

## 1. The Elements and The Periodic Table

元素和周期表

The number of protons in the nucleus of an atom is referred to as the atomic number, or proton number,  $Z$ . The numbers of electrons in an electrically neutral atom is also equal to the atomic number,  $Z$ . The total mass of an atom is determined very nearly **by** the total number of protons and neutrons in its nucleus. This total is called the mass of the number,  $A$ . The number of neutrons in an atom, the neutron number, is given by the quantity  $A-Z$ .

refer to sb. [sth.] as 称某人（物）为

be determined by 由...确定

原子核中质子的数目称为原子序数，或者质子数，以  $Z$  表示。电中性原子中电子的数目也等于原子序数  $Z$ 。经测定，原子的总质量与原子核中质子与中子的总数差不多。（几乎相同）（或者说原子的总质量几乎可以由原子核中质子与中子的总数确定。）这个总数叫质量数，以  $A$  表示。因此，原子中的质子的数目，质子数，可以定量地由  $A-Z$  给出。即原子中质子数= $A-Z$

The term element refers to a pure substance with atoms all kinds of a single kind. To the chemist the “kind” of an atom is specified by its atomic number, **since this is the property that determines its chemical behavior**. At present all the atoms from  $Z=1$  to  $Z=107$  are known; there are 107 chemical elements. Each chemical element has been given a name and a distinctive symbol. For most elements the symbol is simply the abbreviated form of the English name consisting of one or two letters,

for example:

元素这个术语指的是仅仅由同一种类的原子组成的物质。对化学家（化学工作者）来说，原子的种类由原子序数决定（表示），因为这是决定它的化学表现（行为）的性质。现在已经发现了原子序数  $Z=1$  到  $Z=107$  的所有原子；这些是 107 种化学元素。每一种化学元素都被赋予了一个名字和一个特有的（与众不同的）符号。对大部分元素来说，这个含有一个或两个字母的符号仅仅是英文名字的缩写形式，例如：

specify by 用...说明（表示）

Oxygen=O    nitrogen=N    neon=Ne    magnesium=Mg

Some elements; which have been known for a long time, have symbols based on their Latin names, for example:

另外有些早已为人所知的元素的符号是拉丁文名字的缩写（是建立在拉丁文名字的基础上的），例如：

Iron(英文名字)=Fe(缩写)(ferrum)(拉丁文名字)   copper=Cu(cuprum)   lead=Pb(plumbum)

A complete listing of the elements may be found in Table 1.

更完整的元素列表（清单）见表 1。

Beginning in the late seventeenth century with the work of Robert Boyle (罗伯特·波义耳，英国化学家，物理学家)，who proposed the presently accepted concept of an element, numerous investigations produced a considerable knowledge of the properties of elements and their compounds. In 1869, D. Mendeleev and L. Meyer, working independently, proposed the periodic law. In modern form, the law states that the properties of the elements are periodic functions of their atomic numbers. In other words, when the elements are listed in order of

increasing atomic number, elements having closely similar properties will fall at definite intervals along the list. Thus it is possible to arrange the list of elements in tabular form with elements having similar properties placed in vertical columns. Such an arrangement is called a periodic table.

早在 17 世纪末期，罗伯特·波义耳就开始了这项工作，他提出了现在公认的元素概念，大量的研究使我们对元素及其化合物的性质有了相当的了解。1869 年，D. Mendeleev 和 L. Meyer 在各自工作的基础上，分别提出了元素周期律。用现代的话说，这个规律叙述了元素的性质是它们的原子序数的周期性函数。换句话说，当元素按照原子序数逐渐递增的顺序列表（排列时），性质非常接近的元素将占据表格中具有一定间隔的位置。于是，将具有类似性质的元素排成纵列，从而把元素排成表格形式是可能的。这样的排列形式就叫做元素周期表。

Each horizontal row of elements constitutes a period. It should be noted that the lengths of the periods vary. There is a very short period containing only 2 elements, followed by two periods of 8 elements each, and then two long periods of 18 elements each. The next period includes 32 elements, and the last period is apparently incomplete. With this arrangement, elements in the same vertical column have similar characteristics. These columns constitute the chemical families or groups. The groups headed by the members of the two 8-element periods are designated as main group elements, and the members of the other groups are called transition or inner transition elements.

It shoud be noted that. 应当注意的是

(在元素周期表中)，水平的每一排元素组成了一个周期。应当注意的是，周期的长短

是有变化的。首先是一个含有 2 种元素的极短周期，接着是两个短周期，每一周期含有 8 种元素，然后是各有 18 种元素的两个长周期，再下一个周期含有 32 种元素，最后一个周期显然是不完整的（尚未完全发现）。在这种排列下，处于同一纵列的元素具有相似的性质。这些纵列就组成了元素周期表中的族。由两个 8 元素周期中的元素开头的族被指定为主族元素，其它族的元素叫过度元素或内过度元素。

In the periodic table, a heavy stepped line divides the elements into metals and nonmetals. Elements to the left of this line (with the exception of hydrogen) are metals, while those to the right are nonmetals. This division is for convenience only; elements bordering the line –the metalloids-have properties characteristics of both metals and nonmetals. It may be seen that most of the elements, including all the transition and inner transition elements, are metals.

在周期表中，一条粗的阶梯状的线把元素划分为金属元素和非金属元素。处于线左边的元素（H 元素除外）是金属元素，而处于线右边的元素是非金属元素。这种分法仅仅是为了方便。靠近线两边的元素-准金属元素-同时具有金属和非金属元素的性质特征。可以看出，大部分元素，包括过度元素和内过度元素，都是金属元素。

Except for hydrogen, a gas, the elements of group IA make up the alkali metal family. They are very reactive metals, and they are never found in the element state in nature. However, their compounds are widespread. All the members of the alkali metal family form ions having a charge of 1+ only. In contrast, the elements of group IB-copper, silver, and gold-are comparatively inert. They are similar to the alkali metals in that they exist as 1+ ions in many of their compounds. However, as is

characteristic of most transition elements, they form ions having other charges as well.

除了氢，一种气体之外，IA 元素构成了碱金属家族。它们是极其活泼的金属，在自然界中从来没有发现它们的单质状态。但是，它们的化合物却分布广泛。碱金属家族的所有成员都仅仅形成带 1 个正电荷的离子。相反，IB 的元素-铜，银和金却相对惰性。与碱金属相似，它们也以 1+ 离子形式存在于许多化合物中。但是，象许多过度元素所具有的特点一样，它们也形成具有其它电荷的离子。

The elements of group IIA are known as alkaline earth metals. Their characteristic ionic charge is 2+. These metals, particularly the last two members of the group, are almost as reactive as the alkali metals. The group IIB-zinc, cadmium, and mercury are less reactive than are those of group IIA, but are more reactive than the neighboring elements of group IB. The characteristic charge on their ions is also 2+.

IIA 元素被称为碱土金属元素。它们的特征离子电荷为 2+。这些金属，尤其是这一族的最后两个成员，几乎和碱金属一样活泼。IIB 元素-锌，镉，汞不如 IIA 元素活泼，但是比相邻的 IB 的元素活泼得多。它们的离子的特征电荷也是 2+。

With the exception of boron, group IIIA elements are also fairly reactive metals. Aluminum appears to be inert toward reaction with air, but this behavior stems from (来源于, 起源于) the fact that the metal forms a thin, invisible film of aluminum oxide on the surface, which protects the bulk of (大量, 大多数) the metal from further oxidation. The metals of group IIIA form ions of 3+ charge. Group IIIB consists of the metals

scandium, yttrium, lanthanum, and actinium.

除了 B 之外, IIIA 的元素也是相当活泼的金属元素。铝对空气表现出惰性, 但是这种行为是因为金属表面形成了一层肉眼看不见的铝的氧化物薄层, 阻止了大面积的金属被进一步氧化。IIIA 的金属形成带 3+电荷的离子。IIIB 元素包括 Sc、Y、La、Ac。

Group IVA consists of a nonmetal, carbon, two metalloids, silicon and germanium, and two metals, tin and lead. Each of these elements forms some compounds with formulas which indicate that four other atoms are present per group IVA atom, as, for example, carbon tetrachloride,  $\text{CCl}_4$ . The group IVB metals-titanium, zirconium, and hafnium-also form compounds in which each group IVB atom is combined with four other atoms; these compounds are nonelectrolytes when pure.

IVA 由非金属元素 C、两种准金属元素 Si 和 Ge、两种金属元素 Sn 和 Pb 组成。IVA 每一种元素都形成一些这样的化合物, 它们的分子式指出有四个其它的原子存在于 IVA 原子周围 (或四个其它的原子与 IVA 原子结合), 如四氯化碳  $\text{CCl}_4$ 。IVB 的元素 Ti、Zr、Hf 也形成类似的化合物, 即每一个 IVB 原子与四个其它原子结合。纯的这些化合物都是非电解质。

The elements of group VA include three nonmetals-nitrogen, phosphorus, and arsenic-and two metals-antimony and bismuth. Although compounds with the formulas  $\text{N}_2\text{O}_5$ ,  $\text{PCl}_5$ , and  $\text{AsCl}_5$  exist, none of them is ionic. These elements do form compounds-nitrides, phosphides, and arsenides—in which ions having charges of minus three occur. The

elements of group VB are all metals. These elements form such a variety of different compounds that their characteristics are not easily generalized.

VA 包含三种非金属元素-N、P、As 和两种金属元素 Sb 和 Bi。尽管存在分子式为 N<sub>2</sub>O<sub>5</sub>、PCl<sub>5</sub> 和 AsCl<sub>5</sub> 的化合物，它们中没有一个是离子性的。这些元素确实形成氧化数为-3 氮化物、磷化物和砷化物。VB 族元素都是金属元素。这些元素形成如此种类繁多的化合物以至于很难概括出它们的特征。

With the exception of polonium, the elements of group VIA are typical nonmetals. They are sometimes known as the chalcogens, from the Greek word meaning “ash formers”. In their binary compounds with metals they exist as ions having a charge of 2-. The elements of group VIIA are all nonmetals and are known as the halogens, from the Greek term meaning “salt formers.” They are the most reactive nonmetals and are capable of reacting with practically all the metals and with most nonmetals, including each other.

除了 Po 之外，VIA 元素都是典型的非金属元素。有时它们也被叫做硫族元素，来源于希腊名字，意思是成灰元素。它们在与金属形成的二元化合物中，氧化数为-2（形式电荷为 2-）。以卤素闻名的 VIIA 的元素都是非金属元素，“卤素”来源于希腊术语，意思是“成盐的元素”。它们是（同周期中）最活泼的非金属元素，实际上能够和所有金属以及大部分非金属反应，包括卤素之间的反应。

The elements of groups VIB, VIIB, and VIIIB are all metals. They form such a variety of compounds that it is not practical at this point to

present any examples as being typical of the behavior of the respective groups.

