Inorganic Chemistry

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1 Elements and Periodicity

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The elements are found in various states of matter and define the independent constituents of atoms, ions, simple substances, and compounds. Isotopes with the same atomic number belong to the same element. When the elements are classified into groups according to the similarity of their properties as atoms or compounds, the periodic table of the elements emerges. Chemistry has accomplished rapid progress in understanding the properties of all of the elements. The periodic table has played a major role in the discovery of new substances, as well as in the classification and arrangement of our accumulated chemical knowledge. The periodic table of the elements is the greatest table in chemistry and holds the key to the development of material science. Inorganic compounds are classified into molecular compounds and solid-state compounds according to the types of atomic arrangements.

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1.1 The origin of elements and their distribution

All substances in the universe are made of elements. According to the current generally accepted theory, hydrogen and helium were generated first immediately after the Big Bang, some 15 billion years ago. Subsequently, after the elements below iron (Z = 26) were formed by nuclear fusion in the incipient stars, heavier elements were produced by the complicated nuclear reactions that accompanied stellar generation and decay.

In the universe, hydrogen (77 wt%) and helium (21 wt%) are overwhelmingly abundant and the other elements combined amount to only 2%. Elements are arranged below in the order of their abundance,

$$^{1}_{1}\mathrm{H} > {}^{4}_{2}\mathrm{He} \gg {}^{16}_{8}\mathrm{O} > {}^{12}_{6}\mathrm{C} > {}^{20}_{10}\mathrm{Ne} > {}^{28}_{14}\mathrm{Si} > {}^{27}_{13}\mathrm{Al} > {}^{24}_{12}\mathrm{Mg} > {}^{56}_{26}\mathrm{Fe}$$

The **atomic number** of a given element is written as a left subscript and its **mass number** as a left superscript.

1.2 Discovery of elements

The long-held belief that all materials consist of atoms was only proven recently, although elements, such as carbon, sulfur, iron, copper, silver, gold, mercury, lead, and tin, had long been regarded as being atom-like. Precisely what constituted an element was recognized as modern chemistry grew through the time of alchemy, and about 25 elements were known by the end of the 18th century. About 60 elements had been identified by the middle of the 19th century, and the periodicity of their properties had been observed.

The element technetium (Z = 43), which was missing in the periodic table, was synthesized by nuclear reaction of Mo in 1937, and the last undiscovered element promethium (Z = 61) was found in the fission products of uranium in 1947. Neptunium (Z = 93), an element of atomic number larger than uranium (Z = 92), was synthesized for the first time in 1940. There are 103 named elements. Although the existence of elements Z = 104-111 has been confirmed, they are not significant in inorganic chemistry as they are produced in insufficient quantity.

All trans-uranium elements are radioactive, and among the elements with atomic number smaller than Z = 92, technetium, prometium, and the elements after polonium are also radioactive. The half-lives (refer to Section 7.2) of polonium, astatine, radon, actinium, and protoactinium are very short. Considerable amounts of technetium ^{99}Tc are obtained from fission products. Since it is a radioactive element, handling ^{99}Tc is problematic, as it is for other radioactive isotopes, and their general chemistry is much less developed than those of manganese and rhenium in the same group.

Atoms are equivalent to alphabets in languages, and all materials are made of a combination of elements, just as sentences are written using only 26 letters.

1.3 Electronic structure of elements

Wave functions of electrons in an atom are called **atomic orbitals**. An atomic orbital is expressed using three quantum numbers; the **principal quantum number**, n; the **azimuthal quantum number**, l; and the **magnetic quantum number**, m_l. For a principal quantum number n, there are n azimuthal quantum numbers l ranging from 0 to n-1, and each corresponds to the following orbitals.

$$\begin{array}{ll} l: & 0, 1, 2, 3, 4, \dots \\ & s, p, d, f, g, \dots \end{array}$$

An atomic orbital is expressed by the combination of *n* and *l*. For example, *n* is 3 and *l* is 2 for a 3*d* orbital. There are $2l+1$ m_l values, namely *l, l-1, l-2, ..., -l*. Consequently, there are one *s* orbital, three *p* orbitals, five *d* orbitals and seven *f* orbitals. The three aforementioned quantum numbers are used to express the distribution of the electrons in a hydrogen-type atom, and another quantum number m_s (1/2, -1/2) which describes the direction of an electron spin is necessary to completely describe an electronic state. Therefore, an electronic state is defined by four quantum numbers (n, l, m_l, m_s).

The wave function ψ which determines the orbital shape can be expressed as the product of a radial wavefunction *R* and an angular wave function *Y* as follows.

$$\psi_{n,l,ml} = R_{n,l}(r)Y_{l,ml}(\theta,\phi)$$

R is a function of distance from the nucleus, and *Y* expresses the angular component of the orbital. Orbital shapes are shown in Fig. 1.1. Since the probability of the electron's existence is proportional to the square of the wave function, an electron density map resembles that of a wave function. The following conditions must be satisfied when each orbital is filled with electrons.

[The conditions of electron filling]

Pauli principle: The number of electrons that are allowed to occupy an orbital must be limited to one or two, and, for the latter case, their spins must be anti-parallel (different direction).

Hund's rule: When there are equal-energy orbitals, electrons occupy separate orbitals and their spins are parallel (same direction).

The order of orbital energy of a neutral atom is

1*s* < 2*s* < 2*p* < 3*s* < 3*p* < 4*s* < 3*d* < 4*p* …

and the electron configuration is determined as electrons occupy orbitals in this order according to the Pauli principle and Hund's rule. An *s* orbital with one m_l can accommodate 2 electrons, a *p* orbital with three m_l 6 electrons, and a *d* orbital with five m_l 10 electrons.

Exercise 1.1 Describe the electron configuration of a C atom, an Fe atom, and a Au atom.

[Answer] Electrons equal to the atomic number are arranged in the order of orbital energies. Since the electrons inside the valence shell take the rare gas configuration, they may be denoted by the symbol of a rare gas element in brackets.

C: $1s^22s^22p^2$ or $[\mathrm{He}]2s^22p^2$
Fe: $1s^22s^22p^63s^23p^63d^64s^2$ or $[\mathrm{Ar}]3d^64s^2$
Au: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^1$ or $[\mathrm{Xe}]4f^{14}5d^{10}6s^1$

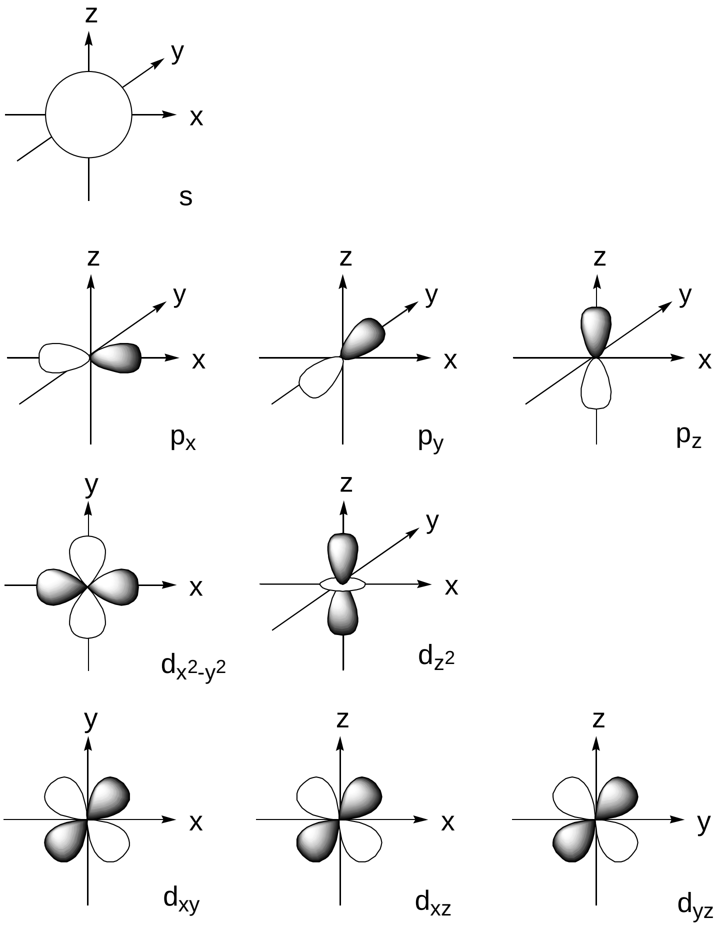

Fig. 1.1 Shapes of *s*, *p*, and *d* orbitals.

Table 1.1 Periodic table of elements. The values are atomic weights.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1.008 $_{1}$H																	4.003 $_{2}$He
2	6.941 $_{3}$Li	9.012 $_{4}$Be											10.81 $_{5}$B	12.01 $_{6}$C	14.01 $_{7}$N	16.00 $_{8}$O	19.00 $_{9}$F	20.18 $_{10}$Ne
3	22.99 $_{11}$Na	24.31 $_{12}$Mg											26.98 $_{13}$Al	28.09 $_{14}$Si	30.97 $_{15}$P	32.07 $_{16}$S	35.45 $_{17}$Cl	39.95 $_{18}$Ar
4	39.10 $_{19}$K	40.08 $_{20}$Ca	44.96 $_{21}$Sc	47.87 $_{22}$Ti	50.94 $_{23}$V	52.00 $_{24}$Cr	54.94 $_{25}$Mn	55.85 $_{26}$Fe	58.93 $_{27}$Co	58.69 $_{28}$Ni	63.55 $_{29}$Cu	65.39 $_{30}$Zn	69.72 $_{31}$Ga	72.61 $_{32}$Ge	74.92 $_{33}$As	78.96 $_{34}$Se	79.90 $_{35}$Br	83.80 $_{36}$Kr
5	85.47 $_{37}$Rb	87.62 $_{38}$Sr	88.91 $_{39}$Y	91.22 $_{40}$Zr	92.91 $_{41}$Nb	95.94 $_{42}$Mo	(99) $_{43}$Tc	101.1 $_{44}$Ru	102.9 $_{45}$Rh	106.4 $_{46}$Pd	107.9 $_{47}$Ag	112.4 $_{48}$Cd	114.8 $_{49}$In	118.7 $_{50}$Sn	121.8 $_{51}$Sb	127.6 $_{52}$Te	126.9 $_{53}$I	131.3 $_{54}$Xe
6	132.9 $_{55}$Cs	137.3 $_{56}$Ba	Lanthanoid	178.5 $_{72}$Hf	180.9 $_{73}$Ta	183.8 $_{74}$W	186.2 $_{75}$Re	190.2 $_{76}$Os	192.2 $_{77}$Ir	195.1 $_{78}$Pt	197.0 $_{79}$Au	200.6 $_{80}$Hg	204.4 $_{81}$Tl	207.2 $_{82}$Pb	209.0 $_{83}$Bi	(210) $_{84}$Po	(210) $_{85}$At	(222) $_{86}$Rn
7	(223) $_{87}$Fr	(226) $_{88}$Ra	Actinoid															
Lanthanoid			138.9 $_{57}$La	140.1 $_{58}$Ce	140.9 $_{59}$Pr	144.2 $_{60}$Nd	(145) $_{61}$Pm	150.4 $_{62}$Sm	152.0 $_{63}$Eu	157.3 $_{64}$Gd	158.9 $_{65}$Tb	162.5 $_{66}$Dy	164.9 $_{67}$Ho	167.3 $_{68}$Er	168.9 $_{69}$Tm	173.0 $_{70}$Yb	175.0 $_{71}$Lu	
Actinoid			(227) $_{89}$Ac	232.0 $_{90}$Th	231.0 $_{91}$Pa	238.0 $_{92}$U	(237) $_{93}$Np	(239) $_{94}$Pu	(243) $_{95}$Am	(247) $_{96}$Cm	(247) $_{97}$Bk	(252) $_{98}$Cf	(252) $_{99}$Es	(257) $_{100}$Fm	(258) $_{101}$Md	(259) $_{102}$No	(262) $_{103}$Lr	

1.4 Block classification of the periodic table and elements

Starting from hydrogen, over 100 elements are constituted as electrons are successively accommodated into 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, and 3*d* orbitals one by one from lower to higher energy levels. When elements with similar properties are arranged in columns, the periodic table of the elements is constructed. The modern periodic table of the elements is based on one published by D. I. Mendeleev in 1892, and a variety of tables have since been devised. The long periodic table recommended by IUPAC is the current standard, and it has the group numbers arranged from Group 1 alkali metals through Group 18 rare gas elements (Table 1.1).

Based on the composition of electron orbitals, hydrogen, helium and Group 1 elements are classified as ***s*-block elements**, Group 13 through Group 18 elements ***p*-block elements**, Group 3 through Group 12 elements ***d*-block elements**, and lanthanoid and actinoid elements ***f*-block elements**. (Fig. 1.2). *s*-Block, *p*-block, and Group 12 elements are called **main group elements** and *d*-block elements other than Group 12 and f-block elements are called **transition elements**. The characteristic properties of the elements that belong to these four blocks are described in Chapter 4 and thereafter. Incidentally, periodic tables that denote the groups of *s*-block and *p*-block elements with Roman numerals (I, II, ..., VIII) are still used, but they will be unified into the IUPAC system in the near future. Since inorganic chemistry covers the chemistry of all the elements, it is important to understand the features of each element through reference to the periodic table.

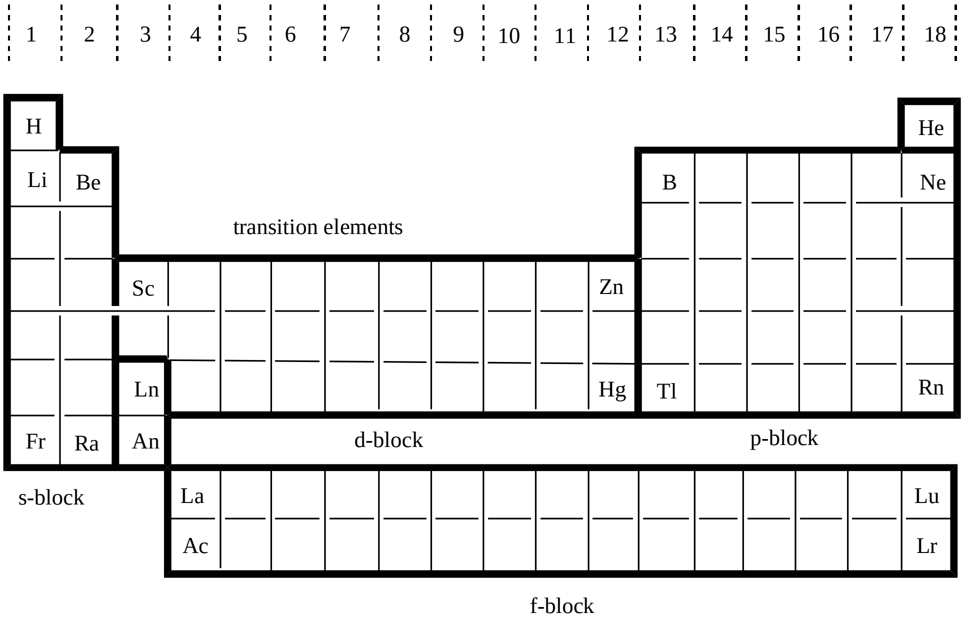

Fig. 1.2 Block classification of elements in the periodic table.

1.5 Bonding states of elements

Organic compounds are molecular compounds that contain mainly carbon and hydrogen atoms. Since inorganic chemistry deals with all compounds other than organic ones, the scope of inorganic chemistry is vast. Consequently, we have to study the syntheses, structures, bondings, reactions, and physical properties of elements, molecular compounds, and solid-state compounds of 103 elements. In recent years, the structures of crystalline compounds have been determined comparatively easily by use of single crystal X-ray structural analysis, and by through the use of automatic diffractometers. This progress has resulted in rapid development of new areas of inorganic chemistry that were previously inaccessible. Research on higher dimensional compounds, such as **multinuclear complexes**, **cluster compounds**, and solid-state inorganic compounds in which many metal atoms and ligands are bonded in a complex manner, is becoming much easier. In this section, research areas in inorganic chemistry will be surveyed on the basis of the classification of the bonding modes of inorganic materials.

(a) Element

Elementary substances exist in various forms. For example, helium and other rare gas elements exist as single-atom molecules; hydrogen, oxygen, and nitrogen as two-atom molecules; carbon, phosphorus, and sulfur as several solid allotropes; and sodium, gold, *etc*. as bulk metals. A simple substance of a metallic element is usually called **bulk metal**, and the word “metal” may be used to mean a bulk metal and “metal atom or metal ion” define the state where every particle is discrete. Although elementary substances appear simple because they consist of only one kind of element, they are rarely produced in pure forms in nature. Even after the discovery of new elements, their isolation often presents difficulties. For example, since the manufacture of ultra high purity silicon is becoming very important in science and technology, many new purification processes have been developed in recent years.

Exercise 1.2 Give examples of allotropes.

[Answer] carbon: graphite, diamond.

Phosphorus: white phosphorus, red phosphorus.

(b) Molecular compounds

Inorganic compounds of nonmetallic elements, such as gaseous carbon dioxide CO_2, liquid sulfuric acid H_2SO_4, or solid phosphorus pentoxide P_2O_5, satisfy the valence requirements of the component atoms and form discrete molecules which are not bonded together. The compounds of main group metals such as liquid tin tetrachloride $SnCl_4$ and solid aluminum trichloride $AlCl_3$ have definite molecular weights and do not form infinite polymers.

Most of the molecular compounds of transition metals are metal complexes and organometallic compounds in which ligands are coordinated to metals. These molecular compounds include not only **mononuclear complexes** with a metal center but also multinuclear complexes containing several metals, or cluster complexes having metal-metal bonds. The number of new compounds with a variety of bonding and structure types is increasing very rapidly, and they represent a major field of study in today's inorganic chemistry (refer to Chapter 6).

(c) Solid-state compounds

Although solid-state inorganic compounds are huge molecules, it is preferable to define them as being composed of an infinite sequence of 1-dimensional (chain), 2-dimensional (layer), or 3-dimensional arrays of elements and as having no definite molecular weight. The component elements of an inorganic solid bond together by means of ionic, covalent, or metallic bonds to form a solid structure. An ionic bond is one between electronically positive (alkali metals *etc*.) and negative elements (halogen *etc*.), and a covalent bond forms between elements with close electronegativities. However, in many compounds there is contribution from both ionic and covalent bonds (see Section 2.1 about bondings).

Exercise 1.3 Give examples of solid-state inorganic compounds.
[Answer] sodium chloride NaCl, silicon dioxide, SiO_2, molybdenum disulfide, MoS_2.

The first step in the identification of a compound is to know its elemental composition. Unlike an organic compound, it is sometimes difficult to decide the empirical formula of a solid-state inorganic compound from elemental analyses and to determine its structure by combining information from spectra. Compounds with similar compositions may have different coordination numbers around a central element and different structural dimensions. For example, in the case of binary (consisting of two kinds of elements) metal iodides, gold iodide, AuI, has a chain-like structure, copper iodide, CuI, a zinc blende type structure, sodium iodide, NaI, has a sodium chloride structure, and cesium iodide, CsI, has a cesium chloride structure (refer to Section 2.2 (e)), and the metal atoms are bonded to 2, 4, 6 or 8 iodine atoms, respectively. The minimum repeat unit of a solid structure is called a **unit lattice** and is the most fundamental information in the structural chemistry of crystals. X-ray and neutron diffraction are the most powerful experimental methods for determining a crystal structure, and the bonds between atoms can only be elucidated by using them. **Polymorphism** is the phenomenon in which different kinds of crystals of a solid-state compound are obtained in which the atomic arrangements are not the same . Changes between different polymorphous phases with variations in temperature and/or pressure, or **phase transitions**, are an interesting and important problem in solid-state chemistry or physics.

We should keep in mind that in solid-state inorganic chemistry the elemental composition of a compound are not necessarily integers. There are extensive groups of compounds, called **nonstoichiometric compounds**, in which the ratios of elements are non-integers, and these non-stoichiometric compounds characteristically display conductivity, magnetism, catalytic nature, color, and other unique solid-state properties. Therefore, even if an inorganic compound exhibits non-integral stoichiometry, unlike an organic compound, the compound may be a thermodynamically stable, orthodox compound. This kind of compound is called a non-stoichiometric compound or **Berthollide compound**, whereas a stoichiometric compound is referred to as a **Daltonide compound**. The law of constant composition has enjoyed so much success that there is a tendency to neglect non-stoichiometric compounds. We should point out that groups of compounds in which there are slight and continuous changes of the composition of elements are not rare.

Problem 1.1 Express the isotopes of hydrogen, carbon, and oxygen using the symbols of the elements with atomic and mass numbers and write the number of protons, neutrons, and electrons in parenthesis.

Superheavy elements

The last element in the ordinary periodic table is an actinoid element lawrencium, Lr, ($Z = 103$). However, elements ($Z = 104 – 109$) "have already been synthesized" in heavy ion reactions using nuclear accelerators. These are 6*d* elements which come under the 5*d* transition elements from hafnium, Hf, to iridium, Ir, and it is likely that their electronic structures and chemical properties are similar. As a matter of fact, only the existence of **nuclides** with very short lives has been confirmed. The trouble of naming the super heavy elements is that the countries of their discoverers, the United States, Russia and Germany, have proposed different names. The tentative names of these elements are:

unnilquadium Une ($Z = 104$), unnilpentium Unp ($Z = 105$), unnilhexium Unh ($Z = 106$), unnilseptium Unq ($Z = 107$), unniloctium Uno ($Z = 108$) and unnilennium Une ($Z = 108$). It has recently been settled that they be named: Rutherfordium $_{104}$Rf, Dubnium $_{105}$Db, Seaborgium $_{106}$Sg, Bohrium $_{107}$Bh, Hassium $_{108}$Hs, and Meitnerium $_{109}$Mt.

"Synthesis" of the element ($Z = 110$), which should come under platinum, was considered the technical limit, but there is a recent report that even the element ($Z = 112$) "was synthesized". In any case, the superheavy elements will run out shortly. It is natural that complications are caused by naming of a new element, because it is a great honor for a scientist to have a new element named after him or her.

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2 Bonding and Structure

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Atomic radii, bond angles, and the valence electrons of the atoms or ions constituting compounds govern the bonding, structure, reactions, and physical properties of the compounds. It is desirable that the chemical properties of known and new compounds can be explained and predicted using universal parameters characteristic of the constituent elements. Inorganic chemistry has developed along with the discovery of new compounds and novel bonding modes. Therefore, it is important to understand the bonding modes, the geometrical and electronic factors governing the bonding, and to learn the basic concepts of molecular orbital theory.

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2.1 Classification of bonding

The bond in which a pair of electrons bind atoms A and B is called a covalent bond, and it is written as A-B or A:B. Since two pairs of electrons are involved in a double bond and three pairs in a triple bond, they are designated by A=B, A≡B or A::B, or A:::B, respectively. The covalent bond is a simple but very useful concept proposed by G. N. Lewis at the beginning of this century and its representation is called the **Lewis structure**. Unshared pair of valence electrons are called lone pairs, and they are expressed by a pair of dots like A:.

Exercise 2.1 Describe the Lewis structures of the nitrogen molecule N_2 and the oxygen molecule O_2.

[Answer] : N:::N: , : O::O :

Eight electrons are required to fill an *s* and three *p* orbitals, and when the total number of electrons used for the bonds and lone pairs is eight, a stable molecular structure results. This is called the **octet rule** and is useful when qualitatively discussing the molecular structures of main group compounds. Of course, this rule is not applied to a hydrogen molecule, H_2, but is applicable to covalent molecules, such as simple two-atomic molecules O_2 or CO and even to complicated organic compounds. For the elements after the 3rd period, the number of covalent bonds is sometimes five (*e.g.* PCl_5) or six (*e.g.* SF_6), and the central atom of these molecules shows **hypervalency**. In this case, because *s* and *p* electrons run short to form more than four 2-electron covalent bonds, it was once believed that *d* electrons were partly involved. The present view is, however, that these hypervalent bonds use only *s* and *p* orbitals but that the bond orders are lower than those of single bonds.

The electrostatic bond between cations (positive ion) and anions (negative ion), such as in sodium chloride, NaCl, is called an ionic bond. Since the total electrical charge in a compound should be zero, the electrical charges of cations and anions are equal. There is a partial contribution from covalent bonds even in an ionic compound, and the ions are not necessarily bonded only by the electrostatic interaction.

Pauling's electroneutrality principle states that the net electrical charge of each component of a compound is essentially neutral. As will be mentioned later, the structures of many solid compounds are described as an alternate array of cations and anions, and are classified into several representative crystal types.

