. It exists in the gaseous phase as a triangular monomeric molecule, and forms Lewis base adducts with ammonia, amines, ethers, phosphines, *etc*. because of its strong Lewis acidity. Diethylether adduct, $(C_2H_5)_2O{:}BF_3$, is a distillable liquid and is used as a common reagent. It is a starting compound for the preparation of diborane, B_2H_6. Tetrafluoroborate, BF_4^-, is a tetrahedral anion formed as an adduct of BF_3 with a base F^-. Alkali metal salts, a silver salt and $NOBF_4$ as well as the free acid HBF_4 contain this anion. Since its coordination ability is very weak, it is used in the crystallization of cationic complexes of transition metals as a counter anion like ClO_4^-. $AgBF_4$ and $NOBF_4$ are also useful for 1-electron oxidation of complexes.

Tetrachlorosilane, $SiCl_4$, is a colorless liquid (mp -70 ^oC and bp 57.6 ^oC). It is a regular tetrahedral molecule, and reacts violently with water forming silicic acid and hydrochloric acid. It is useful as a raw material for the production of pure silicon, organic silicon compounds, and silicones.

Phosphorus trifluoride, PF_3, is a colorless, odorless, and deadly poisonous gas (mp -151.5 ^{o}C and bp -101.8 ^{o}C). This is a triangular pyramidal molecule. Because it is as electron-attracting as CO, it acts as a ligand forming metal complexes analogous to metal carbonyls.

Phosphorus pentafluoride, PF_5, is a colorless gas (mp -93.7 ^{o}C and bp -84.5 ^{o}C). It is a triangular bipyramidal molecule and should have two distinct kinds of fluorine atoms. These fluorines exchange positions so rapidly that they are indistinguishable by ^{19}F NMR. It was the first compound with which the famous Berry's pseudorotation was discovered as an exchange mechanism for axial and equatorial fluorine atoms (refer to Section 6.1). The hexafluorophosphate ion, PF_6^-, as well as BF_4^- is often used as a counter anion for cationic transition metal complexes. $LiPF_6$ and R_4NPF_6 can be used as supporting electrolytes for electrochemical measurements.

Phosphorus trichloride, PCl_3, is a colorless fuming liquid (mp -112 ^{o}C and bp 75.5 ^{o}C). It is a triangular pyramidal molecule and hydrolyzes violently. It is soluble in organic solvents. It is used in large quantities as a raw material for the production of organic phosphorus compounds.

Phosphorus pentachloride, PCl_5, is a colorless crystalline substance (sublimes but decomposes at 160 ^{o}C) It is a triangular bipyramidal molecule in the gaseous phase, but it exists as an ionic crystal $[PCl_4]^+[PCl_6]^-$ in the solid phase. Although it reacts violently with water and becomes phosphoric acid and hydrochloric acid, it dissolves in carbon disulfide and carbon tetrachloride. It is useful for chlorination of organic compounds.

Arsenic pentafluoride, AsF_5, is a colorless gas (mp -79.8 ^{o}C and bp -52.9 ^{o}C). It is a triangular bipyramidal molecule. Although it hydrolyzes, it is soluble in organic solvents. As it is a strong electron acceptor, it can form electron donor-acceptor complexes with electron donors.

Sulfur hexafluoride, SF_6, is a colorless and odorless gas (mp -50.8 ^{o}C and sublimation point -63.8 ^{o}C) It is a hexacoordinate octahedral molecule. It is chemically very stable and hardly soluble in water. Because of its excellent heat-resisting property, incombustibility, and corrosion resistance, it is used as a high voltage insulator.

Sulfur chloride, S_2Cl_2, is an orange liquid (mp -80 ^{o}C and bp 138 ^{o}C). It has a similar structure to hydrogen peroxide. It is readily soluble in organic solvents. It is important as an industrial inorganic compound, and is used in large quantities for the vulcanization of rubber *etc*.