VIB, VIIIB 和 VIIIB 的元素都是金属元素。它们形成了各种不同的化合物，在这一点上我们甚至不能举出任何能表现各族元素典型变化的例子。

The periodicity of chemical behavior is illustrated by the fact that, excluding the first period, each period begins with a very reactive metal. Successive elements along the period show decreasing metallic character, eventually becoming nonmetals, and finally, in group VIIA, a very reactive nonmetal is found. Each period ends with a member of the noble gas family.

元素化学性质的周期性可以由以下事实说明：除了第一周期之外，其它每一周期都从非常活泼的金属开始。同一周期随着原子序数的增加，元素的金属性减弱，最终成为非金属，最后，在第七主族，出现了活泼的非金属元素。每一周期都以惰性气体家族成员结束。

## 2. THE NONMETAL ELEMENTS (非金属元素)

We noted earlier that nonmetals exhibit properties that are greatly different from those of the metals. As a rule, the nonmetals are poor conductors of electricity (graphitic carbon is an exception) and heat; They are brittle, are often intensely colored, and show an unusually wide range of melting and boiling points. Their molecular structures, usually involving ordinary covalent bonds, vary from the simple diatomic molecules of  $H_2$ ,  $Cl_2$ ,  $I_2$ , and  $N_2$  to the giant molecules of diamond, silicon and boron.

我们很早就注意到非金属的性质与金属的性质有显著的区别。通常，非金属单质是电和热的不良导体（石墨碳除外）；易碎，颜色较深，熔点和沸点变化范围很广。它们的分子结构（通常含有一般的共价键）变化很大，从简单的双原子分子  $H_2$ ,  $Cl_2$ ,  $I_2$  和  $N_2$  到巨型的金刚石、硅和硼晶体都有。

The nonmetals that are gases at room temperature are the low-molecular weight diatomic molecules and the noble gases that exert very small intermolecular forces. As molecular weight increases, we encounter a liquid ( $Br_2$ ) and a solid ( $I_2$ ) whose vapor pressures also indicate small intermolecular forces. Certain properties of a few nonmetals listed in Table 2.

室温下为气体的非金属单质是那些分子量低的双原子分子和惰性气体分子，这些分子间的作用力极小。随着分子量的增加，我们就会遇到一种液体  $Br_2$  和一种固体  $I_2$ ，它们的蒸气压也表明它们的分子间作用力较小。一些非金属元素单质的某些性质见表 2。

Table 2 . Molecular Weights and Melting Points of Certain Nonmetals

表 2 一些非金属单质的分子量和熔点

Simple diatomic molecules are not formed by the heavier members of Groups V and VI at ordinary conditions. This is in direct contrast to the first members of these groups, N<sub>2</sub> and O<sub>2</sub>. The difference arises because of the lower stability of  $\pi$  bonds formed from *p* orbitals of the third and higher main energy levels as opposed to the second main energy level. The larger atomic radii and **more dense electron clouds** of elements of the third period and higher do not allow good parallel overlap of *p* orbitals necessary for a strong  $\pi$  bond.

V 和 VI 族元素的较重原子在一般情况下不形成简单的双原子分子。这一点与这些族的第一个元素（分别形成 N<sub>2</sub> and O<sub>2</sub>）恰好相反。差别的出现是由于与第二主能级相反，第三和更高主能级的 *p*-轨道形成的 $\pi$ -键稳定性较低。第三周期和更高周期元素的原子半径较大，电子云更密集，不允许 *p*-轨道进行良好的重叠，而这恰恰是形成强 $\pi$ -键的必要条件。

This is a general phenomenon-strong  $\pi$  bonds are formed only between elements of the second period. Thus, elemental nitrogen and oxygen form stable molecules with both  $\sigma$  and  $\pi$  bonds, but other members of their groups form more stable structures based on  $\sigma$  bonds only at ordinary conditions. Note that Group VII elements form diatomic molecules, but  $\pi$  bonds are not required for saturation of valence.

一般，强 $\pi$ -键的形成只出现在第二周期元素。因此，元素 N 和 O 形成同时含有 $\sigma$ 键和 $\pi$

键的稳定分子，而同族的其它元素在一般情况下仅形成建立在 $\sigma$ 键基础上的较稳定的分子。

请注意 VII 元素也形成双原子分子，但是并不需要 $\pi$ 键来使原子价达到饱和。

Sulfur exhibits allotropic forms. Solid sulfur exists in two crystalline forms and in an amorphous form. Rhombic sulfur is obtained by crystallized on from a suitable solution, such as  $\text{CS}_2$ , and it melts at  $112^\circ\text{C}$ . Monoclinic sulfur is formed by cooling melted sulfur and it melts at  $119^\circ\text{C}$ . Both forms of crystalline sulfur melt into  $\text{S-gamma}$ , which is composed of  $\text{S}_8$  molecules. The  $\text{S}_8$  molecules are puckered rings and survive heating to about  $160^\circ\text{C}$ . Above  $160^\circ\text{C}$ , the  $\text{S}_8$  rings break open, and some of these fragments combine with each other to form a highly viscous mixture of irregularly shaped coils. At a range of higher temperatures the liquid sulfur becomes so viscous that it will not pour from its container. The color also changes from straw yellow at sulfur's melting point to a deep reddish-brown as it becomes more viscous.

硫有几种同素异形体。固态硫通常以两种结晶形式和一种无定形形式存在。菱形硫可以在合适的溶液中例如  $\text{CS}_2$  中经过结晶得到，它的熔点是  $112^\circ\text{C}$ 。单斜硫可以通过冷却熔融的硫获得，它的熔点是  $119^\circ\text{C}$ 。两种形式的结晶硫都可以经过熔融而变为由  $\text{S}_8$  分子组成的  $\text{S}_\gamma$  硫， $\text{S}_8$  分子是一种折叠形的环， $160^\circ\text{C}$  以下可以稳定存在，高于  $160^\circ\text{C}$ ， $\text{S}_8$  环开始破裂，有些碎片互相结合形成高黏度的不规则的线圈型混合物。当加热到一定温度范围时，液体硫的黏度变得如此最大以至不能将熔融硫从容器中倒出。当黏度增加时，硫的颜色也从熔点时的淡黄色一直变到深棕红色。

As the boiling point of  $444^\circ\text{C}$  is approached, the large-coiled

molecules of sulfur are partially degraded and the liquid sulfur decreases in viscosity. If the hot liquid sulfur is quenched by pouring it into cold water, the amorphous form of sulfur is produced. The structure of amorphous sulfur consists of large-coiled helices with eight sulfur atoms to each turn of the helix; the overall nature of amorphous sulfur is described as rubbery because it stretches much like ordinary rubber. In a few hours the amorphous sulfur reverts to small rhombic crystals and its rubbery property disappears.

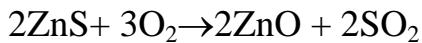
当接近沸点 444°C 时，大的线圈型（铰链型）硫部分降解（破裂），液体硫的黏度降低。热的液体硫如果用冷水淬火，就形成了无定型硫。无定形硫是由大的线圈型螺旋链组成，这些螺旋链是  $S_8$  环断裂后，首尾相连形成的。可以把无定型硫的全部性质描述为弹性硫，因为它伸缩的时候象一般的橡胶一样有弹性。几个小时后，弹性硫就转变为较小的斜方硫，弹性也随之消失。

Sulfur, an important raw material in industrial chemistry, occurs as the free element, as  $SO_2$  in volcanic regions, as  $H_2S$  in mineral waters, and in a variety of sulfide ores such as iron pyrite  $FeS_2$ , zinc blende  $ZnS$ , galena  $PbS$  and such, and in common formations of gypsum  $CaSO_4 \cdot 2H_2O$ , anhydrite  $CaSO_4$  and barytes  $BaSO_4 \cdot 2H_2O$ . Sulfur, in one form or another, is used in large quantities for making sulfuric acid, fertilizers, insecticides, and paper.

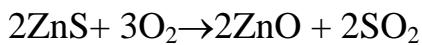
作为化学工业的重要原材料，硫的存在形式多种多样。如单质硫，火山喷发地区的  $SO_2$ ，矿泉水中的  $H_2S$ ，以及各种硫化物矿如黄铁矿  $FeS_2$ ，闪锌矿  $ZnS$ ，方铅矿  $PbS$  和以常见形式

存在的石膏  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 硬石膏(无水石膏)和重晶石。以多种形式存在的硫, 大量地用于制造硫酸、化肥、杀虫剂和纸业。

Sulfur in the form of  $\text{SO}_2$  obtained in the roasting of sulfide ores is recovered and converted to sulfuric acid, although in previous years much of this  $\text{SO}_2$  was discarded through exceptionally tall smokestacks. Fortunately, **it is now economically favorable to recover these gases**, thus greatly reducing this type of atmospheric pollution. A typical roasting reaction involves the change:



通过煅烧硫化物矿获得可以再回收利用的  $\text{SO}_2$ , 进一步转化成硫酸, 而在以前大部分  $\text{SO}_2$  通过高高的烟囱后被废弃。幸运的是, 现在回收这些气体非常经济, 从而大大地减少了此类气体对大气的污染。包含此类变化的一个典型的煅烧反应如下:



Phosphorus, below  $800^\circ\text{C}$ , consists of tetratomic molecules,  $\text{P}_4$ . Its molecular structure provides for a covalence of three, as maybe expected from the three unpaired p electrons in its atomic structure, and each atom is attached to three others. Instead of a strictly orthogonal orientation, with the three bonds  $90^\circ$  to each other, the bond angles are only  $60^\circ$ . This solid supposedly strained structure is stabilized by the mutual interaction of the four atoms (each atom is bonded to the other three), but it is chemically the most active form of phosphorus. This form of phosphorus, the white modification, is spontaneously combustible in air. When heated

to 260°C, it changes to red phosphorus, whose structure is obscure. Red phosphorus is stable in air but, like all forms of phosphorus, should be handled carefully because of its tendency to migrate to the bones when ingested, resulting in serious physiological damage.

磷，在 800°C 以下，是以四面体形分子 P<sub>4</sub> 存在的。它的分子结构中每个原子形成了三个共价键，可预期这三个共价键是由该原子结构中的三个未成对的 p 电子形成的，且每个原子都与另外三个相接。分子中的键角是 60°，键之间不是互相成 90° 的直角取向。可以推测虽然这种张力较大的结构因为四个原子之间的互相作用可以稳定存在(每个原子与其它三个原子键合)，但是它是磷的单质中化学活泼性最强的一种。这种形式的磷，也就是白磷变体，在空气中能够自燃。当加热到 260°C，它就变成了红磷，红磷的结构尚不清楚。红磷在空气中是稳定的，但是象所有其它形式的磷一样，也应该小心处理，因为当误食后，它会向骨头迁移，而造成严重的生理损害。

Elemental carbon exists in one of two crystalline structures-diamond and graphite. The diamond structure, based on tetrahedral bonding of hybridized sp<sup>3</sup> orbitals, is encountered among Group IV elements. We may expect that as the bond length increases, the hardness of the diamond-type crystal decreases. Although the tetrahedral structure persists among the elements in this group-carbon, silicon, germanium, and gray tin-the inter-atomic distances increase from 1.54 Å for carbon to 2.80 Å for gray tin. Consequently, the bond strengths among the four elements range from very strong to quite weak. In fact, gray tin is so soft that it exists in the form of microcrystals or merely as a powder. Typical

of the Group IV diamond-type crystalline elements, it is a nonconductor and shows other nonmetallic properties.