Metal atoms are bound together by means of the **conduction electrons** originating from the valence electrons of metal atoms. The bond due to the conduction electrons in a bulk metal is called the **metallic bond**.

Generally, chemical bonds can be assigned to either of the three kinds mentioned above, but new compounds have been synthesized one after another which cannot always be classified by the simple **2-center electron pair covalent bond**. They include **electron-deficient bonds** in boron hydrides, **coordinate bonds** in transition metal complexes, the **metal-metal bonds** in metal cluster compounds, *etc*., and new concepts have been introduced into bond theory to account for these new kinds of chemical bonds. As has already been described, a weak bonding interaction called the **van der Waals interaction** has been recognized in neutral atomic or molecular compounds. The potential of this interaction is inversely proportional to the 6th power of the distance between atoms. The adjacent but non-bonded distance between atoms is estimated by the sum of the van der Waals radius assigned to each atom.

The weak interaction X-H-Y that a hydrogen atom forms with the atoms X, Y (nitrogen, oxygen, fluoride, *etc*..) with larger electronegativity than that of hydrogen is called the **hydrogen bond**. Hydrogen bonding plays an important role in ice, the structure of the double helix of DNA (deoxyribonucleic acid), *etc*.

2.2 Geometrical factors governing bonding and structure

Two parameters, radii and the electron attracting power of atoms or ions, determine the bonding, structure, and reaction of elementary substances and compounds. Much effort has been devoted to finding numerical values for these two factors applicable to all materials. It is hoped that the chemical properties of a known compound, and of a still non-existent new material, can be predicted with a combination of suitable numerical values. Firstly, geometrical factors will be described.

Table 2.1 Atomic radii (pm)

H 32								
Li 123	Be 89							
Na 154	Mg 136							
K 203	Ca 174	Sc 144	Ti 132	V 122	Cr 118	Mn 117	Fe 117	Co 116
Rb 216	Sr 191	Y 162	Zr 145	Nb 134	Mo 130	Tc 127	Ru 125	Rh 125
Cs 235	Ba 198	La 169	Hf 144	Ta 134	W 130	Re 128	Os 126	Ir 127

			B 82	C 77	N 75	O 73	F 72
			Al 118	Si 111	P 106	S 102	Cl 99
Ni 115	Cu 117	Zn 125	Ga 126	Ge 122	As 120	Se 117	Br 114
Pd 128	Ag 134	Cd 148	In 144	Sn 140	Sb 140	Te 136	I 133
Pt 130	Au 134	Hg 149	Tl 148	Pb 147	Bi 146		

(a) Atomic and ionic radii

The electron density in atoms gradually approaches, but never reaches, zero as the distance from the nucleus increases. Therefore, strictly speaking the radius of an atom or ion is indeterminable. However, it is possible to determine the bond distance between atomic nuclei experimentally. Atomic radii determined experimentally are one of the most important atomic parameters describing the structural chemistry of compounds. It is reasonable to define the metal radius of a bulk metal as half of the distance between metal atoms. Half of the distance between atoms is defined also as the **covalent radius** of a covalent elementary substance (Table 2.1).

Table 2.2 Ionic radii (in pm).*

Li$^+$(4) 59	Be^{2+}(4) 27	B^{3+}(4) 11	N^{3+}(6) 16	O^{2-}(6) 140	F$^-$(6) 133
Na$^+$(6) 102	Mg^{2+}(6) 72	Al^{3+}(6) 54	P^{3+}(6) 44	S^{2-}(6) 184	Cl$^-$(6) 181
K$^+$(6) 138	Ca^{2+}(6) 100	Ga^{3+}(6) 62	As^{3+}(6) 58	Se^{2-}(6) 198	Br$^-$(6) 196
Rb$^+$(6) 152	Sr^{2+}(6) 118	In^{3+}(6) 80		Te^{2-}(6) 221	I$^-$(6) 220
Cs$^+$(6) 167	Ba^{2+}(6) 135	Tl^{3+}(6) 89			

*Numbers in parentheses are the coordination number of the ions.

Since the cations and anions of different elements in an ionic compound are bonded by electrostatic interactions, the bond distance is the sum of **ionic radii** assigned to the cation and anion. The standard ionic radius of one species is fixed first and is then subtracted from the distance between ions to decide the radius of the partner ion. As the standard, the radius of O^{2-} ion in a number of oxides is set to 140 pm (1 pm = 10^{-12} m) (R. D. Shannon). Cationic radii in oxides are the difference between the bond distance and 140 pm. After cation radii in oxides are decided, other anion radii can be calculated by subtraction of the cation radii from the distances between the atoms in ionic compounds. By applying such methods to many ionic compounds, ionic radii have been compiled in such a way that experimental and calculated values are generally consistent (Table 2.2).

Even ionic compounds have some covalent contribution and it is not expected that calculated and experimental bond distances will agree exactly. Even if the ionic radius assigned to a standard ion is changed, we can still compile a set of ionic radii that are consistent across many compounds. Other examples of the proposed radii of O^{2-} ion are 132 pm (V. M. Goldschmidt) or 60 pm (J. C. Slater). We must also be mindful that the cation-anion distances of the same ion pair become larger as the **coordination number** of opposite ions increases. Therefore, in any discussion of the structural features of ionic compounds from a viewpoint of ionic radii, a set of the ionic radii calculated using the same standard radius for the compounds with the same coordination number should be used.

Exercise 2.2 Which ionic radius is larger, Cs$^+$ or F$^-$?

[Answer] Cs$^+$(167 pm) > F$^-$(133 pm). The anion radius is not always larger.

The metal and covalent radii, also called the **atomic radii**, become smaller in the same period of the periodic table as the group of the element goes to the right and then increase again in the next period. The **lanthanide contraction** is responsible for the 5th period (4*d*) elements having almost the same atomic radii as those of the 6th period (5*d*) ones. In the periodic table, the lanthanide elements are inserted before the 5*d* elements. The atomic radii of lanthanide elements decrease noticeably as the effective nuclear charge increases because the screening effects of the 4*f* orbitals of lanthanide elements are weak due to their orbital shapes. Consequently, the atomic radii of the elements following lanthanides are very similar to those of the 4*d* elements.

(b) Lattice enthalpy

Although the stability of a crystal at constant temperature and pressure depends on the Gibbs free energy change of the crystal’s formation from its constituent ions, the stability of a crystal is determined mostly by the enthalpy change alone since the lattice formation is very exothermic, and the entropy term is negligibly small (refer to Section 3.1). **Lattice enthalpy,** ΔH_L, is defined as the standard enthalpy change of the reaction in which an ionic crystal decomposes into gaseous ions (s is solid, g is gas and L is lattice).

$$\mathrm{MX(s)} \rightarrow \mathrm{M^{+}(g)} + \mathrm{X^{-}(g)} \qquad \Delta H_{\mathrm{L}}$$

Lattice enthalpy is indirectly calculated from the values of the enthalpy change at each stage using a Born-Haber cycle (Fig. 2.1). Namely, a closed cycle is formed using enthalpy data; standard enthalpy of formation ΔH_f of an ionic crystal from elements, sublimation enthalpy of an elementary solid, or atomization enthalpy ΔH_{atom} corresponding to the dissociation enthalpy of a gaseous elementary molecule, the ionization enthalpy $\Delta H_{ion,}$ which is the sum of the ionization enthalpy of cation formation and electron acquisition enthalpy of anion formation. Lattice enthalpy is calculated using the relation that enthalpy change in a cycle is zero.

$$\Delta H^{0}_{\mathrm{atom}} + \Delta H^{0}_{\mathrm{ion}} - \Delta H^{0}_{\mathrm{L}} - \Delta H^{0}_{\mathrm{f}} = 0$$

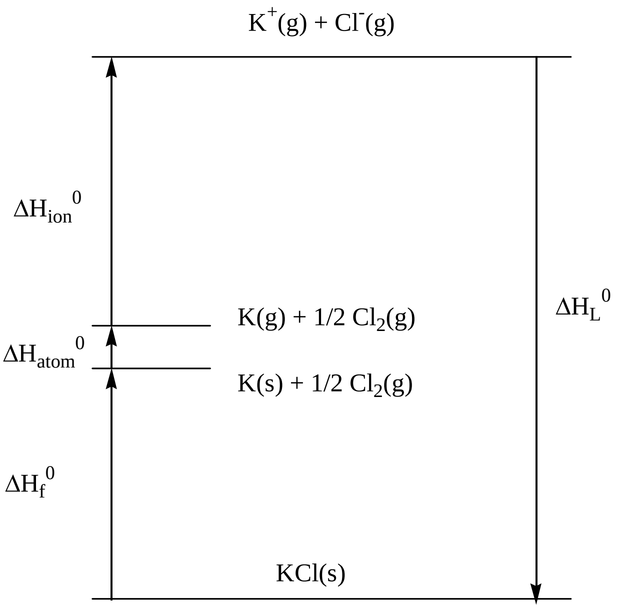


Fig. 2.1 Born-Haber cycle of KCl.

(c) Madelung constant

The total Coulomb potential energy that exists between the ions in an ionic crystal consisting of ions A and B should be the sum of the individual Coulomb potential energies V_{ab}. Since the locations of the ions in the crystal lattice are decided by the structure type, the total Coulomb potential between all ions is calculated by setting the distance between the ions to d. A is the **Madelung constant** that is characteristic of each crystal type (Table 2.3).

$$V = N_A \frac{e^2}{4\pi\varepsilon_0}\left(\frac{z_A z_B}{d}\right) \times A$$

N_A is Avogadro's constant and z_A and z_B are the electric charges of the cation and anion. The electrostatic interaction between contiguous ions is the strongest, and the Madelung constant generally becomes larger as the coordination number increases. Because the electrical charges have opposite signs, the potential becomes negative, indicating the stabilization that accompanies the formation of a crystal lattice from well dispersed, gaseous phase ions. Although it is generally true that the lowest electrostatic potential leads to the most stable structure, this is not strictly correct since there are also other interactions to consider.

Table 2.3 Madelung constants

Structural type	A
Rock-salt	1.748
Cesium chloride	1.763
Sphalerite	1.638
Wurtzite	1.641
Fluorite	2.519
Rutile	2.408

The second largest factor that contributes to the lattice enthalpy is the van der Waals force, and **dispersion forces** or the **London interaction** is the main origin of this force. It is an attractive interaction between electric dipoles, which is inversely proportional to the 6th power of the distance *d* between ions. The van der Waals force is very small.

$$V = -\frac{N_{\mathrm{A}}C}{d^6}$$

The value of the constant *C* is a function of each compound. Since it is at most 1% of the Coulombic force, it may be safely neglected in the calculation of lattice enthalpy.

(d) Structure of metal crystals

If we imagine metal atoms as being hard balls, when densely packed in two dimensions each ball will be in contact with six other balls (A). When another layer of this 2 dimensional arrangement is placed on top of the first, the packing will be densest and the structure most energetically stable when the metal atoms are placed on top of the hollows (B) of the first layer. When a 3rd layer is placed on top of the 2nd layer, there are two possibilities. Namely, the 3rd layer (A) overlaps with the 1st layer (A) or the 3rd layer (C) overlaps with neither (A) nor (B). The ABAB...-type packing is called **hexagonally close-packed** (hcp) (Fig. 2.2), and the ABCABC...-type is called **cubic close-packed** (ccp) (Fig. 2.3). In both cases, each ball is surrounded by 12 balls, that is, it is 12-coordinated. The coordination polyhedron of hcp is anti-cubooctahedron,

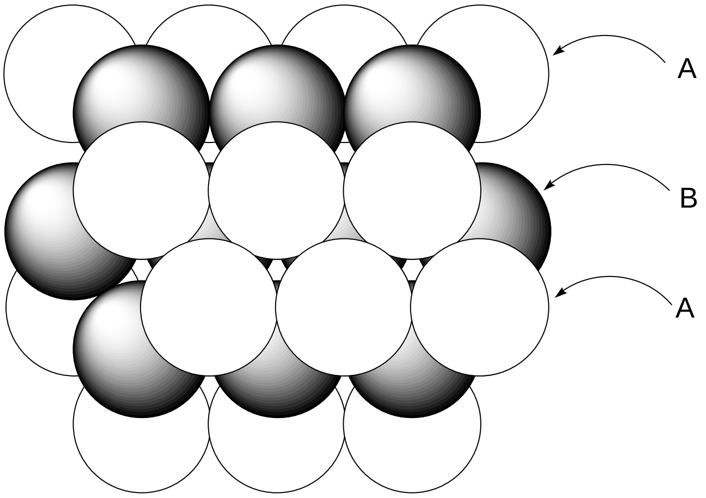


Fig. 2.2 Hexagonally close-packed (hcp) of balls.

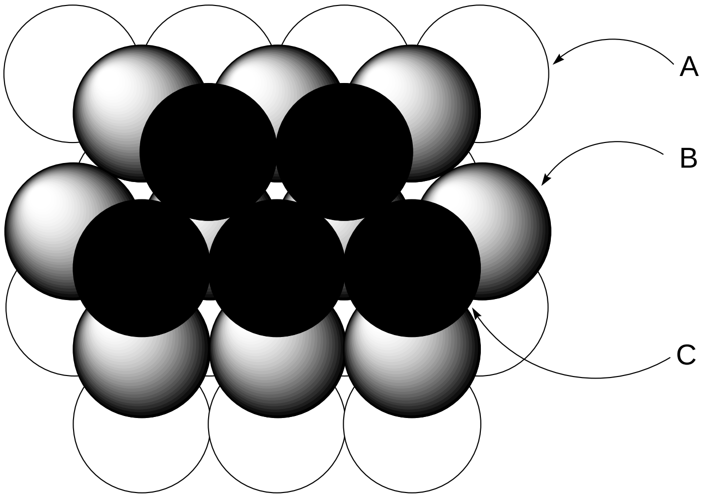
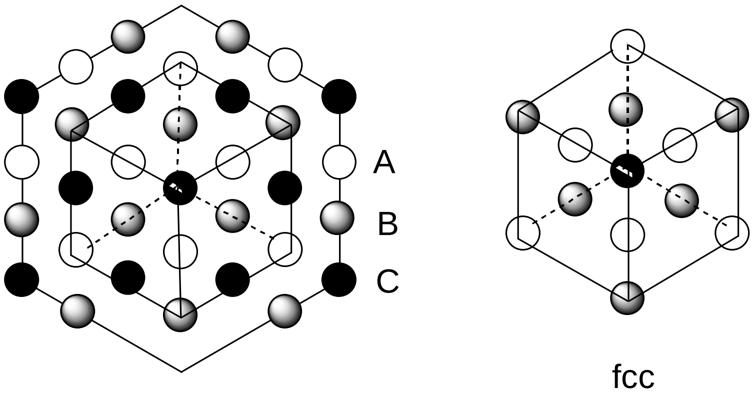


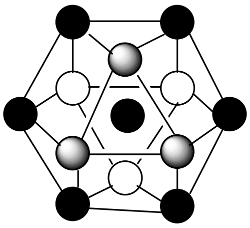
Fig. 2.3 Cubic close-packed (ccp) of balls.

and that of ccp is cubooctahedron. When the lattice is sliced in different planes, the unit lattice of ccp appears to be a **face-centered cubic lattice** (fcc), containing a ball at each cubical apex and on the center of each face (Fig. 2.4). The unit lattice of hcp is a rhombohedral prism in which two balls are located in the positions shown in (Fig. 2.5). There are several different modes of piling up layers other than the normal hcp and ccp,



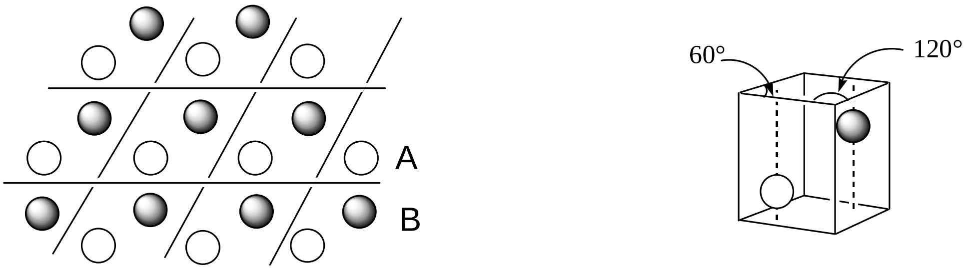
ccp

fcc



cuboctahedron

Fig. 2.4 Different expressions of cubic close-packed.



hcp

rhombohedral prism

Fig. 2.5 Different expressions of hexagonally close-packed.

and many examples are known.

The lattice with another ball at the center of a cubic lattice consisting of eight balls is the **body centered cubic lattice** (bcc), and some metals assume this mode of packing.

The ratio of space occupation in a bcc lattice is smaller than that of close-packed ones but the difference is not large. Although the central ball is formally 8-coordinated, it is essentially 14-coordinated since there are a further six balls only 15.5% more distant than the first eight balls. However, because of the smaller ratio of space occupation, bcc appears relatively rarely and pure metals tend to adopt hcp or ccp.

In both hcp and ccp, the cavities among the balls are either the O_h holes enclosed octahedrally by six balls or the T_d holes enclosed tetrahedrally by four balls (Fig. 2.6). (O_h and T_d are the symmetry symbols used in group theory.) In ionic solids, if the anions are in hcp or ccp arrangements, cations enter into either of these cavities.

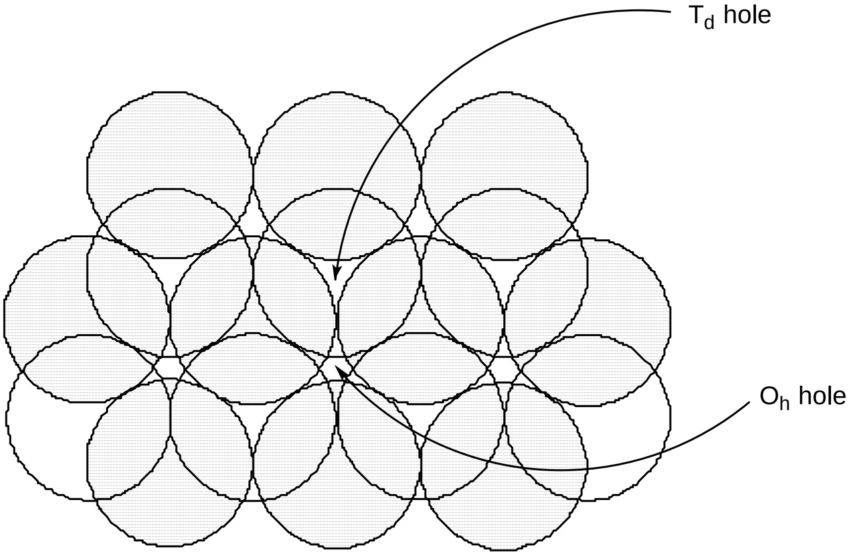


Fig. 2.6 Octahedral and tetrahedral holes.

(e) Ionic crystal

In ionic crystals, such as metal halides, oxides, and sulfides, metal cations and anions are aligned alternately, and the solid is bound together mainly by electrostatic bonding. Many metal halides dissolve in polar solvents, *e.g.* sodium chloride NaCl dissolves in water; whereas metal oxides and sulfides, in which there is a significant contribution of covalent bonding, are usually insoluble even in the most polar of solvents. The fundamental structure of ionic crystals is that larger ions (usually anions) are close-packed and smaller ions (usually cations) enter into the octahedral or tetrahedral cavities between them. Ionic crystals are classified into several typical structures according to the kinds of cations and anions involved and their ionic radii. Each structure type is called by the name of the typical compound, just as the rock salt structure representing the structures of not only NaCl (rock salt) but also various other compounds.

Representative structure types of solid compounds and examples belonging to each type are shown in Table 2.4.

Table 2.4 Crystal types of solid-state compounds

Crystal type	Coordination number	Examples of compounds
Rock-salt	(6,6)	LiCl, NaCl, KBr, RbI, AgCl, MgO, NiO, InP
Cesium chloride	(8,8)	CsCl, CsBr, CsI, CuZn
Sphalerite	(4,4)	ZnS, CdS, HgS, CuCl, GaP
Fluorite	(8,4)	CaF_2, SrF_2, CdF_2, ZrO_2, UO_2
Rutile	(6,3)	TiO_2, SnO_2, RuO_2, NiF_2
Cadmium iodide	(6,3)	CdI_2, CoI_2, $Mg(OH)_2$
Rhenium oxide	(6,2)	ReO_3, WO_3, $Sc(OH)_3$
Perovskite	(6,2)	$CaTiO_3$, $BaTiO_3$, $SrTiO_3$

Rock-salt structure Sodium chloride NaCl is a typical compound in which Cl^- anions are arranged in ccp and Na^+ cations occupy all the octahedral holes (O_h holes) (Fig. 2.7). Each Na^+ cation is surrounded by six Cl^- anions. The same structure results even if the positions of anions and cations are exchanged. In the case of the reversed structure, each Cl^- anion is surrounded by six Na^+ cations. Namely, each ion is 6-coordinated and it is convenient to describe the structure as the (6,6)-structure. The number of ions in a unit lattice is calculated by summing up the ions shown in Fig. 2.7. Since there is one ion inside the lattice, the ions on the faces of the lattice are shared by 2, on the edges by 4, and on the corners by 8 lattices, a net of 4 Cl ions belonging to the unit lattice of NaCl is obtained by multiplying the numbers of ions inside the lattice by 1, on the faces by 1/2, on the edges by 1/4 and on the corners by 1/8. The number of Na ions in the unit lattice is also 4 and the ratio of Cl and Na ions agrees with the formula NaCl.

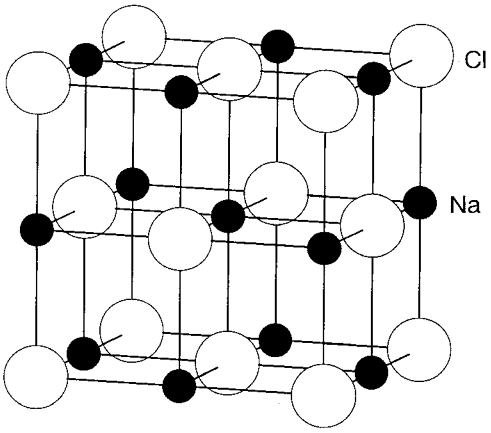


Fig. 2.7 Rock-salt structure.

Cesium chloride structure Cesium chloride, CsCl, is a typical example of the structure shown in Fig. 2.8. There is a Cs^+ ion at the center and eight Cl^- are located at the eight corners of the cube. Conversely, even if a Cl^- comes to the center and eight Cs^+ come to the corners, the number of each ion in the unit lattice is the same. Thus, this is referred to as the (8, 8)-structure. Since there is one Cs^+ and one Cl^- ion belonging to this unit lattice, it coincides with the formula CsCl.

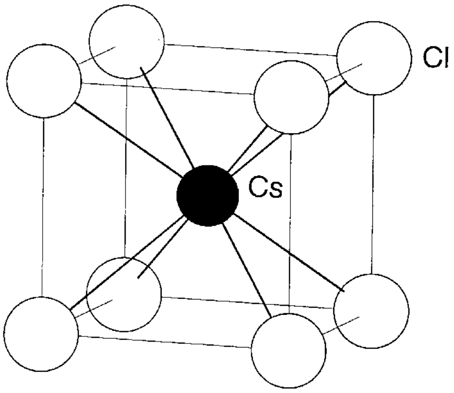


Fig. 2.8 Cesium chloride structure.

Zinc blende structure Zinc blende has the composition ZnS and its unit lattice is shown in Fig. 2.9. S^{2-} anions are arranged in ccp and Zn^{2+} cations occupy half of the tetrahedral holes (T_d holes). In this arrangement, each cation is coordinated by four anions, and each anion by four cations. Hence, this is a (4, 4)-structure. There are both four Zn^{2+} and S^{2-} ions belonging to this unit lattice and the atomic ratio coincides with the formula of ZnS.

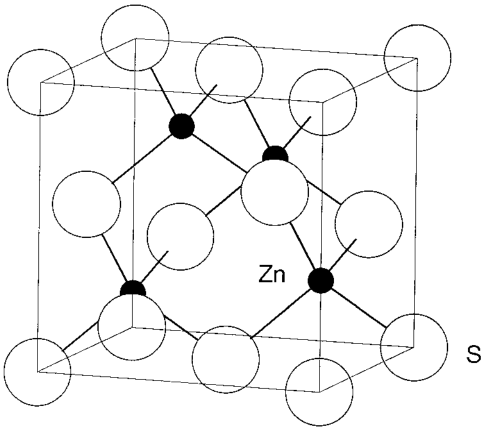


Fig. 2.9 Zinc blende structure.