(d) Metal halides

Many metal halides are made by the combination of about 80 metallic elements and four halogens (Table 4.8, Table 4.9). Since there are more than one oxidation state especially in transition metals, several kinds of halides are known for each transition metal. These halides are most important as starting materials of the preparation of metal compounds, and the inorganic chemistry of metal compounds depends on metal halides. There are molecular, 1-dimensional chain, 2-dimensional layer, and 3-dimensional halides but few of them are molecular in crystalline states. It should be noted that the anhydrous transition metal halides are usually solid compounds and hydrates are coordination compounds with water ligands. As the dimensionality of structures is one of the most interesting facets of structural or synthetic chemistry, typical halides are described in order of their dimensionality.

Table 4.9 Typical chlorides and fluorides of transition metals

Oxidation Number	3	4	5	6	7	8	9	10	11
+1	$ScCl$								$CuCl$
	YCl	$ZrCl$							$AgCl$
	$LaCl$	$HfCl$							$AuCl$
+2		$TiCl_2$	VCl_2	$CrCl_2$	$MnCl_2$	$FeCl_2$	$CoCl_2$	$NiCl_2$	$CuCl_2$
				$MoCl_2$		$RuCl_2$		$PdCl_2$	
				WCl_2				$PtCl_2$	
+3	ScF_3	$TiCl_3$	VCl_3	$CrCl_3$		$FeCl_3$	CoF_3		
	YCl_3	$ZrCl_3$		$MoCl_3$		$RuCl_3$	$RhCl_3$		
	LaF_3			WCl_3	$ReCl_3$	$OsCl_3$	$IrCl_3$		$AuCl_3$
+4		$TiCl_4$	VCl_4	CrF_4				$PtCl_4$	
		$ZrCl_4$	$NbCl_4$	$MoCl_4$					
		$HfCl_4$	$TaCl_4$	WCl_4	$ReCl_4$				
+5			VF_5	CrF_5					
			$NbCl_5$	$MoCl_5$					
			$TaCl_5$	WCl_5	$ReCl_5$	OsF_5	IrF_5	PtF_5	
+6				WCl_6	ReF_6	OsF_6	IrF_6	PtF_6	
+7					ReF_7	OsF_7			

Molecular halides

Mercury(II) chloride, $HgCl_2$. It is a colorless crystal soluble in water and ethanol. It is a straight, three-atomic molecule in the free state. However, in addition to two chlorine atoms bonded to mercury, four additional chlorine atoms of adjacent molecules occupy coordination sites and the mercury is almost hexacoordinate in the crystalline state. The compound is very toxic and used for preserving wood, *etc.*

Aluminum trichloride, $AlCl_3$. A colorless crystal (mp 190 ^{o}C (2.5 atm) and bp183

°C) that sublimes when heated. It is soluble in ethanol and ether. It is a Lewis acid and forms adducts with various bases. It is a molecule consisting of the dimer of tetracoordinate aluminium with chlorine bridges in the liquid and gaseous phases (Fig. 4.21), and takes a lamellar structure when crystalline. It is used as a Lewis acid catalyst of Friedel-Crafts reactions, *etc*.

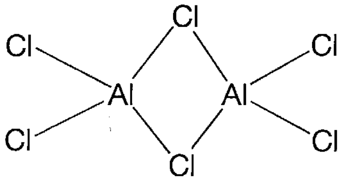


Fig. 4.21 Structure of aluminum chloride.

Tin (IV) chloride, $SnCl_4$. A colorless liquid (mp -33 °C and bp 114 °C). In the gaseous state, it is a tetrahedral molecule.

Titanium(IV) chloride, $TiCl_4$. A colorless liquid (mp -25 °C and bp 136.4 °C). The gaseous molecule is a tetrahedron similar to tin(IV) chloride. It is used as a component of the Ziegler Natta catalyst (refer to Section 8.1 (a)).

Chain-like halides

Gold (I) iodide, AuI. Yellow white solid. Two iodines coordinate to gold, and the compound has a zigzag 1-dimensional chain structure.