碳的同素异形体有两种晶体形式-金刚石和石墨。由  $sp^3$  杂化轨道形成的四面体成键方式的金刚石结构在 IV 族其它元素中也可以见到。可预测，当金刚石型晶体的键长增加的时候，晶体的硬度将降低。尽管四面体结构在这一族的 C、Si、Ge 和灰锡中都存在，但是原子间的距离（键长）却从碳中的  $1.54 \text{ \AA}$  增加到灰锡中的  $2.80 \text{ \AA}$ 。因此，这四种元素的对应单质中的化学键也由极强变为极弱。实际上，灰锡很软，以至它以微晶的形式或仅仅以粉末的形式存在。碳作为典型的第 IV 族金刚石型晶体的元素，它是不良导体，且显示其它非金属性质。

### 3. Groups IB and IIB Elements (IB 和 IIB 元素)

Physical properties of Group IB and IIB (IB 和 IIB 的物理性质)

These elements have a greater bulk use as metals than in compounds, and their **physical** properties vary widely.

这些元素的金属单质比化合物的应用广泛得多，它们的物理性质变化范围较大。

Gold is the most **malleable** (展性的) and **ductile** (延性的) of the metals. It can be **hammered into** (锤成) sheets of **0.00001 (?) inch** in thickness; one **gram** of the metal can be **drawn** (拉, 拖) into a wire 1.8 **mi** (?meter) in length. Copper and silver are also metals that are **mechanically** easy to work. Zinc is a little brittle **at ordinary temperatures** (在通常的温度下), but may be **rolled** (碾薄, 滚压成) into sheets at between 120°C to 150°C; it becomes brittle again about 200°C. The low-melting temperatures of zinc **contribute to** (有助于) the preparation of zinc-coated iron, **galvanized** (镀锌的, 电镀的) **iron** (镀锌铁); clean iron sheet may be dipped into **vats** (装液体的大桶, 大缸) of liquid zinc in its preparation. A different **procedure** (程序, 手续, 工序, 过程, 步骤, 方法) is to **sprinkle** (喷雾, 酒) or air blast (鼓风) zinc dust onto hot iron sheeting for a zinc melt and then coating.

金是延展性最好的金属，它可以压展成仅有 0.00001 英寸 (0.0001mm) 厚的薄片，1 克金能够抽成 1.8 (教材上为 3km) 长的金属丝。铜和银也是机械上容易操作 (或成型) 的金属。锌在常温下较脆，但是在 120°C-150°C 可以碾成薄片。在 200°C 左右又变得较脆。锌低熔点有助于制备包覆锌的铁，也就是镀锌铁。镀锌时可以把洁净的铁片浸泡在装有液体锌

的大桶里。另外一种方法是喷洒或通过鼓风把熔融的锌喷洒到热的铁板上形成融化的锌，然后铁板上就形成了涂层（覆盖层）。

Cadmium has specific uses because of its low-melting temperature in a number of **alloys**. Cadmium rods (细长棒) are used in **nuclear reactors** (核反应堆) because the metal is a good **neutron absorber** (中子吸收体，吸收剂) .

因为熔点较低，所以镉在大量的合金方面有特殊的用途。镉棒可以用在核反应堆中，因为这种金属是良好的中子吸收剂。

Mercury vapor and its salts are **poisonous**, though the free metal may be taken **internally** (内服 to be taken oral internally: 内服 oral administration; take by mouth; to be taken orally) under certain conditions. Because of its relatively low boiling point and hence **volatile** (易挥发的, 挥发性的) nature, free mercury should never be allowed to stand in an open container in the laboratory. Evidence shows that **inhalation** (吸入) of its vapors is **injurious** (有害的) .

尽管汞单质(游离金属)在一定情况下可以内服，但是汞蒸气和它的盐都是有毒的。因为沸点相对较低而导致汞单质容易挥发，在实验室中决不允许直接放在敞口容器中。有证据表明吸入汞蒸气对身体有害。

The metal alloys **readily** (容易地, 乐意地, 欣然地) with most of the metals (except iron and **platinum**) to form **amalgams** (汞齐), the name is given to any alloy of mercury.

汞很容易和大部分金属(铁和铂除外)形成汞齐，即一汞合金的名字。

Copper Sulfate, or **blue vitriol** ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 胆矾, 硫酸铜) is the

most important and widely used salt of copper. On heating, the salt slowly loses water to form first the **trihydrate**( $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ ), then the **monohydrate** ( $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ), and finally the white **anhydrous** salt. The anhydrous salt is often used to test for the presence of water in organic liquids. For example, some of the **anhydrous** (无水的) copper salt **added to** (被加入到...中) **alcohol** (醇, 乙醇) (which contains water) will turn blue because of the **hydration** of the **salt**. Copper sulfate is used in **electroplating** (电镀, 电镀术). Fishermen (渔夫, 钓鱼者, 鱼船) dip their nets in copper sulfate solution to inhibit the growth of **organisms** (生物体, 有机体) that would rot (使腐烂, 使腐败) the **fabric** (织物, 纤维品). Paints **specifically formulated** for use on the bottoms of **marine** (海的, 航海的) craft (飞机, 飞船, 航空器, 飞行器) contain copper compounds to inhibit (防止, 阻止) the growth of **barnacles** (藤壶, 附着在水下船底或柱石上的贝属动物) and other organisms.

硫酸铜, 或者说胆矾, 是最重要和广泛应用的铜盐。加热时, 胆矾慢慢地失水先变成三水合硫酸铜, 即  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , 然后变成单水合硫酸铜  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , 最后是无水  $\text{CuSO}_4$ 。无水  $\text{CuSO}_4$  经常用于检测有机液体中是否含有水。例如, 把无水  $\text{CuSO}_4$  加到含有水的乙醇中, 铜盐就会变蓝色, 因为铜盐发生了水合。硫酸铜也用在电镀工业上。渔民把网浸泡在硫酸铜溶液中, 抑制使鱼网腐烂的有机体的生长。经过特殊配制的用在舰艇底部的涂料含有铜的化合物, 其作用是抑制藤壶或其它有机体的生长。

When dilute(稀释的, 淡的) **ammonium hydroxide** (氢氧化铵) is added to a solution of copper(II) ions, a greenish (微带绿色的) **precipitate** of

**Cu(OH)<sub>2</sub>** or a basic copper(II) salt is formed. This dissolves as more ammonium hydroxide is added. The excess ammonia forms an **ammoniated** (与氨化合了的, 氨合的) **complex** with the copper(II) ion of the **composition** (构成, 组成), Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>. This ion is only slightly dissociated; hence in an **ammoniacal** (氨的) solution very few copper(II) ions are present. **Insoluble** (不可溶的, 不能溶解的) copper compounds, except copper Sulfide, are dissolved by ammonium hydroxids. The formation of the copper(II) ammonia (氨, 氨水) ion is often used as a test for Cu<sup>2+</sup> because of its deep, intense blue color.

当把氨水加到含有 Cu(II)离子的溶液中, 绿色的 Cu(OH)<sub>2</sub>沉淀或碱式铜盐沉淀就形成了。继续加氨水, 这些沉淀又溶解了。过量的氨水可以和 Cu(II)离子形成组成为 Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> 氨的配合物。这种配离子的溶解度很小, 因此在氨水溶液中, 几乎没有 Cu(II)离子存在。铜的难溶解化合物, 除了 CuS 之外, 都能够溶解在氨水溶液中。因为铜氨离子具有深的、强烈的蓝色, 所以它的形成经常用于检验 Cu<sup>2+</sup>的存在。

Copper(II) **ferrocyanide** Cu<sub>2</sub>[Fe(CN)<sub>6</sub>] is obtained as a reddish-brown precipitate on the addition of a **soluble** (可溶的) ferrocyanide to a solution of copper(II) ions. The formation of this salt is also used as a test for the presence of copper(II) ions.

the addition of A to B 把 A 加到 B 中

在 Cu(II)离子的溶液中, 加入可溶性的亚铁氰化物, 就可以得到棕红色 Cu<sub>2</sub>[Fe(CN)<sub>6</sub>] 沉淀。这种盐的形成也可以用来鉴定 Cu(II)。

Compounds of Silver and Gold (银和金的化合物)

Silver **nitrate** (硝酸盐, 硝酸钾), sometimes called **lunar caustic** (医用硝酸银, 含银腐蚀剂), is the most important salt of silver. It melts readily and may be **cast into** (铸造, 铸成) sticks (棍, 棒, 粘贴) for use in cauterizing (灼伤) wounds (创伤, 伤口). The salt is prepared by dissolving silver in **nitric acid** (硝酸) and **evaporating** the solution.



硝酸银, 有时叫做医用硝酸银, 是最重要的银盐。它容易熔化, 可以熔炼为粘贴膏用  
来治疗灼伤的伤口。硝酸银可以通过把银溶解在硝酸中然后蒸发溶剂而制备。制备反应如下:



The salt is the starting material for most of the compounds of silver, including the **halides** (卤化物, 卤化物的) used in **photography** (摄影, 摄影术). It is readily reduced by organic reducing agents, with the formation of a black deposit (沉淀) of finely divided (分开的) silver; this action is **responsible for** (负...责任, 造成...结果) **black spots** (斑点, 污点) left on the fingers from the **handling** of the salt. Indelible (不能拭去的) **marking inks** (不褪色墨水) and pencils **take advantage of** (利用) this property of silver nitrate.

take advantage of: (1) 乘机利用 (2) 利用别人的弱点占便宜, 欺骗, 引诱 (女人)

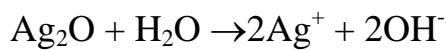
硝酸银是制备大部分银的化合物包括摄影上用的卤化银的原料。它容易被有机还原剂还原, 以细小的银粒形式形成黑色的沉淀 (沉积物)。这个反应可以说明为什么当你的手指接触银盐时, 会留下黑色的斑点。**难以褪色的墨水和铅笔都利用了硝酸银的这种性质。**

The halides of silver, except the **fluoride** (氟化物), are very insoluble

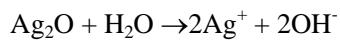
compounds and may be precipitated by the addition of a solution of silver salt to a solution containing chloride, bromide (溴化物), or iodide (碘化物) ions.

卤化银，除了氟化银之外，都是难溶的化合物，可以通过在银盐溶液中加入含有氯、溴、碘离子的溶液而沉淀下来。

The addition of a strong base to a solution of a silver salt precipitates brown silver oxide ( $\text{Ag}_2\text{O}$ ). One might expect the **hydroxide** of silver to precipitate, but it seems likely that silver hydroxide is very unstable and **breaks down into** (分解为..., 打碎(成)... ) the oxide and water-if, indeed, it is ever formed at all. However, since a solution of a silver oxide is **definitely** (明确地, 确切地, 干脆地) basic, there must be hydroxide ions present in solution.