Fluorite structure The composition of fluorite is CaF_2. Since the number of F^- is twice that of Ca^{2+}, all the tetrahedral holes of Ca^{2+} arranged in ccp are occupied by F^-, as shown in Fig. 2.10. There are four Ca^{2+} and eight F^- ions and the number of ions is 4 times the formula. The anti-fluorite structure exchanges the cations and anions, and is exemplified by potassium oxide K_2O, *etc*.

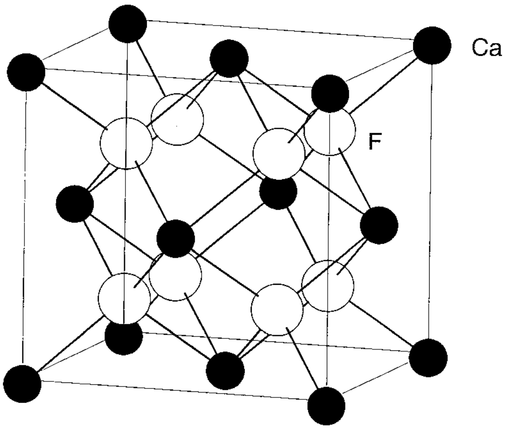


Fig. 2.10 Fluorite structure.

Exercise 2.3 How many cations and anions are there in a unit lattice of zinc blende structure?

[Answer] All four cations are included in a unit lattice . The anions occupy the 8 corners and 6 faces and the number is 8 x 1/8 + 6 x 1/2 = 4.

(f) Radius ratio

Generally, the total Coulombic potential energy E_c of the univalent ionic compound MX is expressed by the following formula.

$$E_{\mathrm{c}} = -\frac{N_{\mathrm{A}} e^2}{4\pi\varepsilon_0 R} A$$

N_A is the Avogadro constant, A the Madelung constant and R the distance between ions. According to this formula, a structure with a larger A / R ratio is more stable. The Madelung constant of an MX compound increases with increasing coordination number. On the other hand, it is advantageous to lower the coordination number and to reduce R in the case of small M, rendering contact between M and X more difficult. In an ionic crystal, the ratio of r_M and r_X with the anions contacting each other and also with the cations depends on the coordination number.

In a partial structure consisting only of anions, the anions form a coordination polyhedron around a cation. The anionic radius r_X is one half of the distance of the edge of the polyhedron and the distance from the cation center to an apex of the polyhedron is the sum of the anion and cation radii $r_\mathrm{X} + r_\mathrm{M}$. The coordination polyhedron of the CsCl structure is a cube, the NaCl structure an octahedron, and the ZnS structure a tetrahedron. The distance from the center of each polyhedron to an apex is $\sqrt{3}r_\mathrm{X}$, $\sqrt{2}r_\mathrm{X}$, $\frac{\sqrt{6}}{2}r_\mathrm{X}$. Therefore, the ratios of the cationic and anionic radii r_M / r_X are $(\sqrt{3}r_\mathrm{X} - r_\mathrm{X})/r_\mathrm{X} = \sqrt{3} - 1 = 0.732$ for CsCl, $(\sqrt{2}r_\mathrm{X} - r_\mathrm{X})/r_\mathrm{X} = \sqrt{2} - 1 = 0.414$ for NaCl, and $\left(\frac{\sqrt{6}}{2}r_\mathrm{X} - r_\mathrm{X}\right)/r_\mathrm{X} = \sqrt{6}/2 - 1 = 0.225$ for ZnS structures (Fig. 2.11) .

It has been explained that the coordination number decreases when these radius ratios are smaller than the given values since cations and anions do not come into contact with each other, causing instability. On the other hand, the coordination number increases for larger cations, increasing the radius ratio. However, the relation between a coordination number and a radius ratio is not simple. For example, halides of alkali metals adopt the NaCl structures at normal temperatures except cesium chloride CsCl, cesium bromide CsBr and cesium iodide CsI. It is not possible to assume structure types from the radius ratios even in the case of simple ionic compounds like alkali metal halides. However, the qualitative trend that smaller cations have smaller coordination numbers is generally correct.

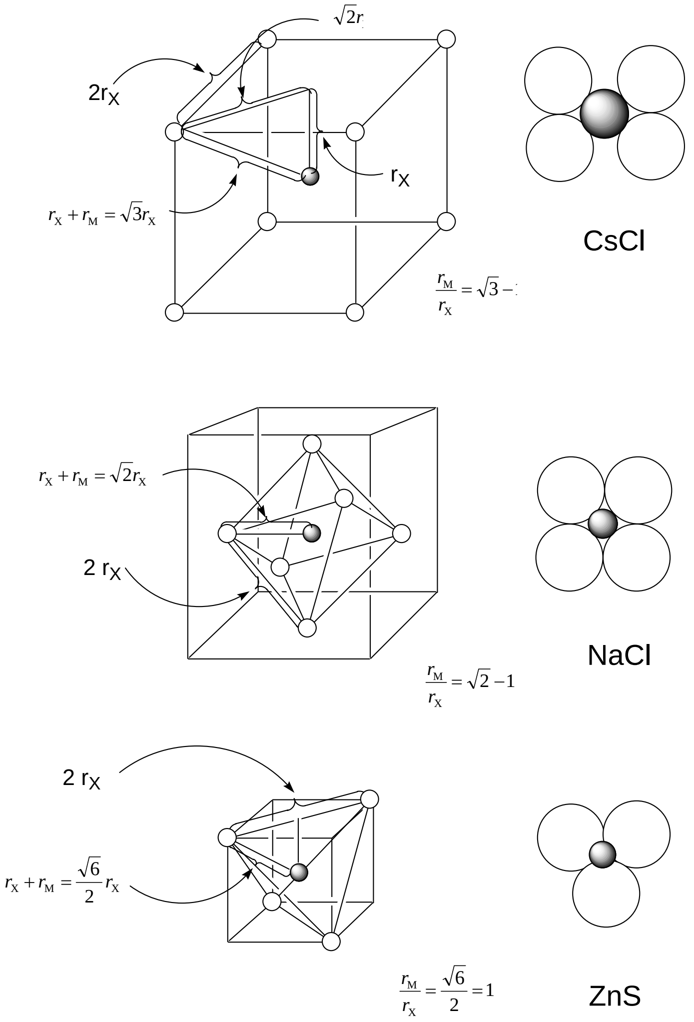


Fig. 2.11 The radius ratio r_M / r_X of cations and anions.

(g) Variation of the solid structure expression

Many solid-state inorganic compounds have complicated three-dimensional structures. Different structural illustrations for the same compound help our understanding of its structure. In the case of complicated inorganic compounds, drawing bond lines between atoms, as in most organic compounds, causes confusion. The anions in many metal oxides, sulfides, or halides form tetrahedra or octahedra around the central metal cations. Although there is no bond between anions, the structures are greatly simplified if they are illustrated by the anion polyhedra sharing apexes, edges, or faces. In such illustrations, cationic metal atoms are usually omitted. As has been mentioned, ionic solid structures can be thought of as a close packed arrays of anions.

Figures 2.12 and 2.13 illustrate these three representations for molecular phosphorus pentoxide P_2O_5 (= P_4O_{10}) and molybdenum pentachloride $MoCl_5$ (= Mo_2Cl_{10}).

Polyhedral representations are much easier to understand for the structures of large molecules or solid-state compounds formed by an infinite number of atoms. However, the bond line representation is suitable for molecular compounds such as the above examples.

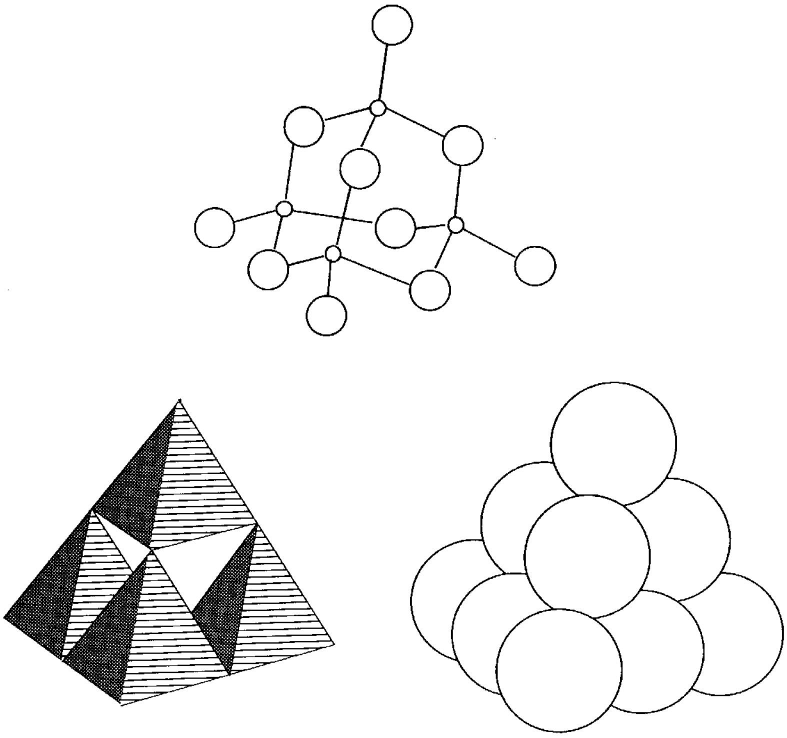


Fig. 2.12 Three expressions for the structure of P_4O_{10}.

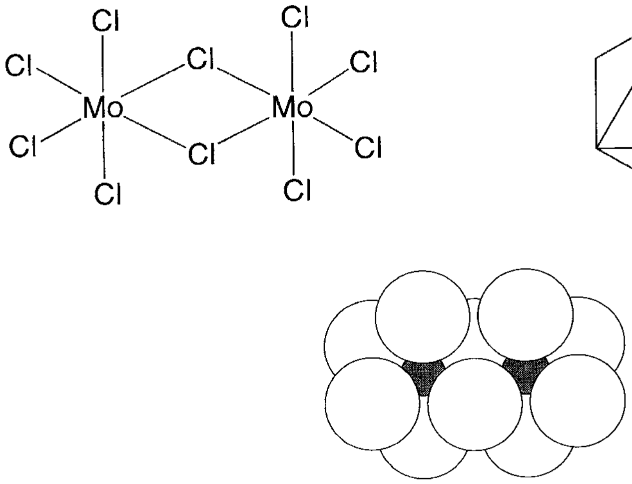


Fig. 2.13 Three expressions for the structure of Mo_2Cl_{10}.

2.3 Electronic factors which govern bonding and structure

The bonding and structure of a compound are determined by electronic properties such as the power of constituent atoms to attract or repel electrons, the molecular orbitals occupied by valence electrons, *etc*. Geometrical arrangements of atoms are also influenced by the electronic interactions between non-bonding electrons. Here, some fundamental concepts are described.

(a) Effective nuclear charge

Since the positive nuclear charge is generally offset by the negative charge of the internal electrons in the electron shell inside the valence electrons, the nuclear charge that valence electrons feel is smaller than the integer charge, Ze for an atomic number Z. This reduction is expressed by the **shielding constant** σ, and the net nuclear charge is called the **effective nuclear charge**, $Z_{\mathrm{eff}}\,\mathrm{e}$.

$$Z_{\mathrm{eff}} = Z - \sigma$$

The effective nuclear charge varies with different electron orbitals and distances from the nucleus.

(b) Ionization energy

Ionization energy is defined as the minimum energy required to remove an electron from the atom in a gaseous phase (g), as shown in the following equation. Ionization energy is expressed in units of electron volt (eV), where 1eV = 96.49 $\mathrm{kJmol^{-1}}$.

$$\mathrm{A(g)} \rightarrow \mathrm{A^{+}(g)} + \mathrm{e^{-}(g)}$$

The 1st ionization energy, which removes the outermost electron, is the smallest, and the 2nd and 3rd ionization energies, which further ionize cations, increase rapidly. The ionization enthalpy, which is the standard enthalpy change of the ionization process and is used in thermodynamic calculations, is the ionization energy multiplied by RT (R is the universal gas constant 8.31451 $\mathrm{JK^{-1}mol^{-1}}$ and T is temperature, 2.479 kJ (0.026 eV), at room temperature). The difference between these two parameters is small. The 1st ionization energy varies periodically with atomic number across the periodic table, with the lower left (cesium, Cs) being the smallest and the upper right (helium, He) the largest.

It is understandable that alkali metals generally have the lowest ionization energies because they are stabilized by removal of an *s* electron to attain the rare gas configuration. Rare gas elements have stable electronic structures, and their ionization energies are the largest. Although the ionization energy increases almost monotonically from alkali metals to rare gases in each period, there are reversals at several places, such as nitrogen N and oxygen O, and phosphorus P and sulfur S. The 1st ionization energies are given in Table 2.5.

Table 2.5 Electronic parameters of atoms (eV). I: 1st ionization energy, A_e: electron affinity, χ_M: electronegativity (Mulliken)

atom	I	A	χ	atom	I	A	χ	atom	I	A	χ
H	13.60	0.75	7.18	Cr	6.77	0.67	3.72	Cd	8.99		
He	24.59			Mn	7.44			In	5.79	0.30	3.10
Li	5.39	0.62	3.01	Fe	7.90	0.15	4.03	Sn	7.34	1.11	4.23
Be	9.32			Co	7.88	0.66	4.27	Sb	8.64	1.07	4.86
B	8.30	0.28	4.29	Ni	7.64	1.16	4.40	Te	9.01	1.97	5.49
C	11.26	1.27	6.27	Cu	7.73	1.24	4.48	I	10.45	3.06	6.76
N	14.53			Zn	9.99			Xe	12.13		
O	13.62	1.46	7.54	Ga	6.00	0.30	3.20	Cs	3.89	0.47	2.18
F	17.42	3.40	10.41	Ge	7.90	1.23	4.61	Ba	5.21	0.15	2.68
Ne	21.56			As	9.82	0.81	5.31	La	5.58	0.50	3.09
Na	5.14	0.55	2.85	Se	9.75	2.02	5.89	Hf	6.83	0.00	3.42
Mg	7.65			Br	11.81	3.36	7.59	Ta	7.89	0.32	4.11
Al	5.99	0.44	3.22	Kr	14.00			W	7.98	0.82	4.40
Si	8.15	1.39	4.77	Rb	4.18	0.49	2.34	Re	7.88	0.15	0.40
P	10.49	0.75	5.62	Sr	5.69	0.11	2.90	Os	8.70	1.10	4.90
S	10.36	2.08	6.22	Y	6.22	0.31	3.27	Ir	9.10	1.60	5.40
Cl	12.97	3.61	8.29	Zr	6.63	0.43	3.53	Pt	9.00	2.13	5.61
Ar	15.76			Nb	6.76	0.89	3.83	Au	9.23	2.31	5.77
K	4.34	0.50	2.42	Mo	7.09	0.75	3.92	Hg	10.44		
Ca	6.11	0.02	3.07	Ru	7.36	1.05	4.26	Tl	6.11	0.20	3.16
Sc	6.56	0.19	3.38	Rh	7.46	1.14	4.30	Pb	7.42	0.36	3.89
Ti	6.83	0.08	3.45	Pd	8.34	0.56	4.45	Bi	7.29	0.95	4.12
V	6.75	0.53	3.64	Ag	7.58	1.30	4.44				

(c) Electron affinity

Electron affinity is the negative of the electron-gain enthalpy ΔH_{eg} of an atom in a gas phase, as shown in the following equation and denoted by A_e (= $-\Delta H_{eg}$) (Table 2.5).

$$\mathrm{A(g) + e^-(g) \rightarrow A^-(g)}$$

It may be regarded as the ionization enthalpy of an anion. Since halogen atoms achieve rare gas electron configurations if an electron is added to them, their electron affinities are large.

(d) Electronegativity

Electronegativity is one of the most fundamental atomic parameters which expresses numerically the tendency to attract electrons to atoms in a molecule. It is very useful in explaining differences in bonding, structure, and reaction from the standpoint of atomic properties. Various schemes have been proposed to explain the theoretical basis of the power of electron attraction, and studies are still actively seeking new numerical values of electronegativity. The Pauling scale, introduced first in 1932, is still the most frequently used , and subsequent new numerical values have been justified if they are close to those of Pauling.

L. Pauling defined electronegativity as the quantitative ionic character of bonds. Originally, the following equation was proposed as a formula to define the ionic character of the bond between atoms A and B.

$$\Delta = D(\mathrm{AB}) - \frac{1}{2}(D(\mathrm{AA}) + D(\mathrm{BB}))$$

where D is the bond energy of a covalent bond. However, it turned out that Δ is not necessarily positive, and Pauling modified the definition

$$\Delta = D(\mathrm{AB}) - \sqrt{D(\mathrm{AA}) \times D(\mathrm{BB})}$$

and redefined it as the ionic character of the A-B bond. Furthermore, electronegativity χ was defined in such a way that the difference of the electronegativities of atoms A and B is proportional to the square root of the ionic character. Here, the coefficient

$$|\chi_{\mathrm{A}} - \chi_{\mathrm{B}}| = 0.208\sqrt{\Delta}$$

0.208 is so determined that the electronegativity of hydrogen H becomes 2.1 when bond energies are expressed in kcal mol^{-1}. Since Pauling electronegativities increase the higher the oxidization states of an atom, these values correspond to the highest oxidization number of each element. The electronegativities calculated using recent values of bond energies are shown in Table 2.6.

Table 2.6 Pauling electronetativities

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.2																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 2.0	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.0
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66	Xe 2.6
6	Cs 0.79	Ba 0.89	Lanthanoid	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 2.04	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	Actinoid															

A. L. Allred and E. G.. Rochow defined electronegativity as the electric field Z_{eff} / r^2 on the atomic surface. They added a constant in order to make the electronegativity χ_{AR} as near as possible to the Pauling values by using *r* for the covalent bond radius of atoms.

$$\chi_{AR} = 0.74 + 0.36 \frac{Z_{eff}}{r^2}$$

It turns out that elements with small covalent radii and large effective nuclear charges have large electronegativities (Table 2.6).

R. Mulliken defined electronegativity χ_M as the average of the ionization energy I and electron affinity A_e as follows (Fig. 2.14).

$$\chi_M = \frac{1}{2}(I + A_e)$$

As ionization energy is the energy of electronic excitation from the HOMO and electron affinity the energy of electron addition to the LUMO (refer to Section 2.3 (e)), in this definition electronegativity can also be called the average value of the energy levels of the HOMO and LUMO. Those elements which are hard to ionize and easy to attract electrons have large values. Although the electronegativity is defined for the atoms in a valence state in a molecule and has the dimensions of energy, it is treated as a dimensionless number (Table 2.5).

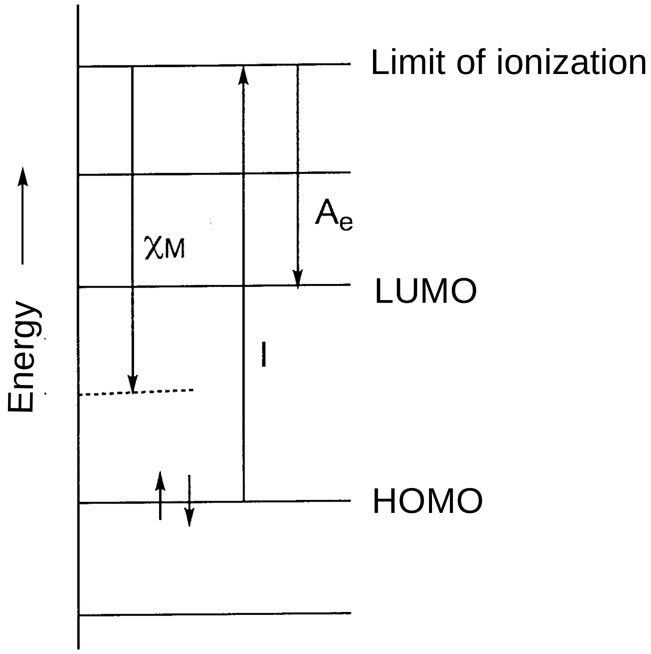


Fig. 2.14 Mulliken electronegativity.

Although the definition of Mulliken is intelligible since it is directly related to atomic orbitals, generally the values of Pauling or Allred-Rochow are used. As these values are not much different, the Pauling electronegativity is appropriate when choosing only one. Electronegativity values change not only by definition, but are also considerably affected by the bonding state of atoms, and they should be used with considerable caution. The electronegativities of the constituent atoms are fundamental to explaining the differences in bonding, structure, and reactions of compounds. Therefore theoretical chemists continue in their efforts firmly to extend the foundations of this parameter.

Exercise 2.4 Describe the numerical tendency of electronegativities of the elements in the periodic table.

[Answer] They increase toward the right and decrease down the table. Namely, the electronegativity of alkali metal Cs is the smallest and that of fluorine F is the largest.

(e) Molecular orbitals

The wave functions of electrons in an atom are called **atomic orbitals**. Since the probability of finding electrons in a molecular orbital is proportional to the square of a wave function, the electron map looks like a wave function. A wave function has domains of positive and negative amplitude called lobes. The overlapping positive lobes or negative lobes of the wave functions of atoms in a molecule amplify each other to form a bond, but the positive and negative lobes cancel each other forming no bond. The extent of this interference effect corresponds to the magnitude of the overlap integral in quantum chemistry.

In the formation of a molecule, atomic orbitals overlap to generate a **molecular orbital** which is the wave function of the electrons in the molecule. The number of molecular orbitals is the sum of the atomic orbitals and these molecular orbitals are classified into **bonding, nonbonding, or antibonding molecular orbitals** by the extent of their participation in the bond between atoms. The conditions of the formation of a bonding molecular orbital are as follows.

[Conditions of the formation of bonding molecular orbitals]

(1) The lobes of the atomic orbitals of the constituent atoms are suitable for an overlap.
(2) The positive or negative sign of the overlapping lobes is the same.
(3) The energy levels of atomic orbitals are close.

The simplest case where a molecular orbital is constructed from atomic orbitals A and B is explained here. A bonding molecular orbital is formed between A and B if the above mentioned conditions (1), (2), and (3) are satisfied, but if the sign of one of the atomic orbitals is reversed, condition (2) is not satisfied and an antibonding molecular orbital, in which the signs of the overlapping lobes are different (Fig. 2.15) results. The energy level of a bonding orbital is lower and the level of an antibonding orbital is higher than those of the constituent atomic orbitals. The larger the energy difference of a bonding and an antibonding orbital, the stronger the bond. When there is no bonding or antibonding interaction between A and B, the resultant molecular orbital is a nonbonding orbital. Electrons occupy the molecular orbitals in order of lowest to highest energy levels. The highest occupied molecular orbital is called the **HOMO** and the lowest unoccupied one the **LUMO**. Ken'ichi Fukui (1981 Nobel prize) named these orbitals **frontier orbitals**.

Two or more molecular orbitals of equal energy are called **degenerate orbitals**. The symbol of a nondegenerate orbital is *a* or *b*, a doubly degenerate orbital *e*, and triply degenerate orbital *t*. The symbol *g* (gerade) is attached as a suffix to the centrosymmetric orbital and *u* (ungerade) to the orbital which changes sign under inversion around an inversion center. The number before the symmetry symbol is used in order of energy to distinguish orbitals of the same degeneracy. Additionally, they are named **sigma(σ) or pi(π) orbitals** according to the orbital character. A sigma orbital has rotation symmetry around the bond axis, and a pi orbital has a nodal plane . Therefore, sigma bonds are formed by the overlap of *s-s, p-p, s-d, p-d,* and *d-d* orbitals (Fig. 2.16) and pi bonds the overlap of *p-p, p-d,* and *d-d* orbitals (Fig. 2.17).