Beryllium chloride, $BeCl_2$. A colorless crystal (mp 405 °C and bp 520 °C). It is deliquescent and soluble in water and ethanol. The tetra-coordinated beryllium forms a 1-dimensional chain via chlorine bridges (Fig. 4.22). In the gaseous phase, it is a straight two-coordinate molecule. It is a Lewis acid and is used as a catalyst for Friedel-Crafts reactions.

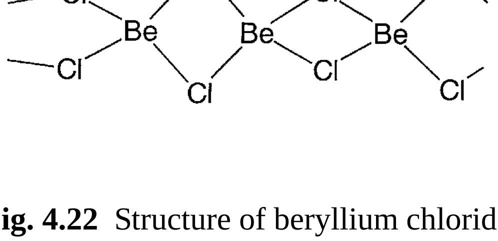


Fig. 4.22 Structure of beryllium chloride.

Palladium chloride, $PdCl_2$. A dark red solid. In the α type, the four-coordinate palladium forms a 1-dimensional chain with double bridges of chlorines . The dihydrate is deliquescent and soluble in water, ethanol, acetone, *etc*. When it is dissolved in hydrochloric acid, it becomes four-coordinate square-planar $[PdCl_4]^{2-}$. It is used as the catalyst for the Wacker process, which is an olefin oxidation process, or in various catalysts for organic syntheses.

Zirconium tetrachloride, (IV) $ZrCl_4$. A colorless crystal (it sublimes above 331 °C). The zirconium is octahedrally coordinated and forms a zigzag chain via chlorine bridges (Fig. 4.23). It is hygroscopic and soluble in water, ethanol, *etc*. It is used as a Friedel-Crafts catalyst and as a component of olefin polymerization catalysts.

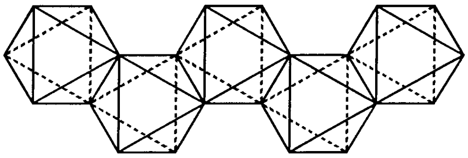


Fig. 4.23 Structure of zirconium tetrachloride.

Stratified halides

Cadmium iodide, CdI_2. A colorless crystal (mp 388 °C and bp 787 °C). It has a cadmium iodide structure where the layers of edge-shared CdI_6 octahedral units are stratified (Fig. 4.24). In the gaseous phase, it comprises straight three atomic molecules. It dissolves in water, ethanol, acetone, *etc*.

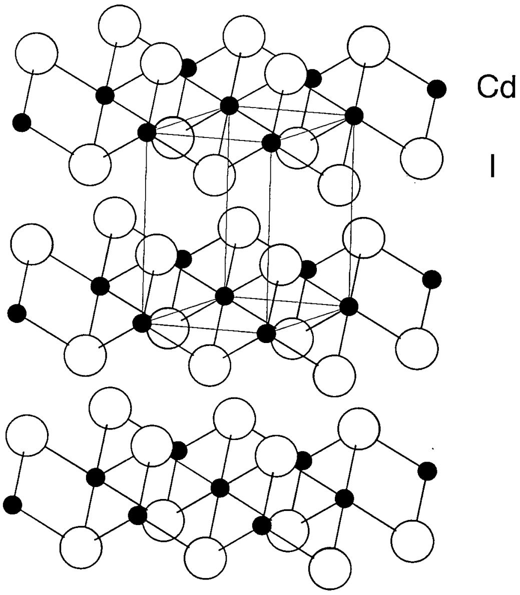


Fig. 4.24 Layers of cadmium and iodine in the cadmium iodide structure.

Cobalt(II) chloride, $CoCl_2$. Blue crystals (mp 735 °C and bp 1049 °C). It has the cadmium chloride structure. It is hygroscopic and becomes light red when water is absorbed. It is soluble also in ethanol and acetone. The hexahydrate is red and is a coordination compound in which water molecules are ligands.