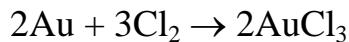


在银盐溶液中加入强碱可以形成棕色的  $\text{Ag}_2\text{O}$  沉淀。你可能想到会形成氢氧化银沉淀，如果说实际上曾经生成了氢氧化银，那么看起来它也不稳定，又分解为氧化物和水。但是，既然形成氧化银的溶液明显是碱性的，溶液中一定存在氢氧根离子。反应如下：



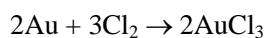
Because of its **inactivity** (不活泼性), gold forms **relatively** few compounds. Two series of compounds are known-**monovalent** and **trivalent**. Monovalent (aurous (亚金的, 一价金的)) compounds **resemble** (象, 类似) silver compounds (**aurous chloride** 氯化亚金) is water insoluble and light sensitive), while the higher **valence** (化合价, 原子价) (**auric** 金的,

三价金的，含金的) compounds tend to form complexes. Gold is **resistant to** (抗...的(作用), 防...的(作用)) the action of most chemicals-air, oxygen, and water have no effect. The common acids do not attack the metal, but a mixture of **hydrocholoric** (**hydrocholoric acid** 盐酸) and nitric acids (**aqua regia** 王水) dissolves it to form gold(III) chloride or **chloroauric acid** (氯金酸). The action is probably due to **free chlorine** (游离氯) present in the **aqua regia**.



chloroauric acid ( $\text{HAuCl}_4 \cdot \text{H}_2\text{O}$  crystallizes from solution).

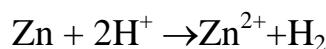
因为它的惰性，金的化合物相对很少。它的化合物通常有两个系列，即氧化数为+1 和+3 的化合物。单价 (亚金) 化合物类似银的化合物，如  $\text{AuCl}$  难溶于水，见光易分解 (对光敏感)，而高氧化数金的化合物倾向于形成配合物。金和大部分的化学物质都不反应 (金可以抵抗大部分化学物质的侵蚀，如空气、氧和水对它都没有作用。常见的酸也很难侵蚀金，但是，金能够溶解在盐酸和硝酸的混合物 (王水) 中形成  $\text{AuCl}_3$  或氯金酸，这个反应大概是由于王水中存在游离氯。



氯金酸 ( $\text{HAuCl}_4 \cdot \text{H}_2\text{O}$  是从溶液中结晶而出)。

**Compounds of Zinc** (锌的化合物)

Zinc is fairly high in the activity series. It reacts readily with acids to produce hydrogen and displaces less active metals from their salts. The action of acids on **impure** (不纯的) zinc is much more rapid than on pure zinc, since bubbles (泡, 起泡, 鼓泡) of hydrogen gas collect on the surface of pure zinc and **slow down** (使...慢下来) the action. If another metal is present as an **impurity** (杂质), the hydrogen is **liberated** (被释放了的) from the surface of the **contaminating metal** (杂质金属) rather than from the zinc. **An electric couple** (电对) to facilitate (促进) the action is probably **set up** (形成, 产生) between the two metals.



锌在金属活动顺序表中是相当靠前的。它很容易与酸反应生成  $\text{H}_2$ , 和比它不活泼的金属的盐发生置换反应。含有杂质的锌和酸反应要比纯的锌和酸反应剧烈得多, 因为  $\text{H}_2$  气泡聚集在纯锌的表面, 减缓了反应。如果存在作为杂质的另外一种金属,  $\text{H}_2$  就会在杂质金属表面形成, 而不是在锌的表面。这样推进反应的电对可能在两种金属间形成了。 $\text{Zn} + 2\text{H}^+$   
 $\rightarrow \text{Zn}^{2+} + \text{H}_2$

Zinc oxide ( $\text{ZnO}$ ), the most widely used zinc compound, is a white powder at ordinary temperatures, but changes to yellow on heating. When **cooled**, it again becomes white. Zinc oxide is obtained by burning zinc in air, by heating the basic (碱性的) **carbonate** (碳酸盐的), or by **roasting** (煅烧) the sulfide. The **principal** (主要的, 首要的) use of  $\text{ZnO}$  is as a **filler** (填料, 填充剂) in rubber manufacture (制造业, 产品), particularly in **automobile** (汽车) tires. As a body (底质, 底料, 坯体) for paints it has the advantage

over white lead of not **darkening** on **exposure** to an atmosphere containing hydrogen sulfide. Its covering power, however, is inferior to that of **white lead** (铅白, 碱式碳酸铅) .

ZnO, 应用最广泛的锌的化合物, 常温下是白色粉末, 但是加热时变成黄色, 冷却后, 又变成白色。ZnO 是通过在空气中燃烧锌, 或者碳酸盐的热分解, 或者煅烧锌的硫化物而获得。ZnO 主要的应用是在橡胶工业上, 尤其是在汽车轮胎上作为填充剂。作为涂料的主要成分, 与铅白相比, 它所具有的优点是: 当暴露在含有 H<sub>2</sub>S 的空气中时, 颜色并不变暗; 但是, 它的覆盖力却不如铅白。

#### 4. Group IIIIB—VIIIB Elements

Group IIIIB includes the elements scandium, yttrium, lanthanum, and actinium, and the two rare-earth series of fourteen elements each—the lanthanide and actinide series. The principal source of these elements is the **high gravity** (地心引力, 重力, 重量) river and beach sands built up by a water-sorting process during long periods of geologic (地质学的) times. Monazite (独居石) sand, which contains a mixture of rare earth phosphates, and an yttrium silicate in a heavy sand now commercial sources of a number of these scarce elements.

注意: riversand 河沙

build up 造成, 逐步建立, 逐步形成, 堆积而成

water-sorting 水 (力) 拣选, 挑选

HIB 包括 Sc、Y、La、Ac 以及各含有 14 种元素的两个稀土系列-镧系和锕系。这些元素主要分布在经过漫长的地质年代由于水的自我冲积、挑选过程而形成的受地心引力较大的河滩和海滩上。(和潮汐现象对比理解)。独居石, 一种混合稀土磷酸盐矿物和一种重沙中的硅酸钇是这些稀有元素的大量的商业来源。

Separation of the elements is a difficult chemical operation. The solubilities of their compounds are so nearly alike that a separation by fractional (分级的) crystallization is laborious and time-consuming (耗时的). In recent years, ion exchange resins (离子交换树脂) in high columns have proved effective. When certain acids are allowed to flow down slowly through a column containing a resin to which ions of Group

IIIB metals are adsorbed, ions are successively released from the resin. The resulting solution is removed from the bottom of the column or tower in bands or sections. Successive sections will contain specific ions in the order of release by the resin. For example, lanthanum ion ( $\text{La}^{3+}$ ) is most tightly held to the resin and is the last to be extracted, lutetium ion ( $\text{Lu}^{3+}$ ) is less tightly held and appears in one of the first sections removed. If the solutions are recycled (多次吸附和脱附 ) and the acid concentrations carefully controlled, very effective separations can be accomplished. Quantities of all the lanthanide series (except promethium, Pm, which does not exist in nature as a stable isotope) are produced for the chemical market.

分离这些元素是非常困难的化学过程。它们化合物的溶解度极为相似，所以分级结晶（过去常用的一种方法）既劳神又耗时（耗时又耗力）。近年来发现填充在长交换柱中的离子交换树脂在分离这些元素方面很有效。当某种酸缓缓流过吸附了 IIIB 金属离子的树脂的交换柱时，IIIB 的离子就连续地从树脂上脱附（释放、淋洗）出来。流出液（交换后的溶液）可以从交换柱或交换塔的底部分段转移开。连续的流出液部分按照树脂释放的顺序含有特定的离子。例如， $\text{La}^{3+}$ 与树脂结合得最紧密，所以它是最后一种被萃取出来的离子；而  $\text{Lu}^{3+}$ 与树脂结合得相对较松，最先被交换，所以它出现在最先流出的那部分溶液中。如果小心控制酸的浓度，经过多次吸附和脱附（淋洗），稀土元素就可以得到有效的分离，从而生产出大量的镧系元素产品（自然界中不存在稳定同位素的 Pm 除外）来供应化学试剂市场。

The predominant group oxidation number of the lanthanide series is +3, but some of the elements exhibit variable oxidation states. Cerium forms

cerium(III) and cerium(IV) sulfates,  $\text{Ce}_2(\text{SO}_4)_3$  and  $\text{Ce}(\text{SO}_4)_2$ , which are employed in certain oxidation-reduction titrations. Many rare earth compounds are colored and are paramagnetic, presumably (推测起来, 大概, 可能) as a result of unpaired electrons in the  $4f$  orbitals.

镧系元素的主要氧化值为+3, 但是有些元素的氧化数是可变的 (呈现出不同的氧化值)。铈可以形成氧化数为+3 和 +4 的硫酸盐,  $\text{Ce}_2(\text{SO}_4)_3$  和  $\text{Ce}(\text{SO}_4)_2$ , 这两种盐可以应用在特定的氧化还原滴定中。许多稀土元素化合物都是有颜色的, 而且是顺磁性的, 大概是因为  $4f$  轨道中存在未成对电子。

All actinide elements have unstable nuclei and exhibit radioactivity. Those with higher atomic numbers have been obtained only in trace amounts. Actinium ( $_{89}\text{Ac}$ ), like lanthanum, is a regular Group IIIIB element.

所有的锕系元素的原子核都不稳定, 表现出放射性。已经获得的较高原子序数的元素仅仅是痕量级的。 $_{89}\text{Ac}$ , 象 La 一样, 也是 IIIIB 元素的一个正式成员。

### Group IVB elements

In chemical properties these elements resemble (象, 类似) silicon, but they become increasing more metallic from titanium to hafnium. The predominant oxidation state is +4 and, as with silica( $\text{SiO}_2$ ), the oxides of these elements occur naturally in small amounts (少量地). The formulas and minerals names of the oxides are  $\text{TiO}_2$ , reutile;  $\text{ZrO}_2$ , zirconia;  $\text{HfO}_2$ , hafnia.

在化学性质方面, 这些元素象硅, 但是, 从 Ti 到 Hf, 它们的金属性增强。IVB 元素的主

要氧化数为+4，象  $\text{SiO}_2$  一样，这些元素的天然氧化物很少。这些氧化物的分子式和矿物的名字如下： $\text{TiO}_2$ ，金红石； $\text{ZrO}_2$ ，锆土（氧化锆）； $\text{HfO}_2$ ，二氧化铪。

Titanium is more abundant than is usually realized. It comprises (包含, 由...组成) about 0.44% of the earth's crust. It is over 5.0% in average composition of first analyzed moon rock. Zirconium and titanium oxides occur in small percentages in beach sands.