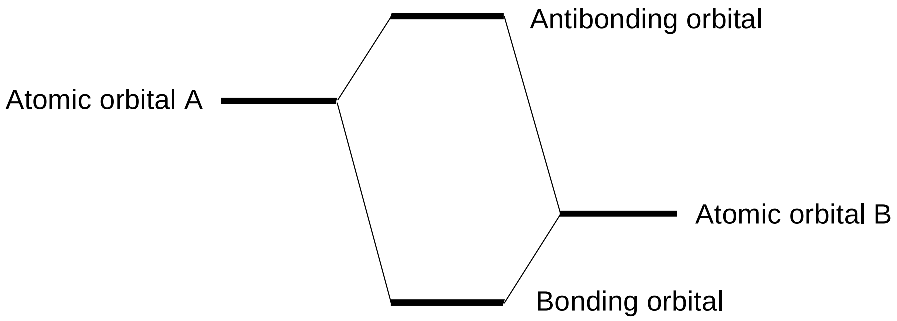
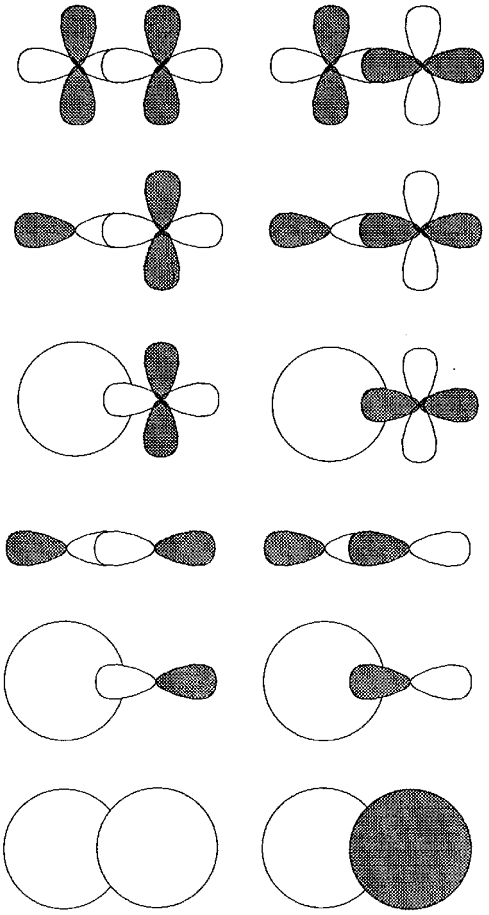


Fig. 2.15 Construction of molecular orbitals.



Bonding σ orbital   Antibonding σ* orbital

Fig. 2.16 The σ molecular orbitals.

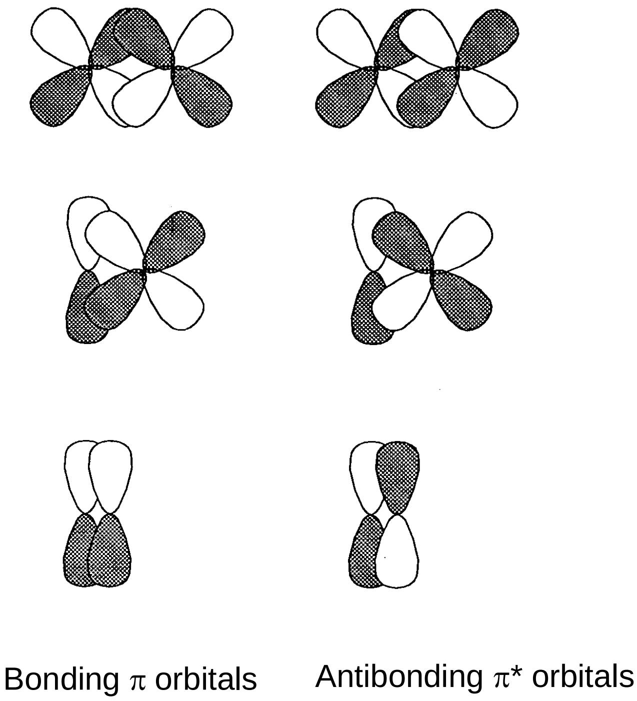


Fig. 2.17 The π molecular orbitals.

When the wave functions of two atoms are set to ϕ_A and ϕ_B, a molecular orbital is a linear combination of the atomic orbitals (LCAO) expressed as

$$\psi = C_A\phi_A + C_B\phi_B$$

Only the atomic orbitals of the valence electron shell are used in the simplest molecular orbital method. Construction of a molecular orbital is illustrated below for the simplest case of the two-atom molecules. All the levels below the HOMO are occupied by electrons and the levels above the LUMO are empty.

In a hydrogen molecule, H_2, the overlap of the 1*s* orbital of each hydrogen atom forms a bonding orbital σ_g if the lobes have equal sign and an antibonding orbital σ_u if they have opposite signs, and two electrons occupy the bonding orbital σ_g (Fig. 2.18).

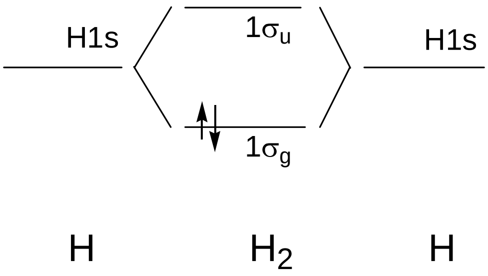


Fig. 2.18 The molecular orbitals of H_2. The arrows indicate the electron spins.

In the two-atom molecules of the 2nd period, from lithium Li_2 to fluorine F_2, if the z axis is set as a bond axis, $1\sigma_g$ and $1\sigma_u$ are formed by the overlap of 2*s* orbital of each atom and $2\sigma_g$ and $2\sigma_u$ from $2p_z$ orbitals and $1\pi_u$ and $1\pi_g$ from $2p_x$, and $2p_y$. The orbital energy levels for the molecules from Li_2 to N_2 are ordered as $1\sigma_g < 1\sigma_u < 1\pi_u < 2\sigma_g < 1\pi_g < 2\sigma_u$ and electrons occupy the levels sequentially from the bottom. The example of an N_2 molecule with ten valence electrons is shown in Fig. 2.19. Since the ordering of orbitals is somewhat different in O_2 and F_2, in which the $2\sigma_g$ orbital comes under that of $1\pi_u$, the molecular orbital of the oxygen molecule, O_2, is illustrated in Fig. 2.20. The 11th and 12th electrons among the 12 valence electrons occupy the doubly degenerate $1\pi_g$ orbital in the ground state and they have parallel spins under **Hund's rule** and hence an oxygen molecule has two unpaired electrons.

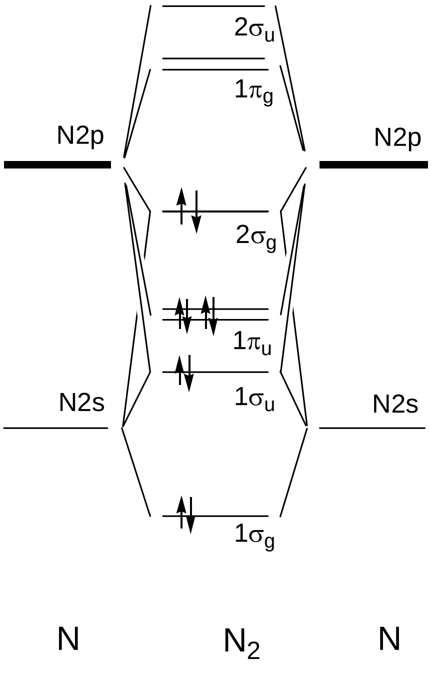


Fig. 2.19 Molecular orbitals of N_2.

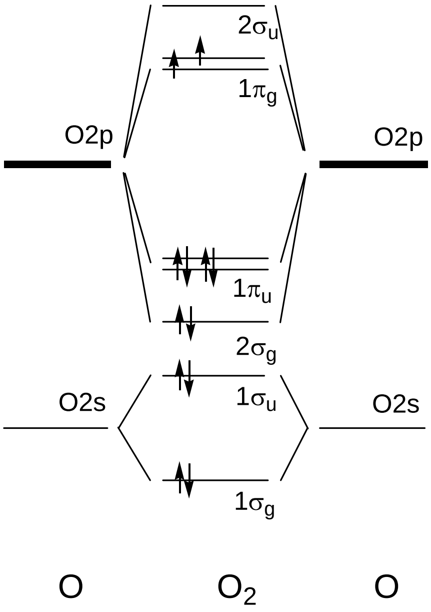


Fig. 2.20 Molecular orbitals of O_2.

The molecular orbitals of two different atoms are formed by the overlap of atomic orbitals with different energy levels. The energy level of the orbital of the atom with larger electronegativity generally is lower, and the molecular orbitals are more characteristic of the atomic orbital with the nearer energy level. Therefore, the bonding orbitals have the character of the atom with the larger electronegativity, and the antibonding orbitals that of the atom with the smaller electronegativity.

For example, five molecular orbitals in hydrogen fluoride, HF, are formed from the 1*s* orbital of hydrogen and the 2*s* and 2*p* orbitals of fluorine, as shown in Fig. 2.21. The bonding 1σ orbital has the 2*s* character of fluorine, and the antibonding 3σ orbital the 1*s* character of hydrogen. Since hydrogen has only one 1*s* orbital, the overlap with the 2*p* orbital of fluorine with π character is not effective, and the fluorine 2*p* orbital becomes a nonbonding orbital. Since HF has eight valence electrons, this nonbonding orbital is the HOMO.

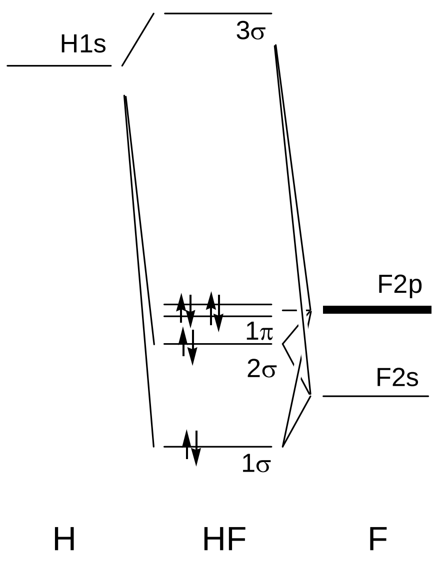


Fig. 2.21 Molecular orbitals of HF.

In carbon monoxide, CO, carbon and oxygen have 2*s* and 2*p* orbitals resulting in both sigma and pi bonds, and a triple bond is formed between the atoms. Although 8 molecular orbitals in this case are qualitatively the same as those of the isolectronic nitrogen molecule N_2 and 10 electrons occupy the orbital up to 3σ, the energy level of each orbital differs from that of the nitrogen molecule. The bonding 1σ orbital has the 2*s* character of oxygen because of its larger electronegativity, and the bonding 1π orbital also has the 2*p* character of oxygen. The antibonding 2π and 4σ orbitals have the 2*p* character of carbon (Fig. 2.22).

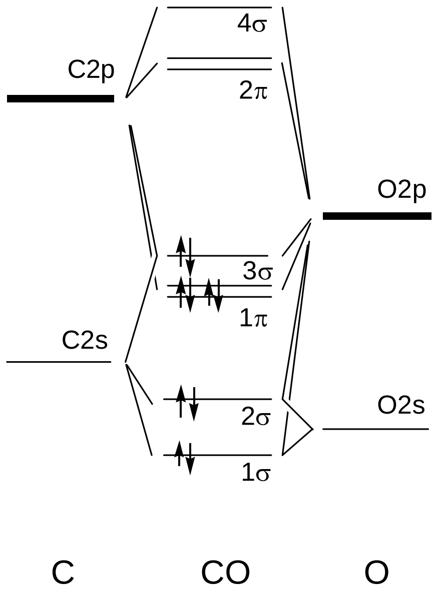


Fig. 2.22 Molecular orbitals of CO.

The bond order between atoms is a half of the number of electrons in the bonding orbitals minus those of the antibonding orbitals. For example, in N_2 or CO, it is equal to 1 / 2(8-2) = 3 and is consistent with the Lewis structure.

Exercise2.5 Why are the atomic orbitals of oxygen atom in the molecular orbital diagram of carbon monoxide, CO, lower than those of carbon?

[Answer] It is because the electronegativity of oxygen is larger than that of carbon.

Problem

2.1 Using the Pauling equation, calculate the electronegativity of chlorine from the bond energies of the hydrogen molecule H_2 (432 $\mathrm{kJmol^{-1}}$), chlorine molecule Cl_2 (239 $\mathrm{kJmol^{-1}}$), and hydrogen chloride HCl molecule (428 $\mathrm{kJmol^{-1}}$) and electronegativity of hydrogen (χ = 2.1).

2.2 Why are the energy levels $\sigma_g<\sigma_u$ in the orbitals of sigma character and $\pi_u<\pi_g$ in those of pi character in the molecular orbital diagram of N_2 or O_2?

Great theory and evaluation

Lewis' valence electron theory proposes that a covalent bond is formed with an electron pair and that there are eight valence electrons around each atom . This is a very important concept with which we understand the bonds between the main group elements. However, the theory was not held in high enough regard for a Nobel prize to be awarded to Lewis. One of the reasons of this disregard seems to be that chemists in the United States, Lewis' homeland, ignored his theory at first, and that a Nobel prize laureate, Langmuir, extended Lewis's theory, which was later known as the Lewis-Langmuir theory. N. Bohr, the eminent physicist who had great influence on the Nobel prize selection, evaluated Langmuir's adsorption theory more highly, which suggests that physicists considered Lewis` theory too simplistic.

There is a similar story about the transition state theory of H. Eyring. Physicists and theoretical chemists, who liked mathematical treatment of chemical phenomena, thought Eyring`s theory too unsophisticated. For this reason, the most important concept in chemical kinetics was not considered for a Nobel prize. It is an episode in the history of chemistry which reminds us of the comment of R. Hoffmann, who pointed out that simple concepts are more important than deceptively complicated mathematical theories.

3 Reaction

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Inorganic reactions can be described in terms of redox or acid-base concepts. Thermodynamics and electrochemistry are closely related to the analyses of redox and acid-base reactions. Although it appears that the theories of thermodynamics and electrochemistry are described by a number of complicated equations and formulae, only a few equations and parameters are required for a proper understanding. A good grasp of the sign and trend of the parameters in these key equations greatly helps this understanding. A more detailed understanding beyond this general level can be acquired by building on these basic concepts.

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3.1 Thermodynamics

Thermodynamic parameters on changes of state are necessary to describe chemical bonding, structure, and reaction. This is true also in inorganic chemistry, and the most important concepts in thermodynamics are described in this section. Even simple thermodynamic knowledge is considerably useful for judging whether structures of compounds are stable and the likelihood of spontaneous reactions, and for the calculations of reaction heat, determination of reaction mechanism, and understanding of electrochemistry.

Enthalpy Since enthalpy is the heat content of a system under constant pressure, the change ΔH is negative in an exothermic reaction, and positive in an endothermic reaction. The standard reaction enthalpy, ΔH^0, is the enthalpy change between 1 mol of products and reactants in the standard state (10^5 Pa and 298.15 K). The **standard enthalpy of formation**, ΔH_f^0, of a compound is the standard reaction enthalpy for the formation of the compound from its constituent elements. Since enthalpy is a state function, the standard reaction enthalpy is calculated by defining the standard enthalpy of formation of simple substances to be zero.
Namely,

$$\Delta H^0 = \Sigma n \Delta H_f^0 (\text{product}) - \Sigma n \Delta H_f^0 (\text{reactant})$$

Entropy Entropy is a state function, and is a criterion determining whether one state can be reached spontaneously from another state. The 2nd law of thermodynamics states that the entropy, S, of an isolated system increases upon a spontaneous change. Namely,

$$\Delta S > 0$$

A thermodynamically irreversible process produces entropy. Entropy is related to the disorder of a system in statistical themodynamics as follows:

$$S = k \ln W$$

k is the Boltzmann constant, and W is the number of the arrangements of atoms or molecules of the system with the same energy, and corresponds to the extent of disorder. As entropy becomes larger, the larger the disorder of a system.

Gibbs energy This quantity is defined as

$$\Delta G = \Delta H - T\Delta S$$

A spontaneous reaction occurs when Gibbs energy of a reaction is negative at constant temperature and pressure. The standard Gibbs free energy ΔG^0 is related to the equilibrium constant K of the reaction $\mathrm{A} \overset{K}{\rightleftharpoons} \mathrm{B}$.

$$\Delta G^0 = -RT \ln K$$

K is larger than 1 when ΔG^0 becomes negative, and the reaction proceeds to the right.

3.2 Electrochemistry

The **standard state** is defined as the one corresponding to 25°C (298.15 K), unit activity for all the substances in an electrochemical zero-current cell under 1 bar of pressure (10^5 Pa). For a reaction in which H^+ ions participate, the standard state is pH = 0 (approximately 1 mol acid).

In the hydrogen electrode used as the standard of electrode potential, 1 atm of hydrogen gas ($a_{H+} = 1$) is slowly contacted with a platinum-black electrode immersed in a strong acid solution of activity $a_{H2} = 1$. The potential is expressed as

$$E = E^0 + \frac{RT}{F}\ln\frac{a_{\mathrm{H}^+}}{a_{\mathrm{H}_2}}$$

and by definition $E^0 = 0$ in the standard state. The hydrogen electrode in the standard state is called the **standard hydrogen electrode**, or NHE. Although reduction potential is usually expressed with reference to the NHE standard, the hydrogen electrode is inconvenient to handle. Therefore a **saturated calomel (SCE)** or an Ag / AgCl electrode is used as a reference electrode for everyday electrochemical measurements and experimental potentials are measured against these electrodes or converted into NHE values. When the NHE value is set to 0, the SCE value is 0.242 V, and the Ag/AgCl value is 0.199 V.

A redox reaction takes place only when redox partners exist and a reactant can be either an oxidant or reductant depending on its reaction partner. The relative redox capability can be expressed numerically by introducing the reduction potentials E^0 of imaginary half-reactions (Table 3.1). The free energy change ΔG^0 of a reaction is related to E^0,

$$\Delta G^0 = -nFE^0$$

where n is the number of transferred electrons and F the Faraday constant 96500 Cmol^{-1}.

Table 3.1 Standard reduction potentials at 25 °C

Couple	E° / *V*
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	+1.77
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$MnO_2^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.09
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	+0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.45
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.37
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

For example, the two reactions

$2H^+(aq) + 2e^- \rightarrow H_2(g), \quad \Delta G_1^0 = -2FE_1^0$
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s), \quad \Delta G_2^0 = -2FE_2^0$

do not occur independently, but if both H^+ (aq) and Zn (s) are present, the redox reaction takes place. The equation for the actual reaction is complete when the latter equation is subtracted from the former.

$2H^+(aq) + Zn(s) \rightarrow H_2(g) + Zn^{2+}(aq)$

The free energy change of the whole redox reaction is the difference between $\Delta G_1^0, \Delta G_2^0$ for the respective half-reactions.

$$\begin{aligned}\Delta G^0 &= \Delta G_1^0 - \Delta G_2^0 \\ &= -2F(E_1^0 - E_2^0)\end{aligned}$$

Because half-reactions are not real and they are used in pairs, the free energy change ΔG_1^0 of H^+ is set to zero for convenience. Since the experimental value of ΔG^0 is -147 kJ, ΔG_2^0 equals 147 kJ. Potential E^0 corresponding to ΔG^0 of a half-reaction is called the **standard reduction potential**.

$$E^0 = -\frac{\Delta G^0}{nF}$$

Therefore,

$$E^0(\mathrm{H^+, H_2}) = 0 \quad \text{(by definition)}$$

$$E^0(\mathrm{Zn^{2+}, Zn}) = \frac{\text{-147 kJmol}^{\text{-1}}}{2 \times 96500\ \text{Cmol}^{\text{-1}}} = -0.76\ \text{V}$$

(1 J = 1 CV).

The standard potentials of various half-reactions are determined using similar procedures to that mentioned above (Table 3.1). The E^0s of redox reactions can be calculated by combining E^0 of these half-reactions.

If E^0 of a redox reaction is positive, ΔG^0 is negative and the reaction occurs spontaneously. Consequently, instead of the free energy change the difference in reduction potentials can be used to judge the thermodynamic spontaneity of a reaction. The higher the reduction potential of a reagent the stronger its oxidation ability. The positive or negative signs are based on the expedient of setting the reduction potential of a proton to 0, and it should be understood that a positive sign does not necessarily mean oxidizing, and a negative sign reducing. The series arranged in the order of redox power is called the **electrochemical series**.

3.3 Oxidation and reduction

(a) Oxidation number

The **oxidation number** is the formal electrical charge of a component atom in a compound or in an ion allocated in such a way that the atom with smaller electronegativity has a positive charge. Since electrical charges do not differ in the case of a molecule composed of the same atoms, the oxidation number of the atoms is the quotient of the net electrical charge divided by the number of atoms. In the case of a compound or an ion consisting of different atoms, the atoms with larger electronegativity can be considered as anions and those with smaller electronegativity as cations. For example, nitrogen is 0 valent in N_2; oxygen is -1 in O_2^{2-}; nitrogen is +4 and oxygen -2 in NO_2; but nitrogen is -3 and hydrogen +1 in NH_3. That is, the oxidation number can be different for the same atom combined with different partners and the atom is said to be in the formal oxidation state corresponding to that oxidation number. Although this does not express the quantitative deviation of the actual electric charge, it is convenient in counting valence electrons or in dealing with redox reactions.

Exercise 3.1 Which halogen has the largest oxidizing power?

[Answer] Since the reduction potential of fluorine is the highest, its oxidizing power is the largest.

(b) Redox reactions

Originally, oxidation meant the formation of oxides from elements or the formation of compounds by the action of oxygen, and reduction is the reverse of oxidation. The present definition of **reduction** is a reaction which gives an electron, and **oxidation** is the reaction which takes an electron. Therefore, a reagent which gives an electron is a **reductant** and one which takes an electron is an **oxidant**. As a result of a redox reaction, a reductant is oxidized and an oxidant is reduced. For example, in the reaction of molybdenum metal and chlorine gas to form molybdenum pentachloride,

$$2\ Mo + 5\ Cl_2 \rightarrow Mo_2Cl_{10}$$

molybdenum is a reductant and changes its oxidation state from 0 to +5 and chlorine is an oxidant and changes its oxidation state from 0 to -1.

(c) Latimer diagram

A **Latimer diagram** is a diagram in which the chemical species in the highest oxidation state is placed at the left end and a series of the reduced chemical species of the same atom are arranged to the right-hand side in the order of the oxidation states, and the standard reduction potentials (/V) are written above the line which connects each state. This diagram is convenient for discussing a redox reaction. Since electric potential differs between an acidic and a basic solution, different diagrams are required depending on the pH of the solution. Taking the series of the oxides and hydrides of nitrogen in acidic solution as an example, ,

$$\begin{array}{ccccccccccc} \mathrm{NO_3^-} & \xrightarrow{0.803} & \mathrm{N_2O_4} & \xrightarrow{1.07} & \mathrm{HNO_2} & \xrightarrow{0.996} & \mathrm{NO} & \xrightarrow{1.59} & \mathrm{N_2O} & \xrightarrow{1.77} & \mathrm{N_2} \\ +5 & & +4 & & +3 & & +2 & & +1 & & 0 \end{array}$$

$$\begin{array}{ccccccc} \xrightarrow{-1.87} & \mathrm{NH_3OH^+} & \xrightarrow{1.41} & \mathrm{N_2H_5^+} & \xrightarrow{1.275} & \mathrm{NH_4^+} \\ & -1 & & -2 & & -3 \end{array}$$

in a basic solution, the series becomes

$$\begin{array}{ccccccccccc} \mathrm{NO_3^-} & \xrightarrow{-0.86} & \mathrm{N_2O_4} & \xrightarrow{0.867} & \mathrm{NO_2^-} & \xrightarrow{-0.46} & \mathrm{NO} & \xrightarrow{0.76} & \mathrm{N_2O} & \xrightarrow{0.94} & \mathrm{N_2} \\ +5 & & +4 & & +3 & & +2 & & +1 & & 0 \end{array}$$

$$\begin{array}{ccccccc} \xrightarrow{-3.04} & \mathrm{NH_2OH} & \xrightarrow{0.73} & \mathrm{N_2H_4} & \xrightarrow{0.1} & \mathrm{NH_3} \\ & -1 & & -2 & & -3 \end{array}$$

The additivity of the state function ΔG^0 is used in order to calculate the standard reduction potential between remote oxidation states.

$$\Delta G^0 = \Delta G_1^0 + \Delta G_2^0$$

$$-(n_1 + n_2)FE^0 = -n_1FE_1^0 - n_2FE_2^0$$

Where the free energy change and electric potential between adjacent states are ΔG_1^0 , E_1^0 , ΔG_2^0 , E_2^0 , respectively, and the number of transferred electrons n_1, n_2. Namely,

$$E^0 = \frac{n_1E_1^0 + n_2E_2^0}{n_1 + n_2}$$

For example, in the reduction of NO_3^- to HNO_2, two electrons are transferred to form HNO_2 via N_2O_4 and the potential becomes

$$E^0 = \frac{0.803\ \mathrm{V} + 1.07\ \mathrm{V}}{2} = 0.94\ \mathrm{V}$$

Exercise 3.2 Calculate the reduction potential of the reduction of NO_3^- to NO_2^- in a basic solution.

[Answer] $E^0 = \dfrac{-0.86\ \mathrm{V} + 0.867\ \mathrm{V}}{2} = 0.004\ \mathrm{V}$

In recent years, whenever a new inorganic compound is synthesized, its redox properties are investigated, usually by electrochemical measurements. **Cyclic voltammetry** is the technique of choice for the study of its redox properties, including the electric potential, the number of transferred electrons, and the reversibility of the reactions, *etc*. because of the simplicity of the measurements. It is approximately correct to consider that the oxidation potential corresponds to the energy level of the HOMO, because oxidation usually takes an electron from the HOMO and the reduction potential to the level of the LUMO since reduction adds an electron to the LUMO. However, various factors, such as solvent effects, should be taken into consideration during quantitative discussions of redox processes.