Iron (II)chloride, $FeCl_2$. Greenish yellow crystals (mp 670-674 ^oC). It has the cadmium chloride structure, and is soluble in water and ethanol. The hydrates, which are coordinated by various numbers (6, 4, 2) of water molecules, are precipitated from aqueous solutions of hydrochloric acid.

Iron(III) chloride, $FeCl_3$. Dark brown crystals (mp 306 ^oC and sublimes). It has a lamellar structure in which iron is octahedrally surrounded by six chlorine ligands. In the gaseous phase, it has a dimeric structure bridged by chlorine atoms similar to that of aluminum chloride.

3-dimensional structure halides

Sodium chloride, NaCl. A colorless crystal (mp 801 ^oC and bp 1413 ^oC). It is the original rock salt-type structure. In the gaseous phase, this is a two-atom molecule. Although it is soluble in glycerol as well as water, it hardly dissolves in ethanol. Large single crystals are used as prisms for infrared spectrometers.

Cesium chloride, CsCl. A colorless crystal (mp 645 ^oC, bp 1300 ^oC). Although it has the cesium chloride type structure, it changes to the rock salt structure at 445 ^oC. In the gaseous phase, it is a two-atom molecule.

Copper(I) chloride, CuCl. A colorless crystal (mp 430 ^oC and bp 1490 ^oC) It has the zinc blende structure and four chlorines tetrahedrally coordinate to copper.

Calcium chloride, $CaCl_{2.}$ A colorless crystal (mp 772 ^oC and bp above 1600 ^oC). It has a deformed rutile-type structure and calcium is octahedrally surrounded by six chlorines. It is soluble in water, ethanol, and acetone. It is deliquescent and used as a desiccant. Hydrates in which 1, 2, 4, or 6 water molecules are coordinated are known.

Calcium fluoride, CaF_2. A colorless crystal (mp 1418 ^oC and bp 2500 ^oC). It has the fluorite type structure. It is the most important raw material for fluorine compounds. Good quality crystals are used also as spectrometer prisms and in photographic lenses.

Chromium(II) chloride, $CrCl_2$. A colorless crystal (mp 820 ^oC and sublimes). It has a deformed rutile-type structure. It dissolves well in water giving a blue solution.

Chromium(III) chloride, $CrCl_3$. Purplish red crystal (mp 1150 ^oC and decomposes at 1300 ^oC). Cr^{3+} occupies two thirds of the octahedral cavities in every other layer of Cl^- ions, which are hexagonally close-packed. It is insoluble in water, ethanol, and acetone.

Exercise 4.6 Why do solid metal halides dissolve in water?

[Answer] It is because water reacts with halides breaking the halogen bridges in the solid structures and coordinates to the resultant molecular complexes.

4.6 Rare gases and their compounds

(a) Rare gases

In the 18th century, H. Cavendish discovered an inert component in air. In 1868, a line was discovered in the spectrum of sunlight that could not be identified and it was suggested to be due to a new element, helium. Based on these facts, at the end of the 19th century W. Ramsay isolated He, Ne, Ar, Kr, and Xe and by studying their properties demonstrated that they were new elements . In spite of the nearly 1% content of argon Ar in air, the element had not been isolated until then and rare gases were completely lacking in Mendeleev's periodic table. The Nobel prize was awarded to Ramsay in 1904 for his achievement.

Rare gases are located next to the halogen group in the periodic table. Since rare gas elements have closed-shell electronic configurations, they lack reactivity and their compounds were unknown. Consequently, they were also called inert gases. However, after the discovery of rare gas compounds, it was considered more suitable to call these elements "noble gases", as is mentioned in the following chapter.

Although the abundance of helium in the universe is next to that of hydrogen, it is very rare on the Earth because it is lighter than air. Helium originated from solar nuclear reactions and was locked up in the earth’s crust. It is extracted as a by-product of natural gas from specific areas (especially in North America). Since helium has the lowest boiling point (4.2 K) of all the substances, it is important for low-temperature science and superconductivity engineering. Moreover, its lightness is utilized in airships *etc*. Since argon is separated in large quantities when nitrogen and oxygen are produced from liquid air, it is widely used in metallurgy, and in industries and laboratories that require an oxygen-free environment.