钛的含量要比人们通常所认识到的要丰富的多。钛在地壳中的丰度大约为 0.44%。首次分析月球岩石的一般组成表明它在（月球中）的丰度超过了 5.0%。锆和钛的氧化物在海滩沙子中占据很小的比例（含量很小）。

Titanium and zirconium metals are prepared by heating their chlorides with magnesium metal. Both are particularly resistant to corrosion and have high melting points.

金属钛和锆可以通过在镁存在下，加热分解它们的氯化物而制备。两种金属都有独特的抗腐蚀能力和较高的熔点。

Pure  $\text{TiO}_2$  is a very white substance which is taking the place of white lead in many paints. Three-fourths of the  $\text{TiO}_2$  is used in white paints, varnishes, and lacquers. It has the highest index of refraction (折光指数) (2.76) and the greatest hiding power of all the common white paint materials.  $\text{TiO}_2$  also is used in the paper, rubber, linoleum, leather, and textile industries.

纯的  $\text{TiO}_2$  的颜色非常白，在很多涂料中可以取代白铅。有 3/4 的  $\text{TiO}_2$  用于白色涂料，清漆和大漆中。在常见的白色涂料中， $\text{TiO}_2$  的折光指数最高，覆盖能力最强。 $\text{TiO}_2$  也用在造

纸业，橡胶业，油毡，皮革和纺织品工业上。

### Group VB Elements: Vanadium, Niobium, and Tantalum

These are transition elements of Group VB, with a predominant oxidation number of +5. Their occurrence is comparatively rare.

这些是 VB 的过度元素，它们的主要氧化数为+5，丰度相对较小。

These metals combine directly with oxygen, chlorine, and nitrogen to form oxides, chlorides, and nitrides, respectively. A small percentage of vanadium alloyed with steel gives a high tensile strength product which is very tough and resistant to shock and vibration. For this reason vanadium alloy steels are used in the manufacture of high-speed tools and heavy machinery. Vandium oxide is employed as catalyst in the contact process of manufacturing sulfuric acid. Niobium is a very rare element, **with limited use as an alloying element in stainless steel.** Tantalum has a very high melting point ( $2850^{\circ}\text{C}$ ) and is resistant to corrosion by most acids and alkalies.

这些金属可以直接和氧、氯和氮反应，分别形成氧化物、氯化物和氮化物。在钢铁中，少量钒的存在可以大大地提高产品的抗张强度，从而使产品非常坚韧，能够有效地抵抗震动和晃动。因此，含有钒的钢铁合金被用来加工高速工具和重机械。五氧化二钒在接触法制造硫酸中用作催化剂。铌是一种非常珍贵的元素，应用有限，如铌的钢铁合金。钽的熔点极高，高达  $2850^{\circ}\text{C}$ ，对大部分酸和碱有抗腐蚀能力。

### Group VIB and VIIIB Elements

Chromium, molybdenum, and tungsten are Group VIB elements.

Manganese is the only chemically important element of Group VIIIB. All these elements exhibit several oxidation states, acting as metallic elements in lower oxidation states and as nonmetallic elements in higher oxidation states. Both chromium and manganese are widely used in alloys, particularly in alloy steels.

铬、钼和钨是VIB元素。锰是VIIB唯一重要的化学元素。所有这些元素都有几种氧化态，它们的低氧化数呈现出金属性，而高氧化数状态呈现非金属性。铬和锰在合金、尤其是钢铁合金上应用很广泛。

### Group VIIIB Metals

Group VIIIB contains the three triads of elements. These triads appear at the middle of long periods of elements in the periodic table, and are members of the transition series. The elements of any given horizontal triad have many similar properties, but there are marked differences between the properties of the triads, particularly between the first triad and the other two. Iron, cobalt, and nickel are much more active than members of the other two triads, and are also much more abundant in the earth's crust. Metals of the second and third triads, with many common properties, are usually grouped together and called the platinum metals.

VIIIB包含了三组元素。这三组元素处于周期表中长周期的中间，是过度元素的一部分。任何水平的一组元素都有许多相似的性质，但是组之间，尤其是第一组和其它两组之间的性质有显著的差别。铁、钴、镍比其它两组元素活泼得多，在地壳中的丰度也大得多。存在许多共同性质的第二组和第三组金属，通常被划分为一组，叫做铂系金属。

These elements all exhibit variable oxidation states and form numerous coordination compounds.

这些元素都呈现出可变的氧化态，形成了大量的配位化合物。

### Corrosion

Iron exposed to the action of moist air rusts rapidly, with the formation of a loose, crumbly deposit of the oxide. The oxide does not adhere to the surface of the metal, as does aluminum oxide and certain other metal oxides, but peels off, exposing a fresh surface of iron to the action of the air. As a result, a piece of iron will rust away completely in a relatively short time unless steps (措施, 步骤) are taken to prevent the corrosion. The chemical steps in rusting are rather obscure, but it has been established that the rust is hydrated oxide of iron, formed by the action of both oxygen and moisture, and is markedly speeded up by the presence of minute amounts of carbon dioxide.

暴露在潮湿空气中的铁很快就会生锈，形成一层松的、脆的氧化物沉积层。这种氧化物并不象氧化铝和某些其它金属氧化物一样附着在金属表面，而是脱落下来，暴露出新鲜的金属表面，继续和空气作用。结果是，如果不采取措施阻止铁的进一步腐蚀，一片铁很快就完全生锈了。生锈的化学过程并不十分清楚，但是已经确认生锈是因为氧和空气的作用而形成的水合氧化铁，并且由于微量二氧化碳的存在而显著加速。

Corrosion of iron is inhibited by coating it with numerous substance, such as paint, an aluminum powder gilt, tin, or organic tarry substances or by galvanizing iron with zinc. Alloying iron with metals such as nickel or

chromium yields a less corrosive steel. “Cathodic protection” of iron for lessened corrosion is also practiced (熟练的, 老练的, 有经验的). For some pipelines and standpipe zinc or magnesium rods in the ground with a wire connecting them to an iron object have the following effect: with soil moisture acting as an electrolyte for an Fe-Zn couple the Fe is lessened in its tendency to become  $\text{Fe}^{2+}$ . It acts as a cathode rather than an anode.

铁的腐蚀可以通过在表面包覆一层其它许多物质来抑制, 如涂料, 铝粉涂层, 锡, 有机焦油状物质或者镀锌。铁和其它金属如镍或铬的合金的抗腐蚀能力也增强。用“阴极保护法”来阻止铁的进一步腐蚀也是一种成熟的方法。对一些铁制品管道和筒形塔, 可以用电线把地下的锌棒或锰棒和铁目标连接起来, 它的作用如下: 当潮湿的空气起到电解质的作用时, 在 Fe-Zn 电对中, Fe 变为  $\text{Fe}^{2+}$  的趋势减弱, 因为它做的是阴极而不是阳极。

## 5. Interhalogen and noble gas compounds

(杂卤素(卤素互化物)和惰性气体)

Interhalogen and noble gas compounds comprise (包含, 由...组成) a relatively limited family of highly reactive and unstable molecules whose primary importance (重要性, 重大, 价值, 傲慢) is their role in testing (测试) chemical bonding theory. At first it may seem rather strange to treat the chemistry of the halogens and the noble gases, two groups that represent the extremes of chemical activity and inertia, in the same section. The superficial(表面的, 肤浅的, 浅薄的) differences between the halogens and the noble gases are much reduced, however, if we focus our attention on the comparison of halide ions (particularly  $F^-$ ) with the isoelectronic noble gas atoms and the noble gas compounds with halogen atoms or the halogens in their higher positive-oxidation states.

杂卤素和惰性气体化合物包含了高度活泼和不稳定分子的比较有限的(我的观点: 相对特别的, 因为后边进一步解释了为什么是 a relatively limited family)一族, 这些化合物的头等重要性(主要价值)是它们在考察化学键理论中的作用。首先, 把卤素和惰性气体的化学内容放在一起论述看起来也许非常奇怪, 因为它们虽然处于同一区域, 但是却分别代表了化学上高度活泼和惰性的两个极端。但是, 如果我们把注意力转向比较卤素离子(尤其是  $F^-$ )和等电子体的惰性气体原子以及把惰性气体化合物和卤素原子或者处于较高氧化数的卤素比较, 卤素和惰性气体间的表面差别就大大减少了。

Noble gases are exceptional (例外的, 异常的) in their reluctance (不愿意, 勉强) to either gain or lose an electron. Halide ions—because of their

excess negative charge, relative to the isoelectronic noble gas atoms—have both a lower **ionization energy** (电离能) and a lesser (较小的, 更少的, 次要的) **electron affinity** (电子亲合能). On the other hand, noble gas cations (阳离子) have greater electron affinities and greater ionization energies than **do** isoelectronic halogen atoms. From such considerations, it is obvious that inert gases should be less reactive than **are** halide ions, but their compounds should show even higher reactivity than the halogens. The big question remaining is: Are there any chemically significant (有意义的, 重大的, 重要的, 2. 有效的, 有影响的) conditions under which noble gases can be persuaded to yield (出产, 生产) electrons sufficiently to produce stable compounds? The answer is definitely (此处应该用 definite), yes! (The same question can be asked of halogen atoms, which have ionization energies comparable to those of the inert gases.)

(与其它原子相比), 惰性气体原子比较异常, 它们既不容易得到电子, 也不容易失去电子。相对于等电子体的惰性气体原子, 因为额外的负电荷, 卤素离子的电离能和电子亲合能都比较低 (易失去电子, 不容易得到电子)。另一方面, 惰性气体阳离子比等电子体的卤素原子具有较高的电子亲合能和较高的电离能 (说明容易得电子, 不容易失电子)。从这些方面来看, 很明显惰性气体应该比卤素离子的活泼性差, 而它们的化合物应该比卤素单质显示出更高的活泼性。目前存在的一个大问题是: 化学上是否存在这样的重要条件, 在此条件下, 惰性气体原子可以失去足够的电子而形成稳定的化合物? 答案是明确的, 有! (对于离子化能可以和惰性气体相比的卤素原子, 也可以提出同样的问题。)

Another obvious point of similarity between halogen and noble gas

compounds is the characteristically large number of electrons that must be accommodated (容纳) in the valence shell. For a noble gas atom bonded to any number of other atoms, the octet rule (八偶体规则) must be exceeded; for a halogen atom to be bonded to more than one other atom, the same must be true. It is a curious (古怪的, 难以理解的, 应该用 curiously) historical fact that the mythical (神话的, 设想的, 虚构的) inertia (惰性, 惯性) of a closed shell did much to diminish (使减少, 使变小) the energy expended (花费, 消耗, 支出) in the search for noble gas compounds, long after (很久以后) numerous examples of superoctet valence shells were known, particularly among interhalogen compounds. (✓)

在卤素和惰性气体化合物间另外一点明显的相似之处是原子核外的价电子层都存在典型的大量的电子。对惰性气体原子来说，不管它与多少个其它原子结合，都会逾越八偶体规则。对于卤素原子，如果与它键合的其它原子超过一个，同样也会逾越八偶体规则。一个说来稀奇的历史事实是，这种闭合壳层的“所谓的”神秘的惰性确实使人们大大地减少了对惰性气体化合物的研究，直到很久以后，人们才了解了大量的超八偶体的化合物的例子，尤其是杂卤素化合物（卤素互化物）。

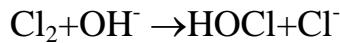
We may roughly (概略地, 粗糙地) classify the interhalogen compounds into two categories (种类, 别): those in oxidation state zero (the binary analogs of the elementary diatomics) and those in which one of the halogens is in a formally (形式上, 正式地) positive oxidation state. Heterodiatomic halogens are generally formed readily on mixing the required pair of halogens in a 1:1 ratio. The bond energies are always higher in the heteropolar (异极的) molecules than are the average bond

energies of the two constituents (组分, 成分) and in some cases higher than either. It is this factor that drives the reactions. All heterodiatomics are more or less stable under ambient conditions except for BrF, which spontaneously (自然地, 本能地) disproportionates (1. 不均衡的 2. 歧化) to BrF<sub>3</sub> and Br<sub>2</sub>. The bonding in the halogen diatomics can be attributed to a single  $\sigma$  bond, formed by overlap of p orbitals. In the heterodiatomics, the principal new features are the poorer orbital overlaps that are possible between atoms of widely (相差大地) different principal quantum number (主量子数 n), the polarity arising from the difference in electronegativity (电负性), the contribution of ionic terms to increase bond energy, and the relief (减轻, 释放, 解除) in interelectronic repulsion in the fluorides, relative to difluorine.