3.4 Acid and base

The definition of acid and base has changed over the course of time. This is not a problem of the orthodoxy of one definition but of the convenience of applying the concept to a particular chemical problem. Therefore, ranking the strength of acids and bases also depends on the definition of acid and base used.

(a) Arrhenius's acid and base

In 1884, Arrhenius defined that an **acid** is a substance that gives H^+ and a **base** one that gives OH^-. Namely, if an acid is HA and a base BOH, then $HA \rightarrow H^+ + A^-$ and $BOH \rightarrow B^+ + OH^-$. Therefore, when an acid and a base react, water is formed.

(b) Brønsted-Lowry's acid and base

In a new theory submitted in 1923 independently by Brønsted and Lowry, an acid is defined as a molecule or an ion which gives H^+ and a molecule or ion that receives H^+ from a partner is a base. A base is not only a molecule or an ion which gives OH^- but anything which receives H^+. Since the acid HA gives H^+ to water in an aqueous solution and generates an **oxonium ion**, H_3O^+, water is also a kind of base according to this definition.

$$HA\text{(acid)} + H_2O\text{ (base)} \rightarrow H_3O\text{(conjugate acid)} + A^-\text{ (conjugate base)}$$

Here H_3O^+ is called a **conjugate acid** and A^- a **conjugate base**. However, since water gives H^+ to ammonia and generates NH_4^+, it is also an acid, as is shown below.

$$H_2O\text{(acid)} + NH_3\text{ (base)} \rightarrow NH_4^+\text{(conjugate acid)} + OH^-\text{ (conjugate base)}$$

That is, water can be an acid or a base dependent on the co-reactant.

Although the definition of Brønsted-Lowry is not much different from that of Arrhenius for aqueous solutions, it is more useful because the theory was extended to non-aqueous acids and bases.

Exercise 3.3 Write the molecular formulae of nitric acid, perchloric acid, sulfuric acid, and phosphoric acid as oxo acids together with the formal oxidation number of the central atom.

[Answer] nitric acid $(HO)N^{5+}O_2$, perchloric acid $(HO)Cl^{7+}O_3$, sulfuric acid $(HO)_2S^{6+}O_2$, and phosphoric acid $(HO)_3P^{5+}O$.

Acid strength

A protonic acid gives H^+ to water and generates the oxonium ion H_3O^+. The strength of an acid in a dilute aqueous solution is estimated from the equilibrium constant K_a

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

for the dissociation equilibrium,

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

but it is more convenient to use,

$$pK_a = -\log K_a \quad \text{or} \quad pH = -\log[H_3O^+]$$

An acid with $pK_a<0$ is classified as a strong acid and one with $pK_a>0$ a weak acid. The conjugate base of a strong acid is a weak base. The p*K*a values of typical acids at 25 °C are shown in Table 3.2.

Table 3.2 Acidity constants for aqueous solutions of acids at 25 °C.

Acid	pK_a
HF	3.17
HCl	-8*
HBr	-9*
HI	-10*
H_2CO_3	6.35
$HClO_4$	<0
HNO_3	<0
H_3PO_3	1.5
H_3PO_4	2.15
H_2SO_4	<0
CH_3COOH	4.56
C_6H_5COOH	4.00
NH_4^+	9.25
$C_5H_5NH^+$	5.25

* Estimated value

Since a solvent also works as an acid or a base, the acidity and its range depend on the solvent dissolving the acid. Full dissociation of an acid stronger than H_3O^+ gives H^+ to water, forming H_3O^+ in an aqueous solution. For example, both HBr and HI dissociate completely to become H_3O^+, and their acidities are similar. This kind of phenomenon is called the **leveling effect**, and all acidities become equal to that of H_3O^+. In measuring the relative acidity of strong acids, it is necessary to use a solvent whose H^+ affinity is smaller than that of water, such as acetic acid or ethanol.

Binary halo acids HX, except for HF, are very strong acids. Although the H_3O^+ concentration itself is also high in an aqueous solution of HF, the stronger hydrogen bond of F^- compared with that of other halide anions decreases the thermodynamic activity of H_3O^+.

The acidity of oxo acids, such as phosphoric acid, sulfuric acid, nitric acid, and perchloric acid, is related to the formal oxidation number of P, S, N, and Cl. Namely, if the oxo acid H_nXO_m is denoted by $(HO)_nXO_{m-n}$, the positive charge on X becomes positive (2m- n), and the acidity is higher for larger value of this number. The number parallels the ease of dissociation of OH to give a proton. Acidity is higher in the following order: perchloric acid $(HO)ClO_3$ > sulfuric acid $(HO)_2SO_2$ > nitric acid $(HO)NO_2$ > phosphoric acid $(HO)_3PO$. Although phosphoric acid can be written as $(HO)_3PO$, phosphorous acid is not $(HO)_3P$ but $(HO)_2HPO$, and has an acid strength comparable to phosphoric acid.

Hammett acidity function

Hydrogen ion concentration and pH are meaningful only in dilute aqueous solutions of acids. The acidity in nonaqueous and concentrated solutions is measured using the **Hammett acidity function**. This function makes it possible to measure the acidities of various acids in a non-aqueous solvent or of an acid in various non-aqueous solvents.

The Hammett acidity function in the equilibrium,

$B + H^+ \rightleftharpoons BH^+$ is defined by

$$H_0 = \mathrm{p}K_{BH^+} - \log\frac{[BH^+]}{[B]}$$

In a very dilute solution

$$K_{BH^+} = \frac{[B][H^+]}{[BH^+]} \quad \text{and}$$

$$H_0 = -\log\frac{[\mathrm{B}][\mathrm{H}^+]}{[\mathrm{BH}^+]} - \log\frac{[\mathrm{BH}^+]}{[\mathrm{B}]} = -\log[\mathrm{H}^+] = \mathrm{pH}$$

An acid with $-H_0$ over 6 is called a **superacid**. This is an acid that is 10^6 times stronger than a 1 molar solution of a strong acid. $-H_0$ for pure sulfuric acid is 12.1, 21.1 for a solution of HF in SbF_5, and 26.5 for the combination of HSO_3F and SbF_5. Superacids have the ability to remove H^- from a hydrocarbon and perform H-D exchange and C-C bond scission, *etc*.

(c) Lewis acid and base

Whereas the concept of Brønsted acid and base is limited to the transfer of protons, a Lewis acid A is generally defined as an acceptor, and a Lewis base B a donor, of an electron pair. An acid A and a base :B bind together to form an adduct A:B. For example, a Lewis acid BF_3 and a Lewis base OEt_2 (diethylether) form an adduct $F_3B{:}OEt_2$. The stability increases by the completion of an octet around boron when such an adduct forms. The stability of an adduct is expressed by the equilibrium constant of the reaction

$$\mathrm{A} + {:}\mathrm{B} \xrightleftharpoons{K_\mathrm{f}} \mathrm{A - B}$$

$$K_\mathrm{f} = \frac{[\mathrm{A:B}]}{[\mathrm{A}][:\mathrm{B}]}$$

Therefore, the Lewis acidities of a series of acids are measured by comparing K_f against a common base :B. Since a proton is also an electron acceptor, Brønsted acids are the special case of the more general Lewis definition of acids . According to this definition, a co-ordinate bond in a transition metal complex is also an acid-base reaction of a ligand (Lewis base) with a metal center (Lewis acid).

V. Gutmann proposed the negative enthalpy of formation (kcal mol^{-1} unit) of the adduct (Cl_5Sb-Sol) of Sol (solvent) with a standard acid ($SbCl_5$) in dichloroethane as a measure of the Lewis basicity of a solvent. This is called the **donor number** (D.N.) of a solvent. On the other hand, the ^{31}P NMR chemical shift of Et_3P in a solvent is defined as the measure of the Lewis acidity of the solvent and is called the **acceptor number** (A.N.).

Hard and soft acids and bases

R. G. Pearson classified Lewis acids and bases according to their **hardness and**

softness. This classification is an extension of the original theory of S. Ahrland, J. Chatt, and N. R. Davies, who proposed that metal cations were classified in the order of the stability constants K_f of the formation of the complexes of the metal cations with halide anions. Namely, the order of K_f is I < Br < Cl < F toward metal ions belonging to class *a* , and F < Cl < Br < I toward those of class *b*. The class *a* type metal cations are hard acids, and class *b* type ones are soft acids. The metal cations which are not much dependent on the kind of halogens have **borderline** character.

What should be noticed here is that K_f tends to become large for the combination of a hard acid and a hard base, or a soft acid and a soft base. If the concept is extended from simple metal cations and halide anions to general Lewis acids and bases, they can similarly be classified in terms of the hard and soft acid-base affinity. Typical hard acids and bases, and soft acids and bases are shown in Table 3.3.

Table 3.3 The classification of Lewis acids and bases

	Hard	Borderline	Soft
Acids	H^+,Li^+,Na^+,K^+ Be^{2+},Mg^{2+},Ca^{2+} Al^{3+},Ti^{4+},Cr^{3+} Fe^{3+},BF_3,Cl^{7+}	Fe^{2+},Co^{2+},Ni^{2+},Cu^{2+} Zn^{2+},Sn^{2+},Pb^{2+} Sb^{3+},Bi^{3+}	Cu^+,Ag^+,Au^+ Tl^+,Cd^{2+},Hg^+,Hg^{2+} Pd^{2+},Pt^{2+},Pt^{4+}
Bases	NH_3,H_2O,R_2O F^-,OH^-,O^{2-} NO_3^-,SO_4^{2-},PO_4^{3-}	N_3^-,N_2,NO_2^- Br^- SO_3^{2-}	H^-,CN^-,R^- I^- PR_3,SR_2,CO

The qualitative expression “softness” is a chemical paraphrasing of the ease of polarization and the larger contribution of covalency than ionicity in bonding. The cations of alkali and alkaline earth metals as well as aluminum are hard and the cations of mercury, copper, silver, and gold, *etc*. are soft. Whereas oxides are hard, sulfides and phosphorus compounds are soft. In the minerals of the Earth’s crust, aluminum, which is hard and oxophilic is found as an oxide, and cadmium, which is soft and chalcophilic is found as a sulfide.

Exercise 3.4 Applying the concept of hard and soft acids for ferric and ferrous ions, what kind of minerals are expected in iron ores?

[Answer] Fe^{3+} is a hard acid and Fe^{2+} is a borderline acid. Therefore, it is likely that the main iron ores are oxide minerals. Although the main ores are actually the oxides hematite Fe_2O_3 or magnetite Fe_3O_4, a Fe^{2+} sulfide pyrite FeS_2 is also widely distributed.

Acid-base and oxidation-reduction

Some people confuse acid-base and redox reactions. This confusion may be caused firstly by the similar terms originating from oxygen and secondly by misunderstanding about electron transfer. Historically, A. L. Lavoisier, who was one of the great founders of modern chemistry in the 18th century, considered that oxygen was the basis of all acids. He also defined oxidation as the formation of oxides from an element and oxygen. It then took a long time before the present definitions of acid-base and redox reactions were proposed and the old definitions were no longer satisfactory. Furthermore, the Lewis acid accepts an electron pair from a base forming a Lewis acid-base complex, and the oxidizing agent accepts electrons from a reducing agent and is reduced. The fact that acids and oxidizing agents are electron acceptors, and that bases and reducing agents are electron donors, is one of the causes of this confusion.

Problem

3.1 The Latimer diagram of oxygen is shown below. Write the oxidation number of oxygen in each compound.

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

Calculate the reduction potential of the reaction which converts an oxygen molecule to water, and judge whether this reaction is a spontaneous reaction.

3.2 Which is the stronger base, ammonia or pyridine?

3.3 The order of the Lewis acidity of boron halides is $BF_3 < BCl_3 < BBr_3$. Is this order reasonable from the standpoint of the electronegativities of halogens?

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 ^{o}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 °C and bp -60.7 °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 °C and bp 19.5 °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.

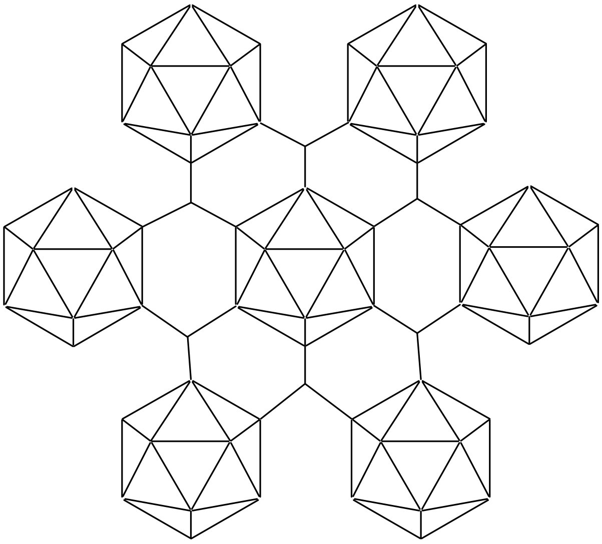


Fig. 4.1 The structure of the elemental boron with B_{12} icosahedra.

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).

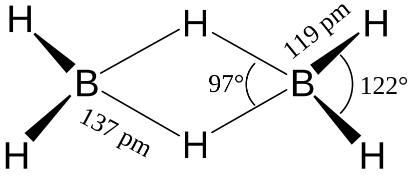
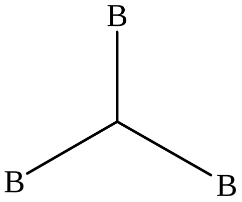


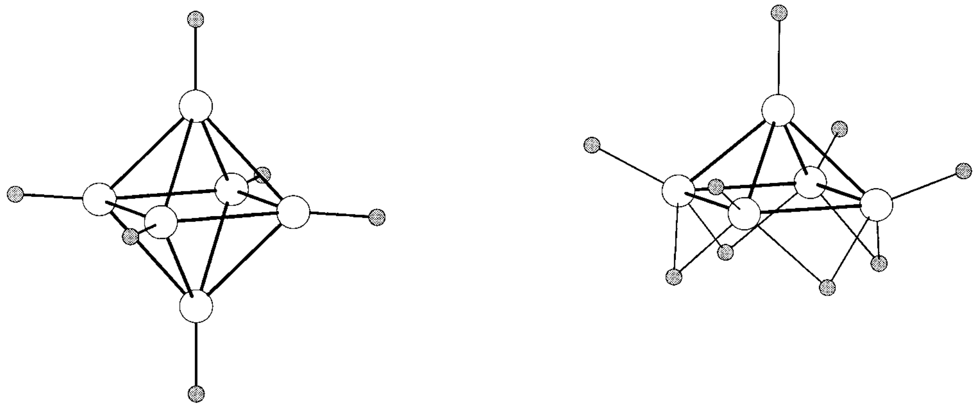
Fig. 4.2 Structure of diborane.

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

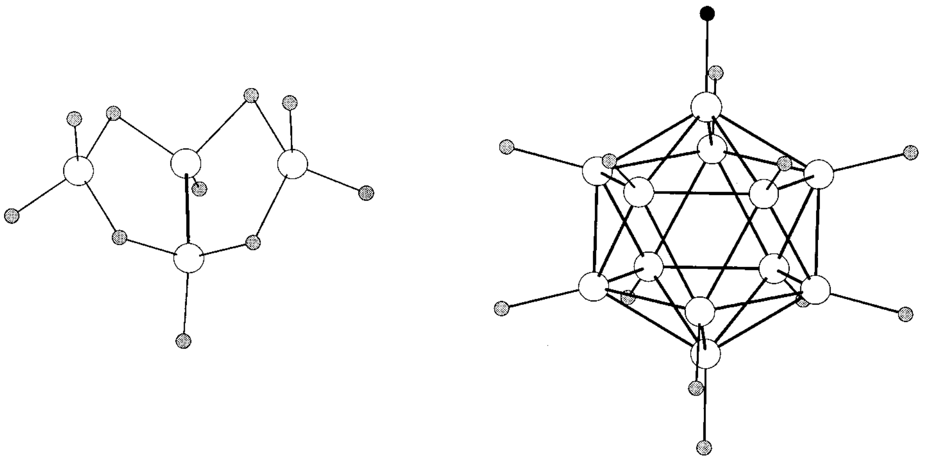


besides the usual 2 center 2 electron covalent bonds (2c-2e bond) B-H and B-B. Such structures can be treated satisfactorily by molecular orbital theory. Boranes are classified into *closo, nido, arachno, etc*. according to the skeletal structures of boron atoms.

C*loso*-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).

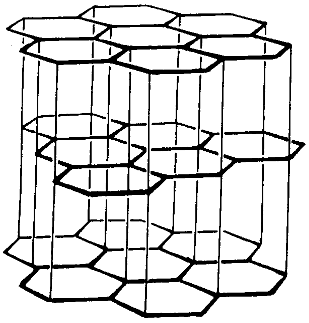


Fig. 4.4 Structure of graphite.

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*.

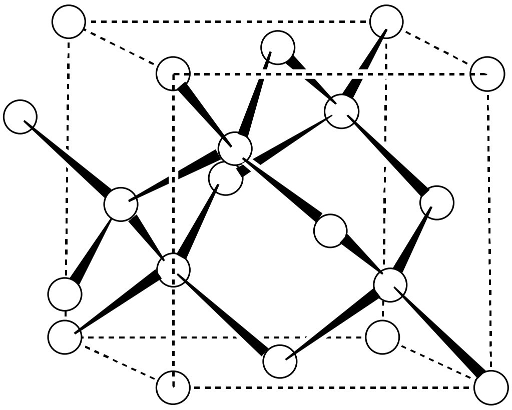


Fig. 4.5 Structure of diamond.

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.

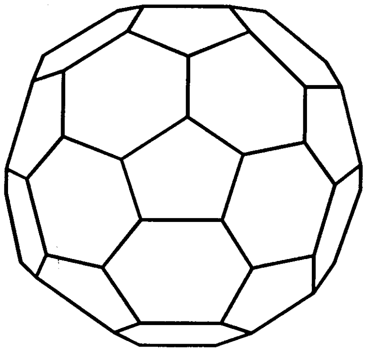


Fig. 4.6 Structure of C_{60}.

(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.

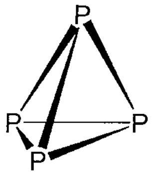


Fig. 4.7 Structure of white phosphorus.

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.

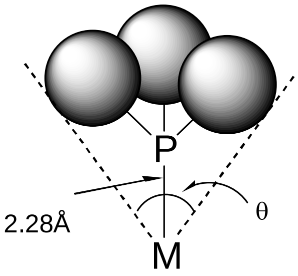


Fig. 4.8 Cone angle.

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*.

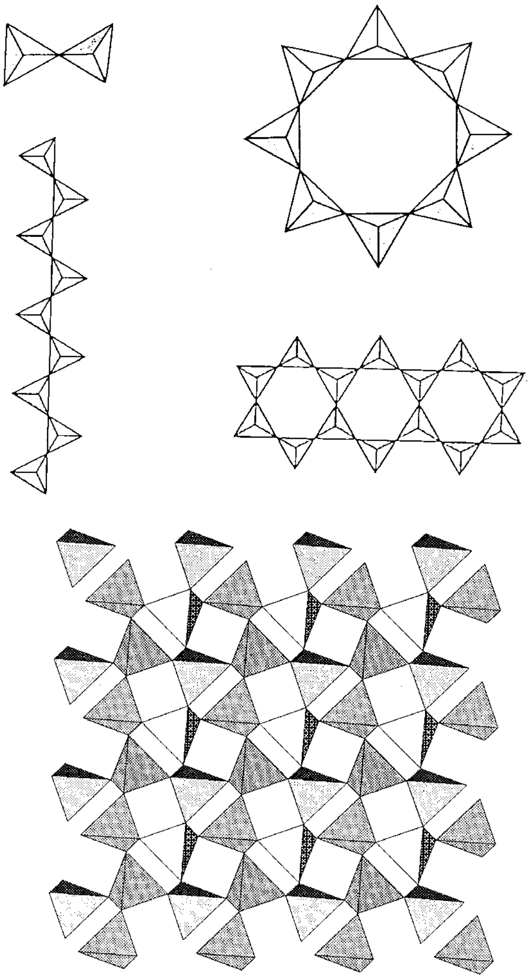


Fig. 4.9 Bridging modes of the SiO_4 tetrahedra.

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.

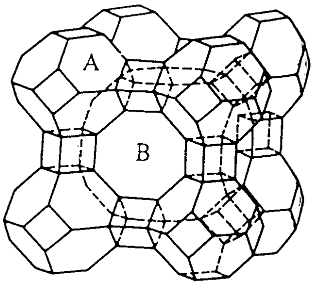


Fig. 4.10 Structure of zeolite A.

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 ^{o}C 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 ^{o}C, 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 $120^o \sim 140^o$ 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 ^oC, and it increases gradually to 15.9% at its boiling point (21.2 ^oC), and becomes 100% at 140 ^oC.

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

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

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 ^oC. 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 ^{o}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 ^{o}C) 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 ^{o}C). 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 ^{o}C), 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						
+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

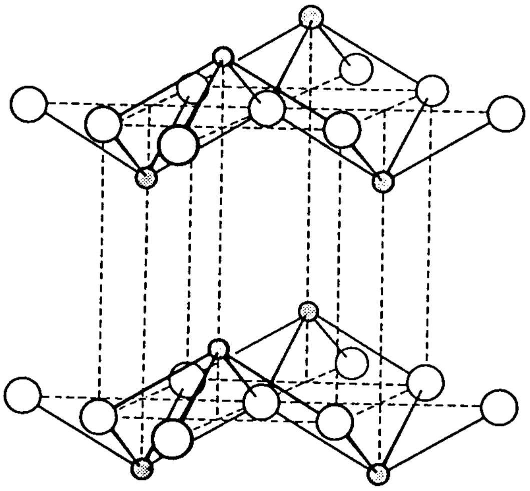


Fig. 4.11 Structure of PbO.

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.

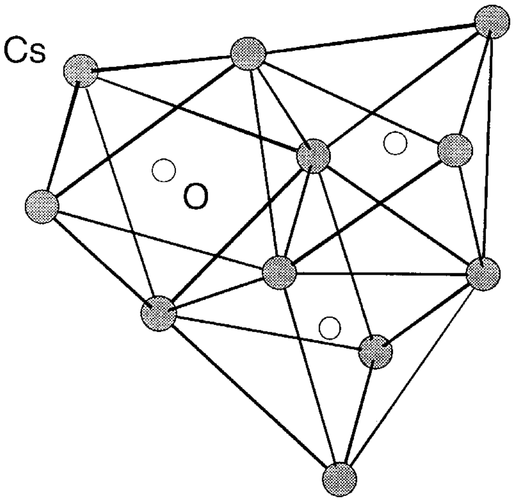


Fig. 4.12 Structure of $Cs_{11}O_3$.

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 ^{o}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.

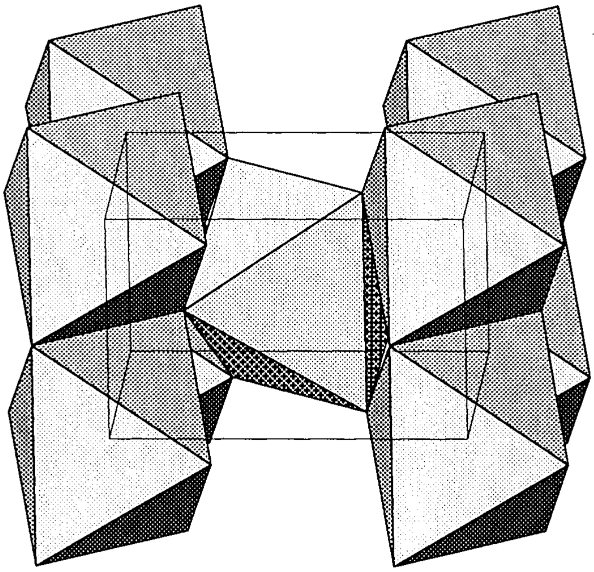


Fig. 4.13 Structure of rutile.

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).