(b) Rare gas compounds

Xenon, Xe, reacts with elements with the largest electronegativities, such as fluorine, oxygen, and chlorine and with the compounds containing these elements, like platinum fluoride, PtF_6. Although the first xenon compound was reported (1962) as $XePtF_6$, the discoverer, N. Bartlett, later corrected that it was not a pure compound but a mixture of $Xe[PtF_6]_x$ (x= 1-2). If this is mixed with fluorine gas and excited with heat or light, fluorides XeF_2, XeF_4, and XeF_6 are generated. XeF_2 has chain-like, XeF_4 square, and XeF_6 distorted octahedral structures. Although preparation of these compounds is comparatively simple, it is not easy to isolate pure compounds, especially XeF_4.

Hydrolysis of the fluorides forms oxides. XeO_3 is a very explosive compound . Although it is stable in aqueous solution, these solutions are very oxidizing. Tetroxide, XeO_4, is the most volatile xenon compound. $M[XeF_8]$ (M is Rb and Cs) are very stable and do not decompose even when heated at 400 ^{o}C. Thus, xenon forms divalent to octavalent compounds. Fluorides can also be used as fluorinating reagents.

Although it is known that krypton and radon also form compounds, the compounds of krypton and radon are rarely studied as both their instability and their radioactivity make their handling problematic.

Discovery of rare gas compounds

H. Bartlett studied the properties of platinum fluoride PtF_6 in the 1960s, and synthesized O_2PtF_6. It was an epoch-making discovery in inorganic chemistry when analogous experiments on xenon, which has almost equal ionization energy (1170 kJmol^{-1}) to that of O_2 (1180 kJmol^{-1}), resulted in the dramatic discovery of $XePtF_6$.

Rare gas compounds had not been prepared before this report, but various attempts were made immediately after the discovery of rare gases. W. Ramsay isolated rare gases and added a new group to the periodic table at the end of the 19th century. Already in 1894, F. F. H. Moisson, who is famous for the isolation of F_2, reacted a 100 cm^3 argon offered by Ramsay with fluorine gas under an electric discharge but failed to prepare an argon fluoride. At the beginning of this century, A. von Antoropoff reported the synthesis of a krypton compound $KrCl_2$, but later he concluded that it was a mistake.

L. Pauling also foresaw the existence of KrF_6, XeF_6, and H_4XeO_6, and anticipated their synthesis. In 1932, a post doctoral research fellow, A. L. Kaye, in the laboratory of D. M. L. Yost of Caltech, where Pauling was a member of faculty, attempted to prepare rare gas compounds. Despite elaborate preparations and eager experiments, attempts to prepare xenon compounds by discharging electricity through a mixed gas of xenon, fluorine, or chlorine were unsuccessful. It is said that Pauling no longer showed interest in rare gas compounds after this failure.

Although R. Hoppe of Germany predicted using theoretical considerations that the existence of XeF_2 and XeF_4 was highly likely in advance of the discovery of Bartlett, he prepared these compounds only after knowing of Bartlett's discovery. Once it is proved that a compound of a certain kind is stable, analogous compounds are prepared one after another. This has also been common in synthetic chemistry of the later period, showing the importance of the first discovery.

Problem

4.1 Write a balanced equation for the preparation of diborane.

4.2 Write a balanced equation for the preparation of triethylphosphine.

4.3 Write a balanced equation for the preparation of osmium tetroxide.

4.4 Describe the basic reaction of the phosphomolybdate method used for the detection of phosphate ions.

4.5 Draw the structure of anhydrous palladium dichloride and describe its reaction when dissolved in hydrochloric acid.

4.6 Describe the reaction of anhydrous cobalt dichloride when it is dissolved in water.

4.7 Draw the structure of phosphorus pentafluoride.