Ambient (周围的, 环境的) temperature: 室温

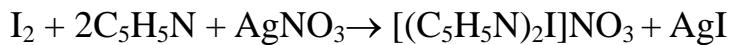
我们可以把杂卤素化合物粗略地分为两类：一类是卤素原子氧化数为 0 的双原子分子的类似物，另一类是卤素形式上为正氧化数的化合物。当把所需要的两种卤素按照 1:1 的比例混合时，卤素的杂双原子分子一般都容易形成。异极分子中的键能通常比组成此分子的两组分的平均键能高，某些情况下，也比任何一种组分的化学键键能高，这正是反应的推动力（正是这种因素推动了反应的进行）。除了 BrF 自然地歧化为 BrF<sub>3</sub> 和 Br<sub>2</sub> 外，所有的杂双原子分子在周围环境下多多少少都能稳定存在。卤素双原子分子中的化学键是由 p 轨道互相重叠形成的  $\sigma$  单键。在杂双原子分子中，主要的新特征分别是可能发生在主量子数 n 有显著差别的原子轨道间的重叠程度较差，因为电负性差而引起的极性，因为离子项的贡献而使键能提高，相对于同核双原子 F<sub>2</sub>，氟化物中的电子间斥力减小。

Dihalogens (except for F<sub>2</sub>) usually react by dissociation into atoms or by heterolytic (异性的) dissociation under the influence of an attacking reagent. Thus, reaction of Cl<sub>2</sub> with hydroxide may be viewed (观察, 观看, 认为, 把...看作是) as displacement (置换, 取代) of Cl<sup>-</sup> from Cl<sub>2</sub> by OH<sup>-</sup>:



卤素单质 (除了 F<sub>2</sub> 外) 反应时通常解离为原子, 或在进攻试剂的影响下, 发生了异极解离。因此, Cl<sub>2</sub> 与氢氧根反应可以认为是 Cl<sub>2</sub> 中的 Cl<sup>-</sup> 被 OH<sup>-</sup> 取代的反应。

The tendency to undergo heterolytic fission (分裂) increases on descending (递减, 下降) the group, and the I<sub>2</sub> molecule can actually be cleaved (劈开) to two stable species:



这种异极间的分裂的趋势在同族中由上而下增加, I<sub>2</sub> 分子实际上可以分裂形成两个稳定的物种:

The increased homolytic (同性的, 均一的) bond energies of the heterodiatomlic halogens decrease the tendency toward homolytic reactions, but the increased polarity increases the tendency toward heterolytic reactions. Thus, ICl is a much better electrophilic (亲电的) iodinating (碘化) agent than is I<sub>2</sub> and unlike I<sub>2</sub> even iodinates aromatic compounds.

杂卤素双原子分子逐渐增加的均裂键的键能降低了均裂反应的趋势, 但是逐渐增加的极性却增加了异裂反应的趋势。因此, ICl 是比 I<sub>2</sub> 更好的亲电碘试剂, 与碘不同, 它甚至能使芳香族化合物碘化。

In the interhalogen (卤间化合物) compounds, one of the halogen atoms may be assigned a positive oxidation state. As may be expected, the general trends reflect the increasing difficulty of withdrawing electrons from the central atom on ascending (上升的, 向上的, 增长的) the group and with increasing oxidation state. As might be anticipated (预期, 预料, 期待), all known stable compounds are fully electronpaired, and the series IF,  $\text{IF}_3$ ,  $\text{IF}_5$ , and  $\text{IF}_7$  give us a homogeneous (同类的, 相似的, 均一的, 均匀的) sequence (顺序, 次序, 序列) of molecules exemplifying (例证, 例示, 作为...的例子) all possible odd-coordination numbers and their associated geometries (there is no known nine-coordinate neutral binary molecule, although many nine-coordinate complexes are known). We may complement (补充, 补足, 使完备) this series with some of the fluorides discussed earlier and with the xenon fluorides to be discussed below, thereby completing the primary family (系列, 族, 家族) of molecular structures and electron configurations for main-group elements. In each state of the cases shown, the experimental evidence indicates that the molecule adopts the structure predicted by VSEPR theory. A valence-bond description (种类) of the molecules with more than eight-valence electrons requires the inclusion of d orbitals in the hybridization scheme. An MO scheme without the participation of d orbitals requires location of electron in antibonding orbitals, and therefore

**bond order** (键级) of less than one, for molecules with more than eight-valence electrons. The mixing of empty d orbitals into the scheme can lower the energy of the antibonding electrons (make them less antibonding) and thereby increase the bond strength.

注意: complement A with B 用 B 补充 A

在杂卤素化合物中, 可以指定其中的一种卤原子为正氧化态。可以预料, 从下到上, 中心原子的氧化数越高, 从中心原子抽回电子越困难。同样可以预料到所有已知的化合物中电子都是完全成对的,  $\text{IF}$ ,  $\text{IF}_3$ ,  $\text{IF}_5$  和  $\text{IF}_7$  为同一序列的分子, 是所有可能的奇配位数化合物和相关构型的例证 (尽管已知许多九配位化合物, 但是尚未发现它们的九配位二元中性分子)。如果把前面讨论过的一些氟化物和下面将要讨论的氟化氙补充到这个系列里来, 就完成了主族元素的分子结构和电子构型的主要系列。在所示情况的任何一种状态下, 实验证明了分子的结构与 VSEPR 理论所预测的相同。分子中多于 8 个价电子的价键类型需要 d 轨道的参与杂化。没有 d 轨道参与的分子系统电子需要填充在反键轨道上, 因此多于 8 个价电子的分子, 键级就小于 1。空的 d 轨道的参与可以降低系统中反键电子的能量 (反键性质降低), 因此增加了键的强度。

## 6. THE CLASSIFICATION OF INORGANIC COMPOUNDS

无机化合物的分类

### The Classes of Compounds (化合物的种类)

Thousands (数千) and **tens of thousands** (好几万) of compounds are known to the chemist today. It would be impossible to learn properties and behavior of even a fraction of this number if it had to be done on the basis of individual compounds. Fortunately, most chemical compounds can be grouped together in a few classes. Then, if we can properly (适当地, 完全地) classify (分类, 分等) a compound, we are at once aware of (知道, 意识到) the general properties of the compound from knowledge of the properties of that class or group of compounds. For example, HCl is classed as an acid, and by becoming familiar with the behavior of acids as a distinct (清楚的, 明显的, 截然不同的, 独特的) class, we are at once aware of the general properties of the compound. A great many of the compounds we are to study may be classified as acids, bases, salts, metallic oxides, or nonmetallic oxides. Of these five classes of compounds, the first three —acids, bases, and salts—are by far the most important.

注释: 1. thousands and tens of thousands 千千万万

2. be aware of 知道, 意识到

3. by far (修饰比较级、最高级, 表示数量、程度等) …得多, 尤其, 更, 显然地

今天, 化学家已经知道了千千万万种的化合物。如果根据个别化合物来了解这么多化合物的性质和行为, 即使其中的一小部分也是不可能的。幸运的是, 大部分化合物可以被划分为几

类。如果我们要把一个化合物完全归类的话，根据这类化合物性质的有关知识，我们马上就会知道这个化合物的一般性质。例如，HCl 归类为酸，由于已经熟悉作为不同类别的酸的性质，我们就会立即知道这一化合物的一般性质。我们要研究的大量的化合物可以划分为酸、碱、盐和金属氧化物或非金属氧化物。在这五类化合物中，前三类显然是最重要的几类。

When an acid, base, or salt is dissolved in water the resulting solution is a conductor of the electric current (电流, 水流, 气流) and is termed an electrolyte. If no conduction of current occurs, the compound is known as a nonelectrolyte.

酸、碱或盐溶解在水中所得的溶液可以导电，因此专业术语为电解质。如果此溶液不导电，那么此化合物就是非电解质。

### Classification of Common Compounds (常见化合物的分类)

By looking at the chemical formulas we may classify many common compounds in the following way.

通过观察化学分子式，我们可以把很多常见的化合物进行以下分类：

1. Acids, in the conventional sense, may be recognized (公认的, 经过验证的) by noting that the H is written first in the formula and that the rest of the compound is generally nonmetallic. Ex., HCl, H<sub>2</sub>SO<sub>4</sub>, HClO.

酸，按照传统的含义，可以通过以下方法进行辨认：一般 H 写在分子式的前边，化合物的其余部分一般是非金属性的基团。例如，HCl, H<sub>2</sub>SO<sub>4</sub>, HClO。

2. Conventional bases have OH radicals written last in the formula. The first part of the formula is usually a metal, Ex., NaOH, Ca(OH)<sub>2</sub>, Fe(OH)<sub>3</sub>.

传统上的碱在分子式的后边都有 OH 基团。分子式的第一部分通常是金属，例如：NaOH, Ca(OH)<sub>2</sub>, Fe(OH)<sub>3</sub>。

3. A salt consists of a metal, written first, combined with a non-metal or radical written last in a formula. Ex., NaCl, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Ca(ClO)<sub>2</sub>.

盐由写在分子式前边的金属和写在分子式后边的非金属或基团组成。例如，NaCl, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Ca(ClO)<sub>2</sub>。

4. Oxides are compounds containing oxygen and only one other element.

氧化物是由氧和只有一种其它元素的组成化合物。

If the element **other than** oxygen is a nonmetal, the oxide is classed as a nonmetal oxide or an acidic anhydride (酐). The latter name **comes about** because water added to nonmetal oxides under certain conditions produces acids. Likewise (同样地, 照样地, 又, 也), if water is removed from an acid containing oxygen, the acid anhydride (without water) results.