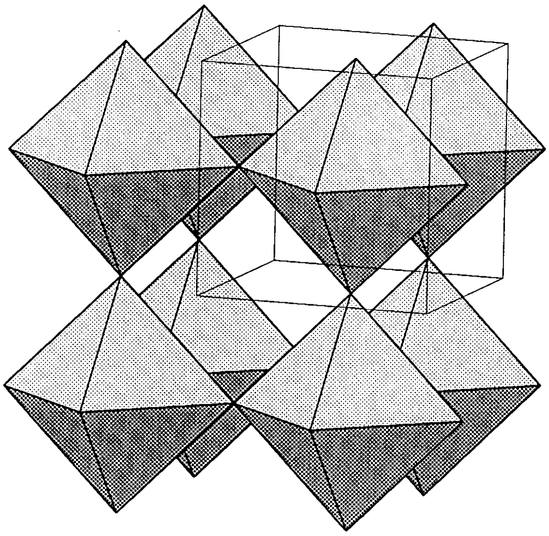


Fig. 4.14 Structure of ReO_3.

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.

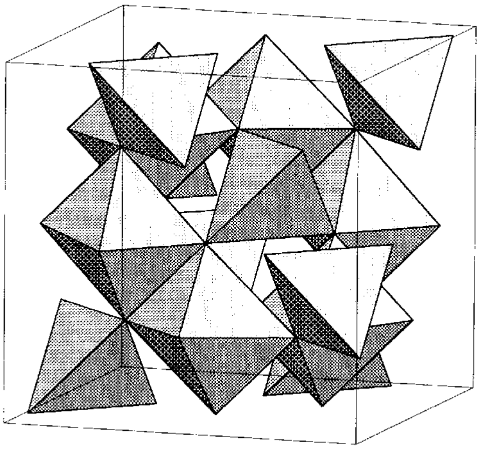


Fig. 4.15 Spinel structure.

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).

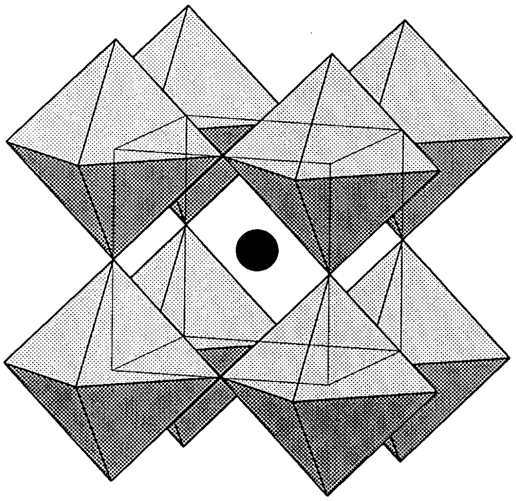


Fig. 4.16 Perovskite structure.

(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.

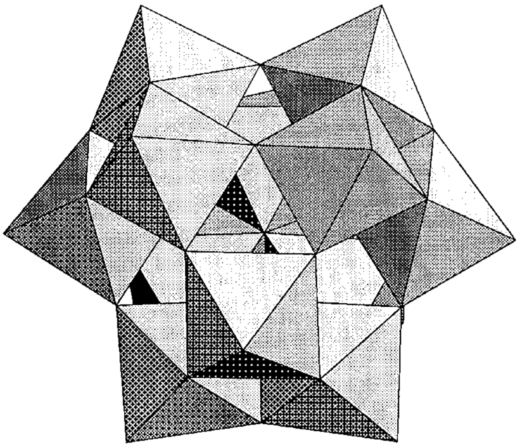


Fig. 4.17 Keggin structure.

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.

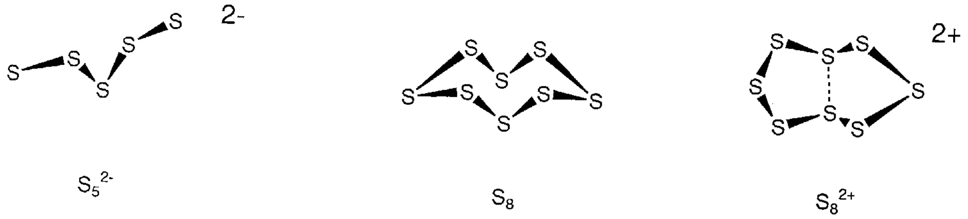
4.4 Chalcogen and chalcogenides

(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.

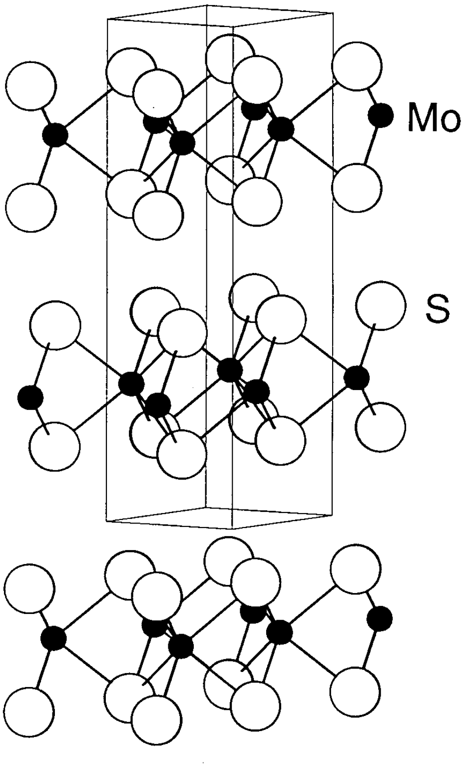


Fig. 4.19 Structure of MoS_2.

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.

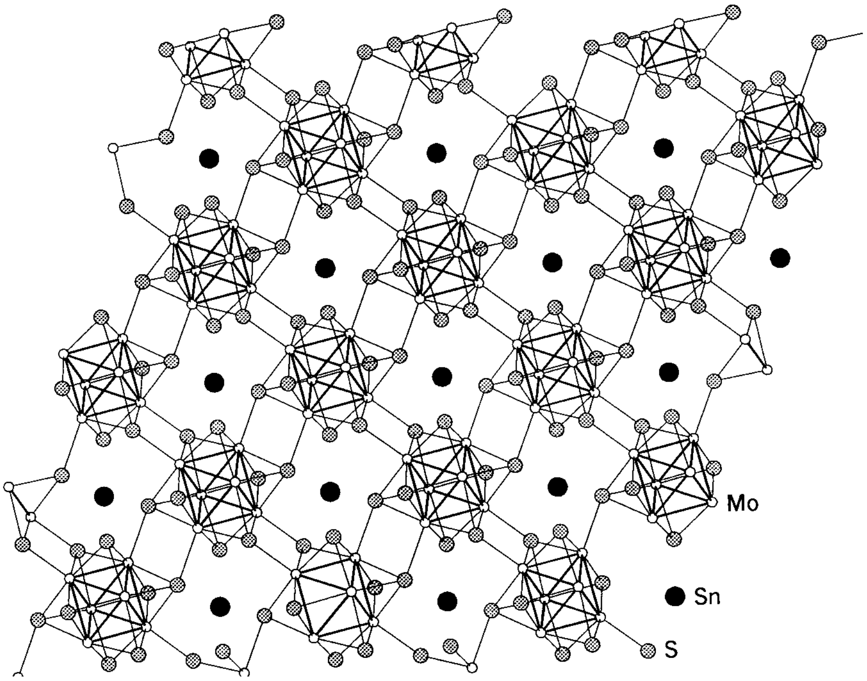


Fig. 4.20 Structure of $SnMo_6S_8$.

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 PCl_5	S_2Cl_2 SF_6	ClF_3 ClF_5	
4	KCl	$CaCl_2$	$ZnCl_2$	$GaCl_3$	GeF_2 $GeCl_4$	$AsCl_3$ AsF_5	Se_2Cl_2 SeF_5	BrF_3 BrF_5	KrF_2
5	RbCl	$SrCl_2$	$CdCl_2$	InCl $InCl_3$	$SnCl_2$ $SnCl_4$	$SbCl_3$ SbF_5	Te_4Cl_{16} TeF_6	IF_5 IF_7	XeF_2 XeF_6
6	CsCl	$BaCl_2$	Hg_2Cl_2 $HgCl_2$	TlCl $TlCl_3$	$PbCl_2$ $PbCl_4$	$BiCl_3$ BiF_5			

Boron trifluoride, BF_3, is a colorless gas (mp -127 ^{o}C and bp -100 ^{o}C) 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 ^{o}C and bp 57.6 ^{o}C). 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 ^oC and bp -101.8 ^oC). 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 ^oC and bp -84.5 ^oC). 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 ^oC and bp 75.5 ^oC). 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 ^oC) 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 ^oC and bp -52.9 ^oC). 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 ^oC and sublimation point -63.8 ^oC) 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 ^oC and bp 138 ^oC). 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*.

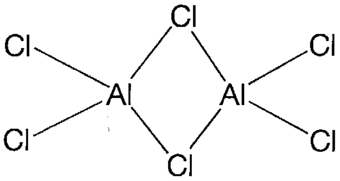


Fig. 4.21 Structure of aluminum chloride.

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.

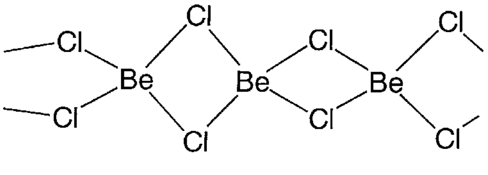


Fig. 4.22 Structure of beryllium chloride.

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.

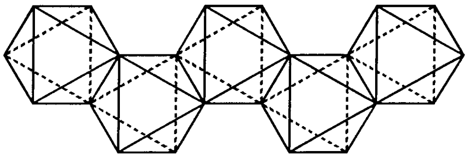


Fig. 4.23 Structure of zirconium tetrachloride.

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*.

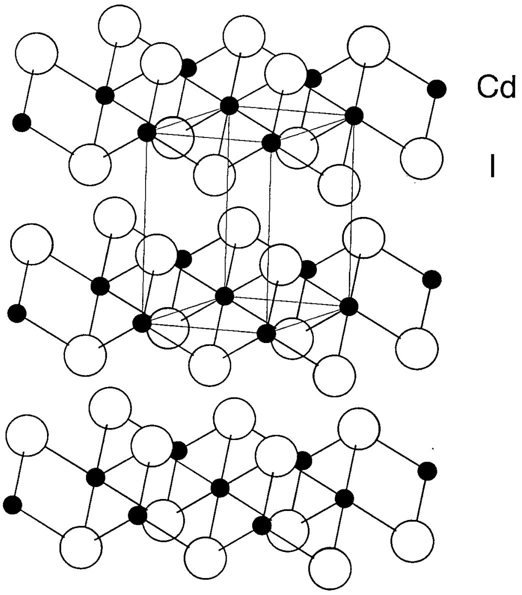


Fig. 4.24 Layers of cadmium and iodine in the cadmium iodide structure.

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 °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.

5 Chemistry of Main-Group Metals

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Metals show metallic luster, are good conductors of electricity and heat, and are very malleable and ductile. Such properties are characteristic of bulk metals, although the definition of metal atoms or ions is not simple. Metallic elements form basic oxides or hydroxides in the +1 or +2 oxidation states, and become cations in aqueous acid solutions. All transition elements are metals, but main group elements are classified into metallic and nonmetallic elements. Germanium and polonium may also be included as metals. Boron, silicon, germanium, arsenic, antimony, selenium, and tellurium exhibit some metallic characteristics and they are sometimes called metalloids.

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5.1 Group 1 metals

Group 1 metals are called **alkali metals**. Alkali metals are abundant in minerals and sea water. Especially the content of sodium, Na, in the Earth's crust is fourth after Al, Fe, and Ca. Although the existence of sodium or potassium ions was recognized for many years, a number of attempts to isolate the metals from aqueous solutions of their salts failed because of their high reactivity with water. Potassium (1807) and subsequently sodium were isolated by the electrolysis of molten salt of KOH or NaOH by H. Davy in the 19th century. Lithium Li was discovered as a new element (1817), and Davy soon isolated it by molten salt electrolysis of Li_2O . Rubidium, Rb and Cesium, Cs, were discovered as new elements by spectroscopy in 1861. Francium, Fr, was discovered using a radiochemical technique in 1939. Its natural abundance is very low.

Table 5.1 Properties of group 1 metals

	mp (°C)	bp (°C)	d(20 °C) (g cm^{-3})	E^0(V) $M^+ + e^-$	I (kJ mol^{-1})
Li	181	1342	0.534	-3.04	520
Na	98	883	0.968	-2.71	496
K	63	759	0.856	-2.93	419
Rb	39	688	1.532	-2.98	403
Cs	28	671	1.90	-3.03	376

As shown in Table 5.1, melting-points, boiling points, and densities of alkali metals are low, and they are soft metals. Since the outer shell contains only one *s*-electron, the ionization energy is very low, and mono cations of alkali metals form easily. Qualitative analysis of alkali metals is possible by means of flame reactions using characteristic luminescence lines. Especially the orange D-line of sodium is used in the sodium lamp. Alkali metals are oxidized by water evolving hydrogen gas due to their low reduction potentials. Except lithium, the heavier alkali metals react violently with water, and sufficient caution should be exercised in their handling.

Exercise 5.1 Describe the reactivity of alkali metals in water.

[Answer] The reactivity of lithium is the lowest, sodium reacts violently, and potassium, rubidium, and cesium react explosively.

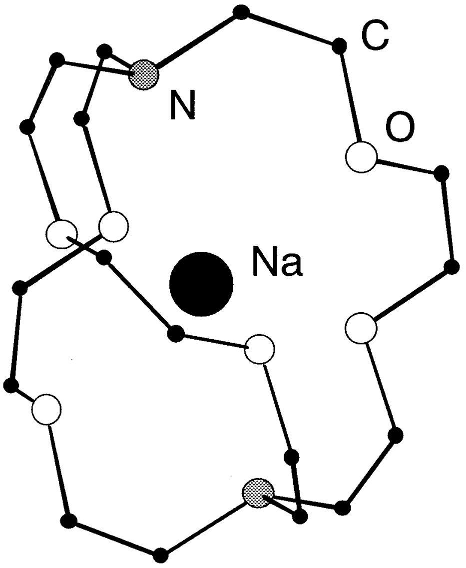

Fig. 5.1 Structure of Na(crypt).

Alkali metals are also highly reactive to oxygen or halogens. As alkali metals are very reducing, they are used widely as reducing agents. Because of the high affinity of alkali metals to halogens, they are important in organic and inorganic syntheses which produce alkali metal halides as the result of condensation and metathesis reactions. Although it is generally difficult to dissolve metals in solvents to make atomic dipersions, alkali metals can be dispersed in liquid ammonia solutions, amalgams, and as cryptand (Fig. 5.1), naphthalene, or benzophenone $(C_6H_5)_2CO$ complexes.

Ammonia boils at -33.35 ^{o}C but liquid ammonia can be easily handled . Alkali metals dissolve readily in liquid ammonia and dilute solutions are blue but concentrated ones show a bronze color. The metal is recovered when ammonia is evaporated from metal solutions. Alkali metal solutions show the same color irrespective of the kind of alkali metals as the color is due to the solvated electrons. Namely, the dissolution is accompanied by the separation of the alkali metal atoms into metal cations and electrons solvated by ammonia, according to the following equation.

$$M + n\ NH_3 \rightarrow M^+[e^-(NH_3)]$$

The liquid ammonia solution of an alkali metal is conductive and paramagnetic. The highly reducing solution is used for special reduction reactions or syntheses of alkali metal complexes and polyhalides.

5.2 Group 2 metals

Group 2 metals from beryllium Be, to radium, Ra, are also called **alkaline earth metals** (Table 5.2). Beryllium is a component of beryl or emerald. Emerald is a mineral that contains about 2% of chromium, Cr, in beryl, $Be_3Al_2Si_6O_{18}$. Beryllium metal is silver white and is used in special alloys and for the window of X-ray tubes, or a moderator of nuclear reactors, *etc*. Compounds of Be^{2+} resemble the compounds of Mg^{2+} or Al^{3+}. Since beryllium is a deadly poison, it should be handled with due care.

Table 5.2 Properties of group 2 metals

	mp	bp	d(20 °C)	E^0(V)	I (kJ mol^{-1})	
	(°C)	(°C)	(g cm^{-3})	$M^{2+}+2e^-$	first	second
Be	1287	2471	1.85	-1.85	899	1757
Mg	650	1090	1.74	-2.37	737	1450
Ca	842	1484	1.55	-2.87	590	1145
Sr	777	1382	2.63	-2.90	549	1064
Ba	727	1897	3.62	-2.91	503	965
Ra	700		5.5	-2.82	509	975

Magnesium, Mg, is mainly produced as carbonates, sulfates, and silicates, and its abundance is between those of sodium and calcium, Ca. It is produced by molten salt electrolysis of magnesium chloride, $MgCl_2$, or the reaction of dolomite, $CaMg(CO_3)_2$, with ferrosilicon alloy FeSi. Magnesium metal is silver white and the surface is oxidized in air. At high temperatures, magnesium reacts with nitrogen gas to become nitride, Mg_3N_2. The metal burns very brightly and is still used for flash lights. The alloy with aluminum is light and strong and used as a structural material in cars and airplanes.

Mg^{2+} is the central metal ion in the porphyrin ring of chlorophyll, and plays an important role in photosynthesis. The Grignard reagent, RMgX, which F. A. V. Grignard of France synthesized in 1900, is a typical organometallic compound of a main-group metal and is widely used for Grignard reactions. This is an important reagent rewarded by a Nobel prize (1912), and is very useful not only for organic reactions but also for the conversion of metal halides into organometallic compounds.

Calcium is contained in silicates, carbonates, sulfates, phosphates, fluorite, *etc*. Calcium is a silver white and soft metal that is manufactured by molten salt electrolysis of calcium chloride $CaCl_2$.

Quick lime, CaO, is produced by the calcination of limestone, $CaCO_3$, at 950-1100 ^oC. Production of quick lime ranks second to sulfuric acid in inorganic chemical industries. Calcium hydroxide, $Ca(OH)_2$, is called also slaked lime. Calcium carbonate is the principal component of limestone and limestone is very important for the production of cement. Gypsum is a dihydrate of calcium sulfate $CaSO_4.2H_2O$ and is obtained in large quantities as a by-product of stack gas desulfurization, and in addition to conventional uses is also used as a building material, *etc*.

Although calcium is not important in either the chemistry of aqueous solution systems or in organometallic chemistry in organic solvents, the element plays very important roles in living organisms. Not only is calcium the structure material of bones and teeth, calcium ions also have a wide range of functions in biological systems, such as protein stabilization, transfer of hormone action, muscular contraction, nerve communication, and blood coagulation.

Strontium, Sr, is a silver white soft metal. The surface is oxidized by air at room temperature, and it becomes a mixture of oxide, SrO, and nitride, Sr_3N_2, at high temperatures. In spite of the relatively high content of strontium in the Earth’s crust, the element has not been studied widely and its application is limited. There are four natural isotopes and ^{88}Sr (82.58%) is the most abundant. Since the artificial isotope ^{90}Sr is obtained cheaply by nuclear reaction, it is used as a source of β particles, and as a radioactive tracer. However, this isotope, as well as ^{137}Cs, has a long half-life (28.8 y) and both are present in the radioactive fallout that accompanies nuclear explosive tests. Both are considered to be very dangerous.

The chemistry of barium, Ba, is unexceptional but $BaSO_4$ is used as a contrast medium for X-ray diagnosis of the stomach because it is insoluble in hydrochloric acid. The Ba^{2+} ion is highly toxic and water-soluble compounds containing the ion should be handled cautiously.

Although radium, Ra, exists in uranium ores, the content is as low as 10^{-6} times that of uranium, U. Mr. and Mrs. Curie isolated a trace quantity of uranium chloride from tons of pitchblende in 1898. Elemental uranium was also isolated by Mrs. Curie via an amalgam. Although radium has historical importance in radiochemistry, it is no longer used as a radiation source.

Exercise 5.2 Show examples of main group organometallic compounds which are often used in synthetic chemistry.

[Answer] Butyl lithium, LiBu, Grignard reagent, RMgBr, triethylaluminum, $AlEt_3$, and diethyl zinc $ZnEt_2$.

5.3 Group 12 metals

Sulfide ores of zinc, Zn, cadmium, Cd, and mercury, Hg, of Group 12 metals (Table 5.3) serve as raw materials in metallurgy. These metals are located immediately after the transition metals in the periodic table but they do not behave like transition metals because their *d* orbitals are filled, and zinc and cadmium exhibit properties intermediate between hard and soft reactivities of magnesium. Mercury is soft and a liquid and it tends to bond to phosphorus or sulfur ligands. Mercury forms monovalent and divalent compounds but monovalent mercury is actually Hg_2^{2+}. This is a cationic species which has a Hg-Hg bond, and mercury further catenates to give, for example, $Hg_4(AsF_6)_2$.

Table 5.3 Properties of group 12 metals

	mp (°C)	bp (°C)	*d*(25 °C) (g cm^{-3})	E^0(V) $M^{2+}+2e^-$	*I*(kJ mol^{-1}) first	second	third
Zn	420	907	7.14	-0.76	906	1733	3831
Cd	321	767	8.65	-0.40	877	1631	3644
Hg	-38.8	357	13.5	0.85	1007	1809	3300

Cadmium and mercury are poisonous, especially organic cadmium and organic mercury compounds are deadly poisons and should be handled carefully.

5.4 Group 13 metals

Aluminum, Al, among Group 13 metals (Table 5.4) exists as aluminosilicates in the Earth's crust and is more abundant than iron. The most important mineral for metallurgy is bauxite, $AlO_x(OH)_{3-2x}$ ($0< x<1$). Although the Al metal was as valuable as noble metals in the 19th century, the price fell dramatically after it came to be manufactured in large quantities by electrolysis of alumina, Al_2O_3, melted in cryolite, Na_3AlF_6. However, because its production requires consumption of a large amount of electrical power, the metallurgy of aluminum is economically feasible only in countries where the price of electrical power is low. Therefore, Japan has withdrawn from aluminum smelting, but Japan's consumption of the metal is second only to the United States. The properties of aluminum are well known as it is widely used and encountered in every day life, for example in one-yen coins, aluminum foil, cooking pans, aluminum window sashes, *etc*. Aluminum metal usually exceeds 99% purity, and the metal itself and its alloys, like duralumin, are widely used.

Table 5.4 Properties of group 13 metals

	mp	bp	d(20 °C)	E^0(V)	I(kJ mol^{-1})		
	(°C)	(°C)	(g cm^{-3})	$M^{3+}+3e^-$	first	second	third
Al	660	2519	2.70	-1.66	577	1816	2744
Ga	29.8	2204	5.90	-0.55	579	1979	2962
In	157	2072	7.31	-0.34	558	1820	2704
Tl	304	1473	11.9	+0.74	589	1971	2877

Aluminum metal dissolves in mineral acids, except concentrated nitric acid, and in aqueous solutions of alkali metal hydroxides evolving hydrogen. Aluminum forms compounds with most nonmetallic elements and shows a rich chemistry, but unlike boron, no cluster hydrides are known. As oxide and halides have already been described (4.3 (c), 4.5 (d)), organo-aluminum compounds will be mentioned here.

Organoaluminum compounds

Organoaluminum compounds are used in large quantities for olefin polymerization, and they are industrially manufactured from aluminum metal, hydrogen, and an olefin as follows.

$$2\,\mathrm{Al} + 3\,\mathrm{H_2} + 6\,\mathrm{CH_2} = \mathrm{CHR} \rightarrow \mathrm{Al_2(CH_2CH_2R)_6}$$

They are dimers except those with bulky hydrocarbyl groups. For example, trimethylaluminum, $Al_2(CH_3)_6$, is a dimer in which methyl groups bridge aluminum atoms by electron deficient bonds (Fig. 5.2). Organnoaluminum compounds are very reactive and burn spontaneously in air. They react violently with water and form saturated hydrocarbons, with aluminium changing to aluminium hydroxide as follows.

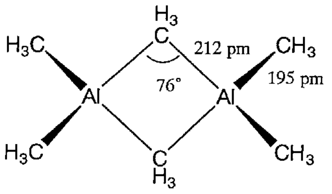

Fig. 5.2 Structure of trimethylaluminum.

$$Al(CH_2CH_3)_3 + 3\,H_2O \rightarrow 3\,C_2H_6 + Al(OH)_3$$

Therefore, they should be handled in the laboratory under a perfectly inert atmosphere. The Ziegler-Natta catalyst, comprising an organoaluminium compound and a transition metal compound was an epoch-making olefin polymerization catalyst developed in the 1950s, for which the Nobel prize (1963) was awarded.

A transition-metal alkyl compound is formed when an organoaluminum compound reacts with a transition-metal compound. The transition-metal alkyl compound so formed can be isolated when stabilization ligands are coordinated to the metal center.

Gallium, Ga, has the largest temperature difference of the melting point and boiling point among all the metals. Since it melts slightly above a room temperature, the temperature range of the liquid state is very wide and it is used as a high temperature thermometer. In recent years, the metal is used for the manufacture of the compound semiconductors gallium arsenide, GaAs, and gallium phosphide, GaP.