注释：1. other than 不同于，除了

2. come about 发生，产生，改变方向，转向

如果除了氧之外的另外一种元素是非金属，这个氧化物就会归类为非金属氧化物或者酸酐。之所以叫做酸酐，是因为非金属氧化物在一定条件下加水后会产生对应的酸。同样，如果从含氧酸中除去水，就得到了不含水的酸酐。

The other class of oxides, metallic oxides or basic anhydrides, consist of oxygen combined with a metal. When water is added under proper conditions to basic anhydrides, bases result and **vice versa** (反之亦然) .

注释: vice versa 反之亦然

另外一类由氧和一种金属元素组成的氧化物，叫做金属氧化物或碱酐。在合适的条件下向碱酐中加入水，就会生成碱，反过来也一样。

All acids in the conventional sense contain hydrogen, which may be replaced by metals. The negative portion of the acid molecule is composed of a nonmetal or a **radical**(原子团, 基团, (数)根, (化)基) (negative valence group). These negative valence groups (except oxide and hydroxide) are often referred to as acid radicals. All acids are covalent compounds in which the atoms are held together by a **sharing** of electrons (应该改为 by sharing electrons) . When an acid is dissolved in water, ions are formed as a result of the transfer of a hydrogen ion (proton) from the acid molecule to the water molecule- for example,

注释: **sharing** 分配, 均分, 共享, 共用, 共价

传统意义上的所有酸都含有可以被金属取代的氢。酸的负电荷部分由非金属或带负电荷的原子团组成。这些负电荷基团(除了氧和氢氧化物之外)经常叫做酸根。所有的酸都是共价化合物，原子间是通过共用电子而互相结合的。当酸溶解在水中时，质子就会从酸分子中向水分子中转移而形成离子，例如：

This is a case of coordinate valence, in which an unused pair of electrons from the water molecule combines with a hydrogen ion to form a hydronium ion. The hydronium ion is a hydrated hydrogen ion or proton ( $\text{H}^+\cdot\text{H}_2\text{O}$ ) and, while the ionization of acids in aqueous solution depends on its formation, we shall ordinarily use the simple  $\text{H}^+$  in writing equations. Such equations are thereby simplified and easier to balance.

这是配位键的一个例子，水分子上未共用的电子对与  $\text{H}^+$ 结合形成水合氢离子。水合氢离子是水合的氢离子或质子  $\text{H}^+\cdot\text{H}_2\text{O}$ ，同时酸在水溶液中的离子化依赖于水合氢离子的形成，在写方程式的时候，我们将通常使用简单的  $\text{H}^+$ 。这样的方程式因此被简化，也容易配平。

The chief characteristic of an acid is its ability to furnish(供应, 提供, 装备, 布置) hydrogen ions (protons); therefore, an acid is usually defined as a substance which may furnish protons.

酸的主要特征是能够提供氢离子  $\text{H}^+$  (质子)，因此，通常也定义酸为质子给予体物质。

Properties of Acids. In general, aqueous solutions of acids are characterized by the following properties:

酸的性质：一般，酸的水溶液具有如下的特征性质：

1. They have a sour (酸味) taste. Lemons, organges, and other citrus (柑橘类的水果) fruits owe their sour taste to the presence of citric acid; the taste of sour milk is due to the presence of the lactic acid.

1. 有酸味。柠檬，橘子以及其它的柑橘类的水果因柠檬酸的存在而拥有酸味；酸奶的味道也是因柠檬酸的存在而产生的。

2. They turn blue **litmus paper** (石蕊试纸) red. Litmus is a dye which has red color in acid solution and a blue color in basic solution; paper which has been soaked (浸湿) in litmus is referred to as litmus paper. Substances of this type, which enable us to determine whether a given solution is acid or basic, are called indicators. Methyl orange (甲基橙) and phenolphthalein (酚酞) are other indicators frequently used by chemists.

使紫色石蕊试纸变蓝。石蕊染料在酸性溶液中呈现红色，而在碱性溶液中呈现蓝色。在石蕊溶液中浸泡后的纸叫做石蕊试纸。这类能够让我们测定所给溶液酸碱性的（是酸还是碱

的) 物质叫做指示剂。甲基橙和酚酞是化学家常用的其它指示剂。

3. They react with certain metals to produce hydrogen. Reactions of this type were studied in connection with the preparation of hydrogen.

酸与某些金属反应产生氢气。这类反应的研究可与制备氢气联系起来。

4. They react with bases to produce salts and water.

与碱反应生成盐和水。

Common strong acids are  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HI}$ . Most other acids are generally only partially ionized and consequently only moderately strong or weak.

$\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HBr}$  和  $\text{HI}$  是常见的强酸。其它的大部分酸一般仅部分解离，因此仅仅是中等强度或者很弱。

### Bases (碱)

All metallic hydroxides are classed as conventional bases. Of the common bases only  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$  are appreciably (略微, 有一点) soluble in water. If these compounds are dissolved in water, the  $\text{OH}^-$  is common to all of their solutions.

所有的金属氢氧化物都归类为传统意义上的碱。在常见的碱中，只有  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$  和  $\text{Ba}(\text{OH})_2$  在水中略微溶解。如果这些化合物溶解在水中， $\text{OH}^-$  的存在是所有这些溶液的共同特征。

An aqueous Solution of  $\text{NH}_3$  is also classed as a base, since  $\text{OH}^-$  ions are present in solution.

$\text{NH}_3$  的水溶液也划分为碱类，因为它的溶液中也存在  $\text{OH}^-$ 。

In each of these compounds we find a combination of a metal (or  $\text{NH}_4$ ) with the hydroxide group. Just as the characteristic part of an acid is hydroxide ion (应该是 hydronium ion) , so the characteristic part of a base in water solution is the hydroxide ion,  $\text{OH}^-$ . Later the concept of a base will be extended to include substances which do not furnish hydroxide ions in solution.

在这些化合物中，我们都会发现金属或  $(\text{NH}_4)$  与氢氧根的结合。正象酸的水溶液的特征部分是水合氢离子，碱的水溶液的特征部分是  $\text{OH}^-$ 。后来碱的概念延伸到包括溶液中不提供（不存在） $\text{OH}^-$  的物质。

**Properties of Bases.** In general, water solution of the metallic hydroxides (bases) exhibit the following properties:

碱的性质：一般，金属氢氧化物（碱）的水溶液表现出以下性质：

1. Bitter taste. (苦味)
2. Soapy or slippery feeling. (滑腻感)
3. Turn red litmus paper blue. 使蓝色石蕊试纸变红。
4. React With acids to form salts and water. 与酸反应产生盐和水。
5. Most metallic hydroxides are insoluble in water. Of the common ones, only  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ , and  $\text{NH}_3$  are soluble.

大部分金属氢氧化物都难溶于水。在常见的金属氢氧化物中，只有  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ , 和  $\text{NH}_3$  易溶解于水。

The common strong bases are  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{Ba}(\text{OH})_2$ .  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$  和  $\text{Ba}(\text{OH})_2$  是常见的强碱。

## Salts (盐)

An acid reacts with a base to produce a salt and water. Hydrogen from the acid combines with hydroxide from the base to form water molecules.

酸与碱反应产生盐和水。酸中的氢与碱中的氢氧根结合形成水分子。

The reaction of an acid with a base is called neutralization. If all the water is removed by evaporation from the solution after the reaction, the positive ions from the base and the negative ions from the acid form a crystal lattice of solid salt.

酸与碱的反应叫做中和反应。如果反应后通过蒸发的方式除去所有的水，来自碱的正离子和来自酸的负离子就形成了固体盐的晶格。

It was shown that the compound sodium chloride, a salt, is an **electrovalent compound** and is ionized in the solid or crystalline state. The crystal is made up of positive sodium ions and negative chloride ions oriented in a definite pattern. In general, most salts in the crystalline state are electrovalent and are composed of ions oriented in a definite way.

注释: **electrovalent compound** 电价化合物

事实表明 NaCl, 一种盐是电价化合物，在固体或晶体状态是离子化的。晶体由按照一定的型式取向的钠正离子和氯负离子组成。一般，大部分盐在晶体状态时都是电价化合物，由离子按照一定的空间取向组成。

## 7. THE NOMENCLATURE OF INORGANIC COMPOUNDS (无机化合物的命名)

With the discovery of **thousands of** (数千的) new inorganic compounds it has become necessary to revise the traditional rules of nomenclature. An international committee has recommended **a set of** (一套, 一组) rules for naming compounds, and these are now being adopted throughout the world. Many of the older names are still used, **however, and our ensuing** (跟着发生, 继起) **discussion** will include in many cases both the old and new, with emphasis on the latter. One of the principal changes is that proposed by Albert Stock and now known as the Stock system for the naming of compounds of metals (oxides, hydroxides, and salts) in which the metal may exhibit more than one oxidation state. In these cases, the oxidation state of the metal is shown by a Roman numeral in parentheses (圆括号) immediately following the English name of the metal which corresponds to its oxidation number. If the metal has only one common oxidation number, no roman numeral is used. Another important change is in the naming of complex ions and coordination compounds. **We will defer** (推迟, 延期, 服从, 听从) **the nomenclature of the latter until these compounds are discussed.**

注释: 1. thousands of 数千 thousands of people 成千上万的人 thousands of times 几千遍, 千遍万遍, 千万倍, 无数次

### 2. a set of 一套

随着成千上万新的无机化合物的发现, 修正传统的命名规则成为必然。有个国际委员会建议了一套命名化合物的规则, 现在这套规则正在全世界范围内采用。很多比较陈旧(古老)的名字仍然使用, 而我们接下来的讨论将包括许多旧的和新的命名的例子, 重点是后者。一

个主要的变化是由 Albert Stock 建议的、现在已经广为人知的命名金属化合物（氧化物、氢氧化物和盐）的 Stock 命名系统，其中金属化合物中，金属可能表现出不止一种氧化态。在这些例子中，金属的氧化态用与氧化数一致的罗马数字标在紧随着金属英文名字的圆括号中。（后边注释：在这种情况下，金属氧化态是紧接着金属的英语名称之后在圆括号中用罗马数字表示，该数字与金属的氧化数一致。）如果金属只有一种常见的氧化数，就不用罗马字母标出了。另外一个重要的变化是配离子和配位化合物的命名。有关后者（配离子和配位化合物）的命名我们将等到讨论这些化合物时再说。

#### Naming Metal Oxides. Bases, and Salts 金属氧化物、碱和盐的命名

The student should have a good start in learning nomenclature if he has learned the Valence (化合价, 原子价) Table 3 which gives both charges on ions and names for the more common ones. A compound is a combination of positive and negative ions in the proper ratio to give a balanced charged and the name of the compound follows from names of the ions, for example, NaCl, is sodium chloride; Al(OH)<sub>3</sub> is aluminum hydroxide; FeBr<sub>2</sub> is iron(II) bromide or ferrous bromide; Ca(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> is calcium acetate; Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is chromium(III) sulfate or chromic sulfate, and so on. Table 4 gives some additional examples of the naming of metal compounds. Of the two common systems used, the Stock system is preferred. Note that even in this system, however, the name of the negative ion will need to be obtained from Valence Table 4.