Indium In is a soft metal also with a low melting-point. It is the raw material for compound semiconductors InP, InAs, *etc*. Indium has two stable states, In (I) or In (III), and In (II) compounds are considered to be **mixed-valence compounds** of monovalent and trivalent In.

Thallium Tl also has two stable states, Tl (I) and Tl (III), and Tl (II) is a mixed valence compound of monovalent and trivalent Tl. Since the element is very poisonous, the metal and its compounds should be handled carefully. As it is a weak reductant compared to $Na(C_5H_5)$, thallium cyclopentadienide, $Tl(C_5H_5)$, is sometimes used for the preparation of cyclopentadienyl compounds, and is a useful reagent in organometallic chemistry.

Exercise 5.3 Give the example of the metals for which stable ions differing in oxidation numbers exist.

[Answer] In(I), In(III), Tl(I), Tl(III), Sn(II), Sn(IV).

The reaction of organoaluminum compounds

Organoaluminum compounds were synthesized for the first time in 1859, but they were not regarded as important as Grignard reagents or organolithium compounds as synthetic reagents for some time. This is in part due to the low reactivity of the ether adducts, $R_3Al:OEt_2$, which were present because of the frequent use of ether as a solvent. The studies of K. Ziegler changed this situation. K. Ziegler also discovered oligomerization of ethylene by organoaluminum compounds and the formation of higher organoaluminum compounds by the insertion of ethylene in aluminum-carbon bonds. Since alcohols were formed by hydrolysis of organoaluminum compounds, these discoveries were important for organic synthesis.

The discovery of the action of trace amount of nickel in the reaction vessel to give only butene from ethylene led to investigation of the effect of transition metals upon this reaction. Many transition metal salts were examined and Ziegler discovered that titanium compounds gave the highest degree of polymerization of ethylene. This was the birth of the so-called Ziegler catalysts. It should be remembered that this great discovery of the 1950s occurred when the petrochemical industry was beginning to develop and revolutionized the chemical industry of higher polymers.

5.5 Group 14 metals

Of the ten isotopes of tin, Sn, ^{118}Sn (24.22%) and ^{120}Sn (33.59%) are the most abundant. Metallic tin is present as α tin (gray tin), which is stable below 13.2 ^{o}C and β tin which is stable at higher temperatures. At low temperatures, the phase transition is quick. Divalent and tetravalent compounds are common, and divalent compounds are reducing agents.

^{208}Pb (52.4%) is the most abundant among the four stable isotopes of lead, Pb. Lead is the end product of natural radioactive decay and has 82 protons. The atomic number 82 is important as it is especially stable. Thus, Pb exhibits high abundance for a heavy element. The divalent and tetravalent oxidation states are most common and usually lead is present as Pb^{2+} except in organometallic compounds. PbO_2 is a tetravalent compound and readily becomes divalent, hence it is a very strong oxidizing agent. Although tetraethyl lead was previously used as an anti-knock agent in gasoline, only unleaded gasoline is now permitted for use in Japan.

It has been known since the 1930s that when Ge, Sn, or Pb are reduced by sodium in liquid ammonia, multi nuclear anions such as Ge_9^{4-}, Sn_5^{2-}, and Pb_9^{4-}, are formed. These are called Zintl phases. These multi-atom anions were crystallized as $[Na(crypt)]_4 [Sn_9]$ *etc*. recently using a cryptand, and cluster structures have been elucidated.

Problem

5.1 Write a balanced equation for the formation of butyllithium.
5.2 Potassium permanganate is insoluble in benzene but it dissolves in this solvent in the presence of a crown ether which is a cyclic polyether. Why is the solubility of potassium permanganate increased in the presence of a crown ether?
5.3 Why is trimethylaluminum called an electron deficient compound?

6 Chemistry of Transition Metals

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Simple substances of transition metals have properties characteristic of metals, *i.e.* they are hard, good conductors of heat and electricity, and melt and evaporate at high temperatures. Although they are used widely as simple substances and alloys, we typically encounter only iron, nickel, copper, silver, gold, platinum, or titanium in everyday life. However, molecular complexes, organometallic compounds, and solid-state compounds such as oxides, sulfides, and halides of transition metals are used in the most active research areas in modern inorganic chemistry.

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Transition elements are metallic elements that have incomplete *d* or *f* shells in the neutral or cationic states. They are called also transition metals and make up 56 of the 103 elements. These transition metals are classified into the *d*-block metals, which consist of 3*d* elements from Sc to Cu, 4*d* elements from Y to Ag, and 5*d* elements from Hf to Au, and *f*-block metals, which consist of lanthanoid elements from La to Lu and actinoid elements from Ac to Lr. Although Sc and Y belong to the *d*-block, their properties are similar to those of lanthanoids. The chemistry of *d*-block and *f*-block elements differs considerably. This chapter describes the properties and chemistry of mainly *d*-block transition metals.

6.1 Structures of metal complexes

(a) Central metals

Properties of *d*-block transition metals differ considerably between the first (3*d*) and the second series metals (4*d*), although the differences in properties between the second and the third series (5*d*) metals is not pronounced. Metallic radii of elements from scandium, Sc, to copper, Cu, (166 to 128 pm) are significantly smaller than those of yttrium, Y, to silver, Ag, (178 to 144 pm) or those of lanthanum, La, to gold, Au, (188 to 146 pm). Further, metal compounds of the first series transition metals are rarely 7 co-ordinate, whereas transition metals from the second and third series may be 7 to 9 coordinate. Cerium, Ce, (radius 182 pm) ~ lutetium, Lu, (radius 175 pm) fall between La and Hf and, because of the lanthanide contraction, metallic radii of the second and third series transition metals show little variation.

Higher oxidation states in the second and third series transition metals are considerably more stable than those in the first series transition metals. Examples include tungsten hexachloride, WCl_6, osmium tetroxide, OsO_4, and platinum hexafluoride, PtF_6. Compounds of the first series transition metals in higher oxidation states are strong oxidants and thus are readily reduced. On the other hand, whereas M(II) and M(III) compounds are common among the first series transition metals, these oxidation states are generally uncommon in compounds of second and third series metals. For example, there are relatively few Mo(III) or W(III) compounds compared with many Cr(III) ones. Aqua ions (ions with water ligands) are very common among compounds of first series metals but few are known amongst the second and third metal compounds.

Metal carbonyl cluster compounds of first series transition metals with M-M bonds in low oxidation states exist but halide or sulfide cluster compounds are rare. In general, metal-metal bonds are formed much more easily in the 4*d* and 5*d* metals than in the 3*d* ones. Magnetic moments of the first series transition metal compounds can be explained in terms of spin-only values (*cf.* Chapter 6.2 (d)) but it is difficult to account for the magnetic moments of the second and third series compounds unless complex factors such as spin-orbital interactions are taken into account.

Thus, it is necessary to acknowledge and understand the significant differences in chemical properties that exist between metals of the first and later series metal compounds, even for elements in the same group.

Properties of the *d*-block transition metals are different not only in the upper and lower positions in the periodic table but also in the left and right groups. The Group 3 to 5 metals are now often referred to as **early transition metals** and they are generally oxophilic and halophilic. Smaller numbers of *d* electrons and the hardness of these elements explain their affinity toward hard oxygen and halogens. In the absence of bridging ligands, the formation of metal-metal bonds is difficult for these elements. Organometallic compounds of these metals are known strongly to activate C-H bonds in hydrocarbons. **Late transition metals** in the groups to the right of the periodic table are soft and have a high affinity toward sulfur or selenium.

The *d*-block transition metals have *s*, *p*, and *d* orbitals and those with n electrons in the *d* orbitals are termed **ions with a d^n configuration**. For example, Ti^{3+} is a d^1 ion, and Co^{3+} a d^6 ion. The number of electrons occupying the orbitals split by the ligand field (*cf.* 6.2(a)) is denoted by a superscript on the orbital symbol. For example, an ion with 3 electrons in t_{2g} and 2 electrons in e_g is described as $t_{2g}^3e_g^1$.

(b) Ligands

Compounds of metal ions coordinated by ligands are referred to as **metal complexes**. Most ligands are neutral or anionic substances but cationic ones, such as the tropylium cation, are also known. Neutral ligands, such as ammonia, NH_3, or carbon monoxide, CO, are independently stable molecules in their free states, whereas anionic ligands, such as Cl^- or $C_5H_5^-$, are stabilized only when they are coordinated to central metals. Representative ligands are listed in Table 6.1 according to the ligating elements. Common ligands or those with complicated chemical formula are expressed in abbreviated forms.

Those ligands with a single ligating atom are called **monodentate ligands**, and those with more than one ligating atoms referred to as **polydentate ligands,** which are also called **chelate ligands**. The number of atoms bonded to a central metal is the **coordination number**.

Table 6.1 Representative ligands

Name	Abbreviation	Formula
hydrido		H^-
carbonyl		CO
cyano		CN^-
methyl	Me	CH_3^-
cyclopentadienyl	Cp	$C_5H_5^-$
carbonato		CO_3^{2-}
ammine		NH_3
pyridine	py	C_5H_5N
bipyridine	bipy	$C_{10}H_8N_2$
triphenylphosphine	PPh_3	$P(C_6H_5)_3$
aqua	aq	H_2O
acetylacetonato	acac	$CH_3C(O)CH_2C(O)CH_3^-$
thiocyanato		SCN^-
chloro		Cl^-
ethylenediaminetetraacetato	edta	$(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{4-}$

(c) Coordination number and structures

Molecular compounds which consist of *d*-block transition metals and ligands are referred to as complexes or **coordination compounds**. The coordination number is determined by the size of the central metal, the number of *d* electrons, or steric effects arising from the ligands. Complexes with coordination numbers between 2 and 9 are known. In particular 4 to 6 coordination are the most stable electronically and

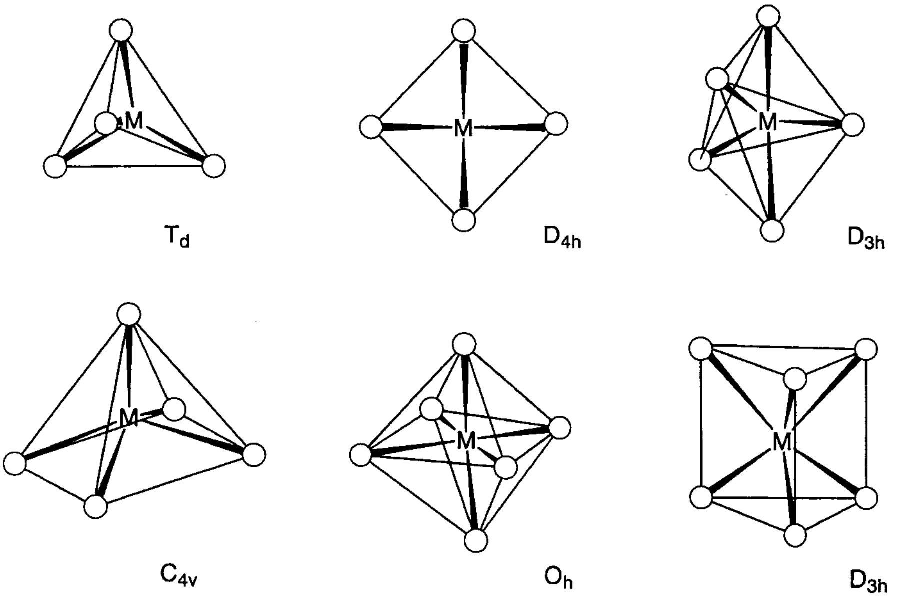


Fig. 6.1 Structure of 4 ~ 6 coordination.

geometrically and complexes with these coordination numbers are the most numerous (Fig. 6.1). Complexes with the respective coordination numbers are described below.

Two co-ordinate complexes

Many electron-rich d^{10} ions, *viz*: Cu^+, Ag^+, and Au^+, form linear complexes such as $[Cl\text{-}Ag\text{-}Cl]^-$ or $[H_3N\text{-}Au\text{-}NH_3]^-$. A zero-valent complex $[Pd(PCy_3)_2]$ with very bulky tricyclohexylphosphine ligands is also known. Generally, stable 2-coordinate complexes are known for the late transition metals.

Three co-ordinate complexes

Although $[Fe\{N(SiMe_3)_3\}_3]$ is one example, very few 3-coordinate complexes are known.

Four co-ordinate complexes

When four ligands coordinate to a metal, tetrahedral (T_d) coordination is the least congested geometry, although a number of square planar (D_{4h}) complexes are known. $[CoBr_4]^{2-}$, $Ni(CO)_4$, $[Cu(py)_4]^+$, $[AuCl_4]^-$ are all examples of tetrahedral complexes. There are a few known examples of square planar complexes with identical ligands, such as $[Ni(CN)_4]^{2-}$, or $[PdCl_4]^{2-}$. In the case of **mixed ligand complexes**, a number of square planar complexes of d^8 ions, Rh^+, Ir^+, Pd^{2+}, Pt^{2+}, and Au^{3+}, have been reported. Examples include $[RhCl(PMe_3)_3]$, $[IrCl(CO)(PMe_3)_2]$, $[NiCl_2(PEt_3)_2]$, and $[PtCl_2(NH_3)_2]$ (Et = C_2H_5).

Cis and trans **geometrical isomers** are possible for complexes with two different kinds of ligands, and were first noted when A. Werner synthesized 4-coordinate $[PtCl_2(NH_3)_2]$. As tetrahedral complexes do not give geometrical isomers, Werner was able to conclude that his 4-coordinate complexes were square planar. Recently *cis*-$[PtCl_2(NH_3)_2]$ (Cisplatin) has been used for the treatment of tumors and it is noteworthy that only the *cis* isomer is active.

Exercise 6.1 Write the formal name of *cis*-$[PtCl_2(NH_3)_2]$.
[Answer] *cis*-diamminedichloroplatinum.

Five co-ordinate complexes

Trigonal bipyramidal (D_{3h}) $Fe(CO)_5$ or square pyramid (C_{4v}) $VO(OH_2)_4$ are examples of 5-coordinate complexes. Previously, 5-coordinate complexes were rare but the number of new complexes with this coordination is increasing. The energy difference between the two coordination modes is not large and structural transformation readily occurs. For example, the molecular structure and infrared spectrum of $Fe(CO)_5$ are consistent with a trigonal bipyramid structure, but the ^{13}C NMR spectrum shows only one signal at the possible lowest temperature, which indicates that the axial and equatorial carbonyl ligands are fluxional in the NMR time scale (10^{-1}~10^{-9} s). Structural transformation takes place via a square pyramid structure and the mechanism is well known as **Berry's pseudorotation**.

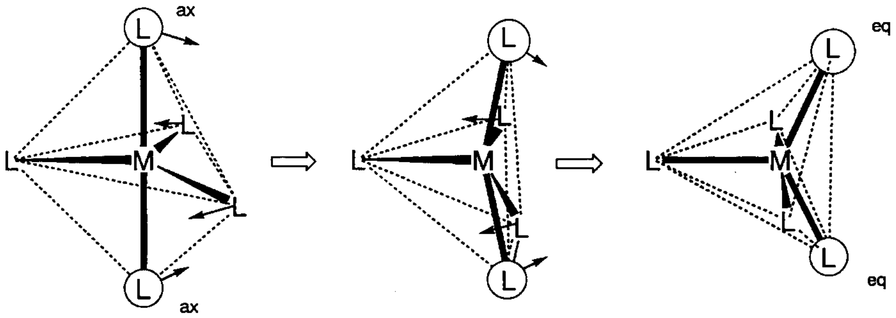
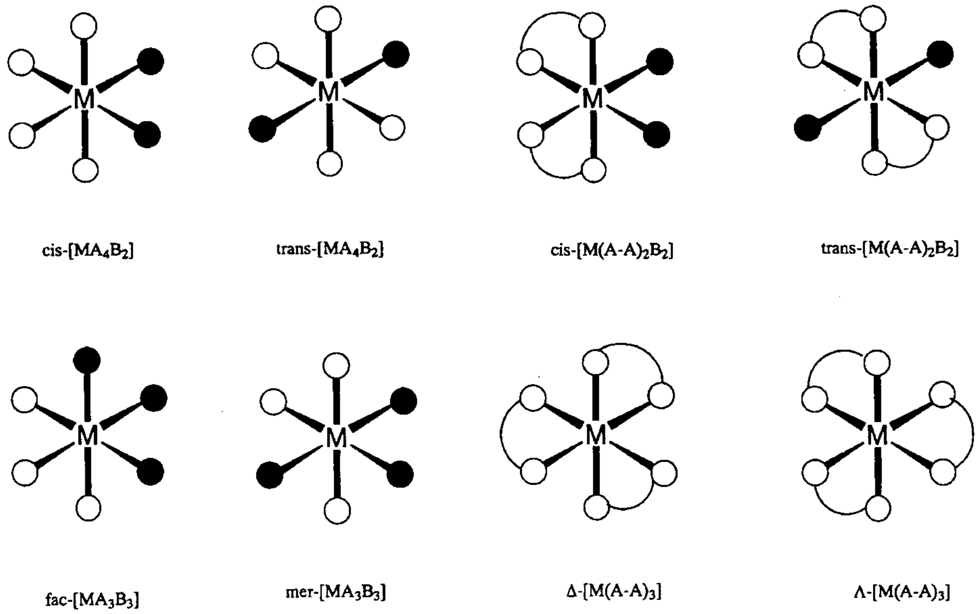


Fig. 6.2 Berry's pseudorotation.

Six co-ordinate complexes

When six ligands coordinate to a central metal, octahedral (O_h) coordination is the most stable geometry and the majority of such complexes assume this structure. In particular, there are a number of Cr^{3+} and Co^{3+} complexes which are inert to ligand exchange reactions, represented by $[Cr(NH_3)_6]^{3+}$ or $[Co(NH_3)_6]^{3+}$. They have been particularly important in the history of the development of coordination chemistry. $[Mo(CO)_6]$, $[RhCl_6]^{3-}$, *etc*. are also octahedral complexes. In the case of mixed ligands, *cis*- and *trans*-$[MA_4B_2]$ and *mer*- and *fac*-$[MA_3B_3]$ geometrical isomers, and for chelate ligands, Δ-$[M(A\text{-}A)_3]$ and Λ-$[M(A\text{-}A)_3]$ **optical isomers** (Fig. 6.3) are possible. The octahedral structure shows tetragonal (D_{4h}), rhombic (D_{2h}), or trigonal (D_{3h}) distortions caused by electronic or steric effects. The tetragonal distortion of $[Cu(NH_3)_6]^{2+}$ by an electronic factor is a typical example of the Jahn-Teller effect (refer to 6.2(a)).



cis-$[MA_4B_2]$ trans-$[MA_4B_2]$ cis-$[M(A\text{-}A)_2B_2]$ trans-$[M(A\text{-}A)_2B_2]$

fac-$[MA_3B_3]$ mer-$[MA_3B_3]$ Δ-$[M(A\text{-}A)_3]$ Λ-$[M(A\text{-}A)_3]$

Fig. 6.3 Geometrical isomers of 6-coordination.

Six ligating atoms can assume trigonal prism coordination. Although this coordination is seen in $[Zr(CH_3)_6]^{2-}$ or $[Re\{S_2C_2(CF_3)_2\}_3]$, few metal complexes with this coordination structure are known because octahedral coordination is sterically less strained. This notwithstanding, it has long been known that the bonding mode of sulfur atoms around a metal is trigonal prism in solid-state MoS_2 and WS_2.

Exercise 6.2 Write the chemical formula of potassium diamminetetra(isothiocyanato)chromate(III).

[Answer] $K[Cr(NCS)_4(NH_3)_2]$.

Higher co-ordinate complexes

Metal ions of the second and third transition metal series can sometimes bond with more than seven ligating atoms and examples are $[Mo(CN)_8]^{3-}$ or $[ReH_9]^{2-}$. In these cases, smaller ligands are favorable to reduce steric congestion.

6.2 Electronic structure of complexes

It is necessary to learn a few concepts to understand the structure, spectrum, magnetism, and reactivity of complexes which depend on *d* electron configurations. In particular, the theory of electronic structure is important.

(a) Ligand field theory

Ligand field theory is one of the most useful theories to account for the electronic structure of complexes. It originated in the application of the **crystal field theory** of ionic crystals to metal complex systems.

Six co-ordinate octahedral complexes

The five *d* orbitals of transition metal cations are degenerate and have equal energy.

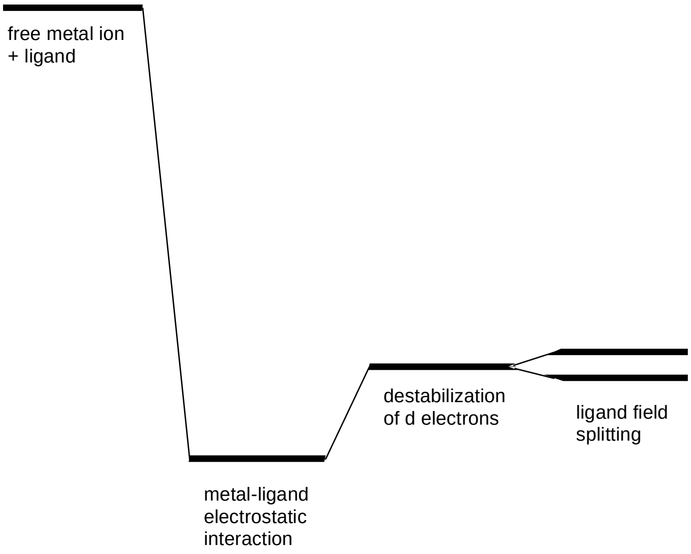
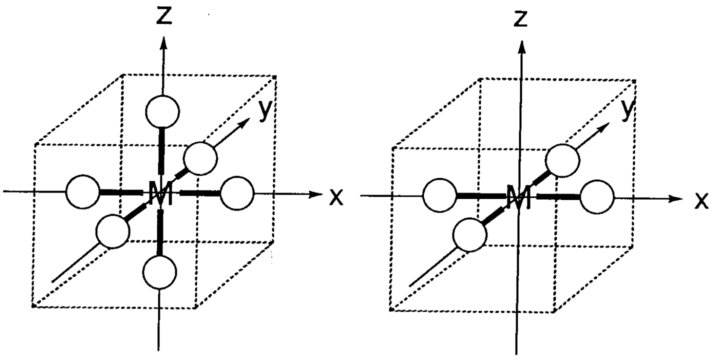
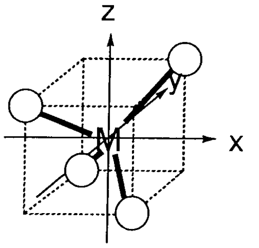


Fig. 6.4 Change of electronic energy upon complex formation.

The spherical negative electric field around a metal cation results in the total energy level being lower than that of a free cation because the electrostatic interactions. The repulsive interaction between the electrons in the metal orbitals and the negative electric field destabilizes the system and compensates for the stabilization to some extent (Fig. 6.4).



octahedral coordination square planar coordination



tetrahedral coordination

Fig. 6.5 Ligand positions in the Cartesian coordinate with a metal ion at the origin.

Let us assume that instead of a uniform spherical negative field, the field is generated by six ligands coordinating octahedrally to a central metal. The negative field of the ligands is called the **ligand field.** Negative charge, in the case of anionic ligands, or a negative end (lone pair), in the case of neutral ligands, exert a repulsive force on the metal *d* orbitals which is anisotropic depending on the direction of the orbitals. The position of the metal cation is taken as the origin and Cartesian coordinates are constructed (Fig. 6.5). Then, d_{x2-y2} and d_{z2} orbitals are aligned along the directions of the axes and the d_{xy}, d_{yz}, and d_{xz} orbitals are directed between the axes. If ligands are placed on the axes, the repulsive interaction is larger for the e_g orbitals (d_{x2-y2}, d_{z2}) than for the t_{2g}

orbitals (d_{xy}, d_{yz}, d_{xz}), and the e_g orbitals are destabilized and the t_{2g} orbitals are stabilized to an equal extent. In the following discussion, only the energy difference between the t_{2g} and e_g orbitals is essential and the average energy of these orbitals is taken as the zero of energy. If the energy difference between the two e_g and three t_{2g} orbitals is set to Δ_o, the energy level of the e_g orbitals is $+3/5\Delta_o$ and that of the t_{2g} orbitals is $-2/5\Delta_o$ (Fig. 6.6). (Δ_o may also be expressed as 10 Dq. In this case, the energy level of the e_g orbitals is +6 Dq and that of the t_{2g} orbitals -4 Dq.)

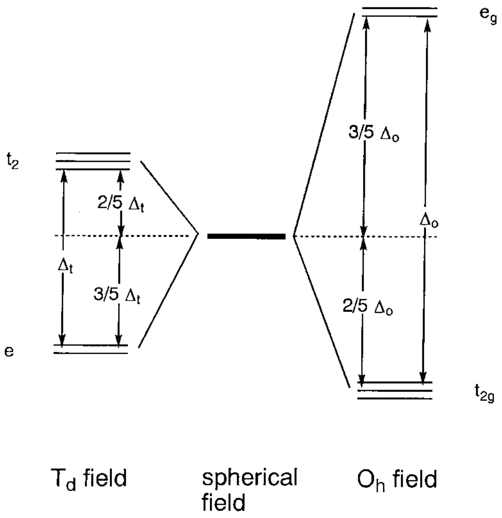


Fig. 6.6 Ligand field splitting in tetrahedral and octahedral complexes.

Transition metal ions have 0 to 10 *d* electrons and when the split *d* orbitals are filled from a lower energy level, the electron configuration $t_{2g}^{x}e_g^{y}$ corresponding to each ion is obtained. With the zero energy level chosen as the average energy level, the energy of the electron configuration relative to zero energy becomes

$$\text{LFSE} = (-0.4x + 0.6y)\ \Delta o$$

This value is called the **ligand field stabilization energy**. The electron configuration with smaller value (taking the minus sign into consideration) is more stable. LFSE is an important parameter to explain some properties of *d*-block transition metal complexes.

A condition other than the orbital energy level is required to explain the filling of electrons being populated into the split t_{2g} and e_g orbitals,. Two electrons can occupy an orbital with anti-parallel spins but a strong electrostatic repulsion occurs between two electrons in the same orbital. This repulsive interaction is called **pairing energy,** *P*.

When the number of *d* electrons is less than three, the pairing energy is minimized by loading the electrons in the t_{2g} orbital with parallel spins. Namely, the electron configurations arising are t_{2g}^1, t_{2g}^2, or t_{2g}^3.

Two possibilities arise when the fourth electron occupies either of the t_{2g} or e_g orbitals. The lower energy orbital t_{2g} is favorable but occupation of the same orbital gives rise to pairing energy, *P*. The total energy becomes

$$-0.4\Delta o \text{ x } 4 + P = -1.6\Delta o + P$$

If the fourth electron occupies the energetically unfavorable e_g orbital, the total energy becomes

$$-0.4\Delta o \text{ x } 3 + 0.6\Delta o = -0.6\Delta o$$

The choice of the electron configuration depends on which of the above values is larger. Therefore if $\Delta o > P$, t_{2g}^4 is favoured and this is called the strong field case or the **low spin electron configuration**. If $\Delta o < P$, $t_{2g}^3 e_g^1$ is favoured and this is called the weak field case or the **high spin electron configuration**. A similar choice is required for d^5, d^6, and d^7 octahedral complexes, and in the strong field case, t_{2g}^5, t_{2g}^6, or $t_{2g}^6 e_g^1$ configurations are favoured, whereas in the weak field case, $t_{2g}^3 e_g^2$, $t_{2g}^4 e_g^2$, or $t_{2g}^5 e_g^2$ configurations are favoured. The ligand field splitting parameter Δo is decided by the nature of the ligands and metal, whereas the pairing energy, *P*, is almost constant and shows only a slight dependence on the identity of the metal.

Square planar complexes

Complexes with four ligands in a plane containing the central metal are termed square planar complexes. It is easier to understand the electronic energy levels of the *d* orbitals in square planar complexes by starting from those for hexacoordinate octahedral complexes. Placing the six ligands along the Cartesian axes, the two ligands on the z axis are gradually removed from the central metal and finally only four ligands are left on the x,y plane. The interaction of the two z coordinate ligands with the d_{z2}, d_{xz}, and d_{yz} orbitals becomes smaller and the energy levels of these ligands lower. On the other hand, the remaining four ligands approach the metal and the d_{x2-y2} and d_{xy} energy levels rise as a result of the removal of the two ligands. This results in the order of the energy levels of five d orbitals being $d_{xz}, d_{yz} < d_{z2} < d_{xy} << d_{x2-y2}$ (Fig. 6.7). Rh^+, Ir^+, Pd^{2+}, Pt^{2+}, and Au^{3+} complexes with a d^8 configuration tend to form square planar structures because eight electrons occupy the lower orbitals leaving the highest d_{x2-y2} orbital empty.

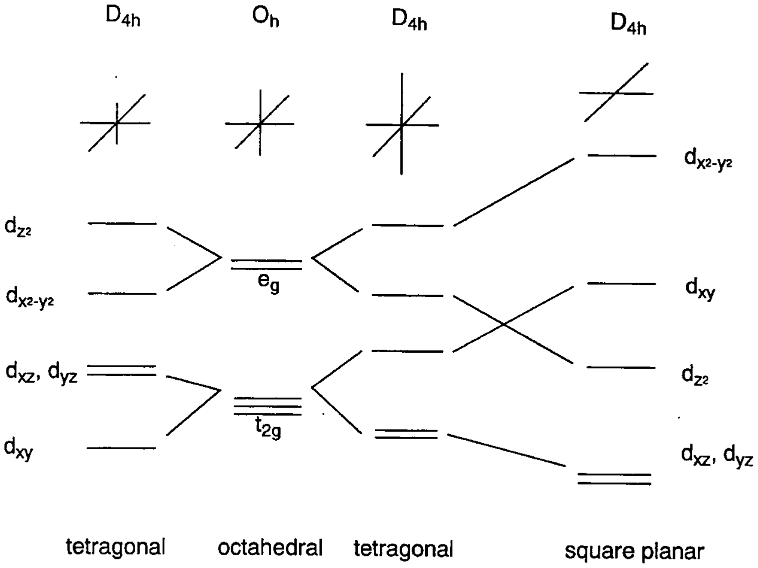


Fig. 6.7 Change of the orbital energy from octahedral to square planar complexes.

Tetrahedral complexes

Tetrahedral complexes have four ligands on the apexes of a tetrahedron around the central metal. $[CoX_4]^{2-}$ (X = Cl, Br, I), $Ni(CO)_4$, *etc.* are all examples of 4-coordination complexes (Fig. 6.5). When a metal is placed on the origin of the Cartesian axes, as in the octahedral complexes, *e* orbitals (d_{x2-y2}, d_{z2}) are distant from ligands and t_2 orbitals (d_{xy}, d_{yz}, d_{xz}) are nearer ligands. Consequently, the electronic repulsion is larger for the t_2 orbitals, which are destabilized relative to the *e* orbitals. The ligand field exerted by four ligands splits the fivefold degenerate orbitals of the central metal into twofold degenerate *e* and threefold degenerate t_2 sets (Fig. 6.6). The t_2 set has energy of +2/5 Δ_t and the *e* set -3/5 Δ_t with a ligand field splitting of Δ_t. As the number of the ligands is 4/6 = 2/3 of that in hexacoordinate octahedral complexes, and overlap of the ligands with the orbitals is smaller, and the ligand splitting Δt is about a half of Δo. Consequently, only high-spin electron configurations are known in tetrahedral complexes. The ligand field splitting energies calculated by the above method are shown in Table 6.2.

Table 6.2 Ligand field stabilization energy (LFSE)

		Octahedral				Tetrahedral	
		Strong field (LS)		Weak field(HS)			
d^n	Example	n	Δo	n	Δo	n	Δt
d^1	Ti^{3+}	1	0.4	1	0.4	1	0.6
d^2	V^{3+}	2	0.8	2	0.8	2	1.2
d^3	Cr^{3+},V^{2+}	3	1.2	3	1.2	3	0.8
d^4	Cr^2,Mn^{3+}	2	1.6	4	0.6	4	0.4
d^5	Mn^{2+},Fe^{3+}	1	2.0	5	0	5	0
d^6	Fe^{2+},Co^{3+}	0	2.4	4	0.4	4	0.6
d^7	Co^{2+}	1	1.8	3	0.8	3	1.2
d^8	Ni^{2+}	2	1.2	2	1.2	2	0.8
d^9	Cu^{2+}	1	0.6	1	0.6	1	0.4
d^{10}	Cu^1	0	0	0	0	0	0

Jahn-Teller effect

When orbitals of a highly symmetrical nonlinear polyatomic molecule are degenerate, the degeneracy is resolved by distorting the molecular framework to attain lower symmetry and thus lower energy. This is the **Jahn-Teller effect** and a typical example is seen in the tetragonal distortion of an octahedral coordination structure of hexacoordinate Cu^{2+} complexes.

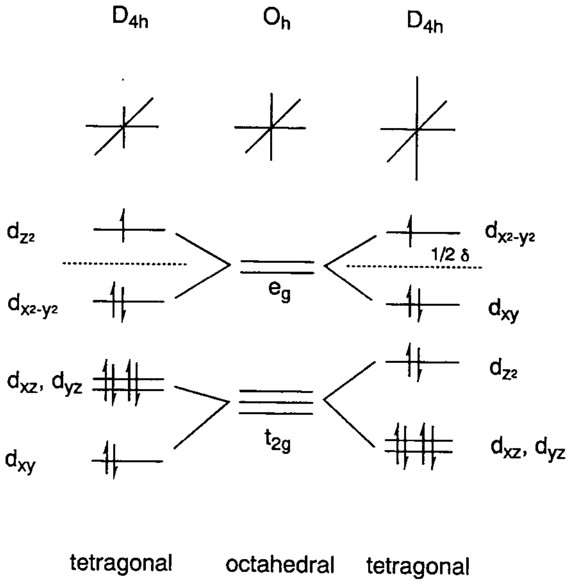


Fig. 6.8 Jahn-Teller splitting in a Cu^{2+} ion.

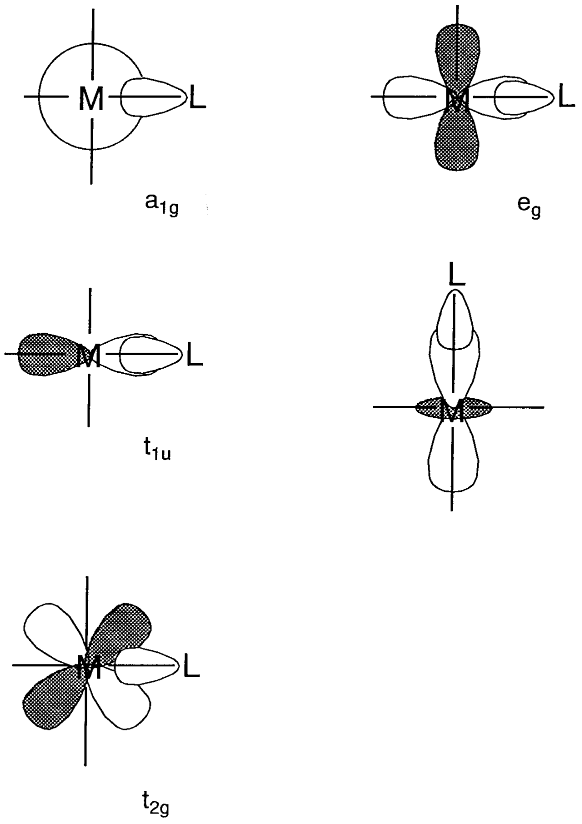


Fig. 6.9 The relation between the metal and ligand orbitals during formation of σ bonds.

They have a d^9 configurations and the e_g orbitals in the octahedral structure are occupied by three electrons. If the e_g orbitals split and two electrons occupy the lower orbital and one electron the upper orbital, the system gains energy of a half of the energy difference, δ, of two split orbitals. Therefore a tetragonal distortion in the z axis becomes favorable.

Molecular orbital theory of transition metal complexes

The characteristics of transition metal-ligand bonds become clear by an analysis of the molecular orbitals of a 3*d* metal coordinated by six identical ligands in octahedral complexes [ML_6]. As the result of the interaction between the metal *d* and ligand orbitals, bonding, non-bonding and anti-bonding complex molecular orbitals are formed.

Generally, the energy levels of the ligand orbitals are lower than those of the metal orbitals, bonding orbitals have more ligand character and non-bonding and anti-bonding orbitals have more metal character. The processes of formation of the σ and π molecular orbitals are described step by step below.

σ bond

Firstly, consider the M-L σ bond among interactions of the metal *s*, *p*, *d* and ligand orbitals by assuming the position of a metal at the origin of the Cartesian coordinate system and locating ligands on the coordinate axes. As the σ bond is a nodeless bond along the bonding axes, the metal *s* orbital (a_{1g}, non-degenerate), p_x, p_y, p_z orbitals (t_{1u}, triply-degenerate), and $d_{x2\text{-}y2}$, d_{z2} orbitals (e_g, doubly-degenerate) fit symmetry (+, - signs) and orbital shapes with the ligands' σ orbitals (Fig. 6.9).

When the ligand orbitals are σ_1 and σ_2 along the x-axis, σ_3 and σ_4 along the y-axis, and σ_5 and σ_6 along the z-axis in Fig. 6.5, six ligand atomic orbitals are grouped by making linear combinations according to the symmetry of the metal orbitals. Then the orbital to fit with the metal a_{1g} orbital is a_{1g} ($\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6$), the one to fit with the metal t_{1u} orbitals is t_{1u} ($\sigma_1-\sigma_2$, $\sigma_3-\sigma_4$, $\sigma_5-\sigma_6$) and the one to fit with the metal e_g orbitals is e_g ($\sigma_1+\sigma_2-\sigma_3-\sigma_4$, $2\sigma_5+2\sigma_6-\sigma_1-\sigma_2-\sigma_3-\sigma_4$). There is a bonding interaction between the metal e_g orbitals and the ligand group orbitals and bonding and anti-bonding molecular orbitals are formed. The relation is shown in Fig. 6.10.

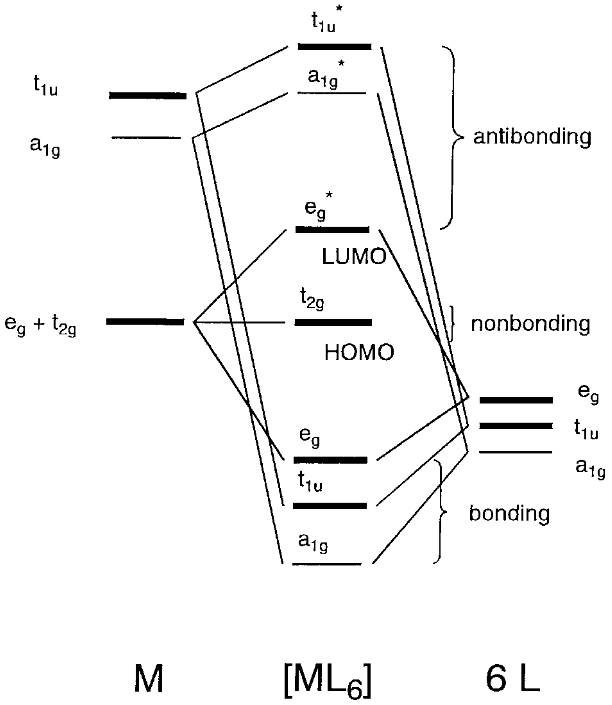


Fig. 6.10 Bonding and anti-bonding M(metal)-L(ligand) molecular orbitals.

The levels of the molecular orbitals from the lowest energy are bonding ($a_{1g}<t_{1u}<e_g$) < non-bonding (t_{2g}) < anti-bonding ($e_g^*<a_{1g}^*<t_{1u}^*$). For example, in a complex like $[Co(NH_3)_6]^{3+}$, 18 valence electrons, 6 from cobalt and 12 from ammonia, occupy 9

orbitals from the bottom up, and t_{2g} is the HOMO and e_g^* the LUMO. The energy difference between the two levels corresponds to the ligand field splitting. Namely, the e_g set ($d_{x2-y2,}$ d_{z2}) and the ligands on the corner of the octahedron form the bonding σ orbitals but the t_{2g} set (d_{xy}, d_{yz}, d_{xz}) remain non-bonding because the orbitals are not directed to the ligand σ orbitals.

π bond

When the ligand atomic orbitals have π symmetry (i.e. with nodes) through the bond axis, the e_g orbitals (d_{x2-y2}) are non-bonding and the t_{2g} orbitals (d_{xy}, d_{yz}, d_{xz}) have bonding interactions with them (Fig. 6.11). In halide ions, X^-, or aqua ligands, H_2O, the π

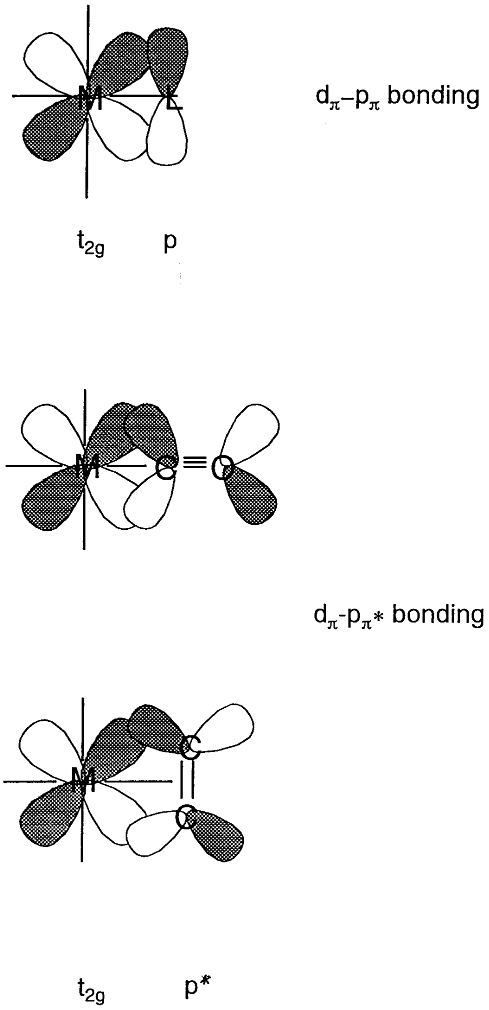


Fig. 6.11 The relation between the metal and ligand orbitals in formation of a *π* bond.

symmetrical *p* orbitals have lower energy than the metal t_{2g} orbitals and a bonding molecular orbital, which is lower than the t_{2g} orbital, and an anti-bonding molecular orbital, which is higher than the t_{2g} orbitals, form. Consequently, the energy difference Δ_o between e_g and the anti-bonding orbitals becomes smaller. On the other hand, for the ligands having anti-bonding π orbitals within the molecule, such as carbon monoxide or ethylene, the π^* orbitals match the shape and symmetry of the t_{2g} orbitals and the molecular orbitals shown in Fig 6.12 (b) form. As a result, the energy level of the bonding orbitals decreases and Δ_o becomes larger.

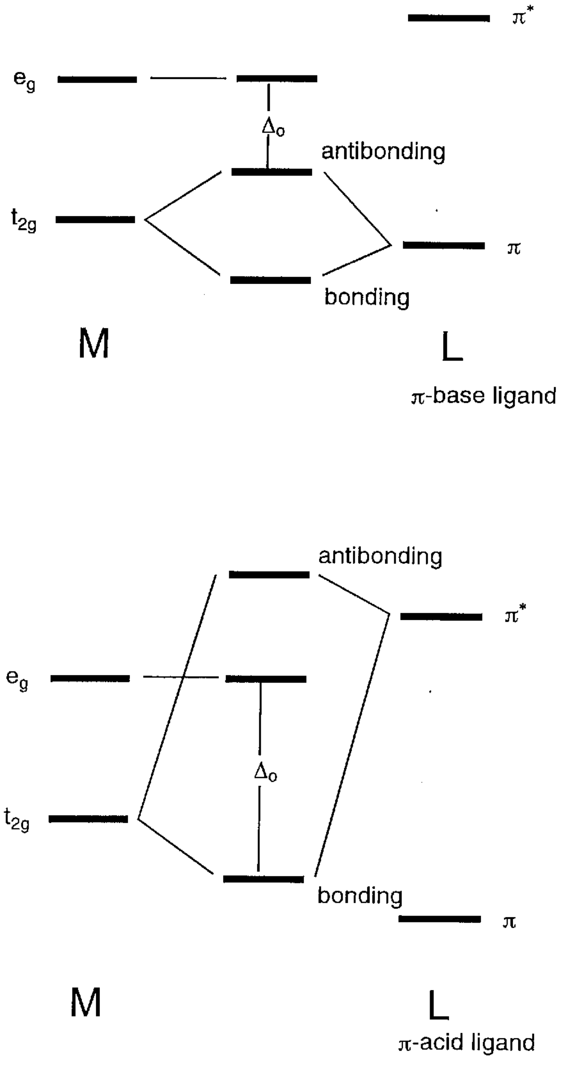


Fig. 6.12 The energy change upon formation of M-L_π bonds.

Using these simple molecular orbital considerations, the effects of σ and π orbital interactions between the metal and ligands upon the molecular orbitals are qualitatively understandable.

(c) Spectra

Many transition metal complexes have characteristic colors. This means that there is absorption in the visible part of the spectrum resulting from an electron being excited by visible light from a level occupied by an electron in a molecular orbital of the complex to an empty level. If the energy difference between the orbitals capable of transition is set to ΔE, the absorption frequency ν is given by $\Delta E = h\nu$. Electronic transitions by optical pumping are broadly classified into two groups. When both of the molecular orbitals between which a transition is possible have mainly metal *d* character, the transition is called a ***d-d* transition** or **ligand-field transition**, and absorption wavelength depends strongly on the ligand-field splitting. When one of the two orbitals has mainly metal character and the other has a large degree of ligand character, the transition is called a **charge-transfer transition**. Charge transfer transitions are classified into metal (M) to ligand (L) charge-transfers (MLCT) and ligand to metal charge-transfers (LMCT).

Since the analysis of the spectra of octahedral complexes is comparatively easy, they have been studied in detail for many years. When a complex has only one *d* electron, the analysis is simple. For example, Ti in $[Ti(OH_2)_6]^{3+}$ is a d^1 ion, and an electron occupies the t_{2g} orbital produced by the octahedral ligand field splitting. The complex is purple as the result of having an absorption at 492 nm (20300 cm^{-1}) (Fig. 6.13) corresponding to the optical pumping of a *d* electron to the e_g orbital. However, in a complex with more than one *d* electrons, there are repellent interactions between the electrons, and the *d-d* transition spectrum has more than one absorptions. For example, a d^3 complex $[Cr(NH_3)_6]^{3+}$ shows two *d-d* absorptions in the 400 nm (25000 cm^{-1}) region, suggesting that the complex has two groups of molecular orbitals between which an electronic transition is possible with a high degree of transition probability. This means that, when three electrons in the t_{2g} orbital are excited to the e_g orbital, there are two energy differences due to repellent interactions between the electrons.

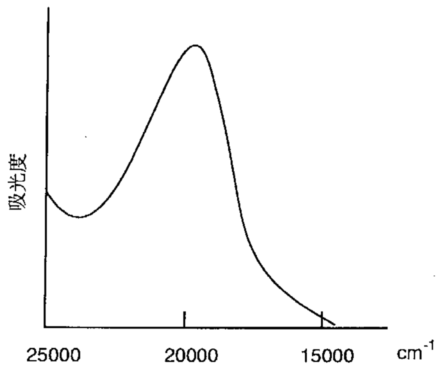


Fig. 6.13 A visible absorption spectrum of $[Ti(OH_2)_6]^{3+}$.

Tanabe-Sugano diagrams are constructed from calculations based on ligand field theory and have been widely used in the analysis of absorption spectra of d^1 to d^9 ions. The analysis becomes increasingly difficult for ions with many electrons. In any case, the existence of a *d-d* spectrum requires that the energy difference of an occupied orbital and an empty orbital is equivalent to the energy of the UV-visible spectrum, the transition is allowed by the selection rule, and the transition probability is high enough. Generally, a charge-transfer absorption is stronger than a ligand field absorption. An LMCT emerges when ligands have a non-bonding electron pair of comparatively high energy or the metal has empty low energy orbitals. On the other hand, an MLCT tends to appear when the ligands have low energy π^* orbitals, and bipyridine complexes are good examples of this. Since the lifetime of the excited state of a ruthenium complex $[Ru(bipy)_3]^{2+}$ is extraordinarily long, many studies have been performed on its photoredox reactions.

Spectrochemical series

The magnitude of the ligand field splitting parameter Δo is determined mainly by the identity of the ligands. An empirical rule called the **spectrochemical series** was proposed by a Japanese scientist Ryutaro Tsuchida. The rule was constructed from empirical data collected when spectra of complexes that have the same central metal, oxidation state, coordination number, *etc.* were measured. It is noteworthy that ligands with π acceptor properties are in a higher position in the series.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < H_2O < NH_3 < NO_2 < PPh_3 < CN^- < CO$