Table 3. Some Common Ions

1+	2+	2+	3+
ammonium    NH <sub>4</sub> <sup>+</sup>	barium           Ba <sup>2+</sup>	Magnesium    Mg <sup>2+</sup>	aluminum      Al <sup>3+</sup>
copper(I)    Cu <sup>+</sup>	calcium        Ca <sup>2+</sup>	manganese(II) Mn <sup>2+</sup>	chromium(III) Cr <sup>3+</sup>

hydrogen	$H^+$	chromium(II)	$Cr^{2+}$	mercury(II)	$Hg^{2+}$	iron(III)	$Fe^{3+}$
potassium	$K^+$	copper(II)	$Cu^{2+}$	mercury(I)	$Hg_2^{2+}$		
silver	$Ag^+$	iron(II)	$Fe^{2+}$	tin(II)	$Sn^{2+}$		
sodium	$Na^+$	lead(II)	$Pb^{2+}$	strontium	$Sr^{2+}$		
				zinc	$Zn^{2+}$		
3-		2-		1-		1-	
arsenate	$AsO_4^{3-}$	carbonate	$CO_3^{2-}$	acetate	$C_2H_3O^-$	hydrogen sulfite	$HSO_3^-$
arsenite	$AsO_3^{3-}$	chromate	$CrO_4^{2-}$	bromide	$Br^-$	hydride	$H^-$
phosphate	$PO_4^{3-}$	dichromate	$Cr_2O_7^{2-}$	chlorate	$ClO_3^-$	hydroxide	$OH^-$
phosphite	$PO_3^{3-}$	oxalate	$C_2O_4^{2-}$	chloride	$Cl^-$	hypochlorite	$ClO^-$
		oxide	$O^{2-}$	chlorite	$ClO_2^-$	iodate	$IO_3^-$
		sulfide	$S^{2-}$	cyanide	$CN^-$	iodide	$I^-$
		sulfate	$SO_4^{2-}$	fluoride	$F^-$	nitrate	$NO_3^-$
		sulfite	$SO_3^{2-}$	hydrogen	carbonate	nitrite	$NO_2^-$
				(bicarbonate)	$HCO_3^-$	perchlorate	$ClO_4^-$
					hydrogen sulfate $HSO_4^-$	permanganate	$MnO_4^-$

注释： in the ratio 按照比例

2. follow from 是从（根据）...得...出的

一个学生如果掌握了给出离子电荷和较常见离子名称的价键表 3，他在掌握命名方面就必定有了一个好的开端。化合物是正离子和负离子按照合适的比例给出的电中性的结合，化合物的名字是根据离子的名字得出的，例如  $NaCl$  叫做氯化钠；  $Al(OH)_3$  叫氢氧化铝；  $FeBr_2$  叫溴化亚铁；  $Ca(C_2H_3O_2)_2$  叫乙酸钙；  $Cr_2(SO_4)_3$  叫硫酸铬等等。表 4 给出了金属化合物名字的另

外的一些例子。在所用的两个常见的系统中，首选 Stock 系统。但是，要注意即使在这个系统中，负离子的名字仍然需要从价键表 4 获得。

Table 4. Names of some metal oxides, bases, and salts

FeO	iron(II) oxide	ferrous oxide
Fe <sub>2</sub> O <sub>3</sub>	iron(III) oxide	ferric oxide
Sn(OH) <sub>2</sub>	tin(II) hydroxide	stannous hydroxide
Sn(OH) <sub>4</sub>	tin(IV) hydroxide	stannic hydroxide
Hg <sub>2</sub> SO <sub>4</sub>	mercury(I) sulfate	mercurous(I) sulfate
HgSO <sub>4</sub>	mercury(II) sulfate	mercuric sulfate
NaClO	sodium hypochlorite	sodium hypochlorite
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	potassium dichromate	potassium dichromate
Cu <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	copper(II) arsenate	curic arsenate
Cr(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>3</sub>	chromium(III) acetate	chromic acetate

Negative ions, anions, may be monatomic or polyatomic. All monatomic anions have names ending with ide. Two polyatomic anions which also have ending with ide are the hydroxide ion, OH<sup>-</sup>, and the cyanide ion, CN<sup>-</sup>.

负离子，即阴离子，可以是单原子的，也可以是多原子的。所有的单原子阴离子的名字都是以-ide 结尾的。有两个也是以-ide 结尾的多原子阴离子是氢氧根离子 OH<sup>-</sup> 和氰根离子 CN<sup>-</sup>。

Many polyatomic anions contain oxygen in addition to another element. The number of oxygen atoms in such oxyanions is denoted (指示, 表示) by the use of the suffixes (应该为 suffixes, 后缀) ite and ate, meaning fewer and more oxygen atoms,

respectively. In cases, where it is necessary to denote more than two oxyanions of the same element, the prefixes hypo and per, meaning still fewer and still more oxygen atoms, respectively, may be used. A series of oxyanions is named in Table 5.

注释: in case 以防, 可能, 倘若 in cases

许多多原子阴离子除了其它的元素之外还含有氧。在这样的含氧阴离子中, 氧原子的数目用后缀 ite 和 ate 表示, 意思分别是较少的和较多的氧原子。在一种元素形成的含氧阴离子多于两种的情况下, 有必要用前缀 hypo 和 per 来表示, 仍然分别表示较少的和较多的原子。一系列含氧阴离子的命名见表 5。

Table 5. Names of oxyanions

Fewest Oxygen Atoms hypo-ite	Fewer Oxygen Atoms -ite	More Oxygen Atoms -ate	Most Oxygen Atoms per-ate
$\text{ClO}^-$ hypochlorite	$\text{ClO}_2^-$ chlorite	$\text{ClO}_3^-$ chlorate	$\text{ClO}_4^-$ perchlorate
$\text{BrO}^-$ hypobromite	$\text{BrO}_2^-$ bromite	$\text{BrO}_3^-$ bromate	$\text{BrO}_4^-$ perbromate
$\text{IO}^-$ hypoiodite	$\text{IO}_2^-$ iodite	$\text{IO}_3^-$ iodate	$\text{IO}_4^-$ periodate
$\text{PO}_2\text{3}$ hypophosphite	$\text{PO}_3^{3-}$ phosphite $\text{NO}_2^-$ nitrite $\text{SO}_3^{2-}$ sulfite	$\text{PO}_4^{3-}$ phosphate $\text{NO}_3^-$ nitrate $\text{SO}_4^{2-}$ sulfate $\text{SO}_3^{2-}$ sulfite	

### Naming Nonmetal oxides (非金属氧化物的命名)

The older system of naming and one still widely used employs Greek prefixes for both the number of oxygen atoms and that of the other element in the compound. The prefixes used are (1) mono-, sometimes reduced to mon-, (2) di-, (3) tri-, (4)

tetra-, (5) penta-, (6) hexa-, (7) hepta-, (8) octa-, (9) nona- and (10) deca-. Generally the letter a is omitted from the prefix (from tetra on) when naming a nonmetal oxide and often mono- is omitted from the naming altogether.

在化合物中，氧原子的数目和其它元素原子的数目，不管是旧的命名系统，还是现在广泛使用的命名系统都使用了希腊语前缀。这些前缀是：(1) mono-, 有时简化为 mon-, (2) di-, (3) tri-, (4) tetra-, (5) penta-, (6) hexa-, (7) hepta-, (8) octa-, (9) nona- and (10) deca-。当命名非金属氧化物的时候，从 tetra 开始，一般省略前缀中的字母 a，mono-也经常从命名中一起省略。

The Stock system is also used with nonmetal oxides. Here the Roman numeral refers to the oxidation state of the element other than oxygen.

Stock 系统也经常用于非金属氧化物。其中罗马数字代表了除了氧之外的元素的氧化数。

In either system, the element other than oxygen is named first, the full name being used followed by oxide. Table 6 shows some examples.

在任意一种系统中，都是首先命名氧以外的元素，在全名中后边跟着 oxide。表 6 给出了一些例子。

Table 6. Names of some nonmetal oxides

Formula		
CO	carbon(II) oxide	carbon monoxide
CO <sub>2</sub>	carbon(IV) oxide	carbon dioxide
SO <sub>3</sub>	sulfur(VI) oxide	sulfur trioxide
N <sub>2</sub> O <sub>3</sub>	nitrogen(III) oxide	dinitrogen trioxide
P <sub>2</sub> O <sub>5</sub>	phosphorus(V) oxide	diphosphorus pentoxide

$\text{Cl}_2\text{O}_7$	chlorine(VII) oxide	dichlorine heptoxide
-------------------------	---------------------	----------------------

### Naming Acids (酸的命名)

Acid names may be obtained directly from a knowledge of Valence Table 3 by changing the name of the acid ion (negative ion) in the table as follows:

酸的名字可以直接从价键表 3 的知识通过改变酸根离子（阴离子）的名字而获得，见

下表: Ion Table 3

Corresponding Acid

\_\_\_\_\_ate                    \_\_\_\_\_ic

\_\_\_\_\_ite                    \_\_\_\_\_ous

\_\_\_\_\_ide                    hydro\_\_\_\_\_ic

Table 7 shows examples of this relationship. 表 7 给出了这种关系的例子。

Table 7. Names of some acids

Formula of Acid	Acid Ion in Table 3	Name of Acid
$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$ acetate	acetic acid
$\text{H}_2\text{CO}_3$	$\text{CO}_3^{2-}$ carbonate	carbonic acid
$\text{HClO}_2$	$\text{ClO}_2^-$ chlorite	chlorous acid
$\text{HClO}_4$	$\text{ClO}_4^-$ perchlorate	perchloric acid
$\text{HCN}$	$\text{CN}^-$ cyanide	hydrocyanic acid
$\text{HBr}$	$\text{Br}^-$ bromide	hydrobromic acid
$\text{H}_2\text{SiO}_4$	$\text{SiO}_4^{2-}$ silicate	silicic acid
$\text{H}_3\text{AsO}_4$	$\text{AsO}_4^{3-}$ arsenate	arsenic acid
$\text{HMnO}_4$	$\text{MnO}_4^-$ permanganate	permanganic acid

There are a few cases where name of the acid is changed slightly from that of the

acid radical; for example  $\text{H}_2\text{SO}_4$  is sulfuric acid rather than sulfic. Similarly,  $\text{H}_3\text{PO}_4$ , is phosphoric acid rather than phosphic.

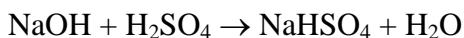
存在这样的一些例子，酸的名字与酸根的名字相比有轻微的改变，例如： $\text{H}_2\text{SO}_4$  叫 sulfuric acid 而不是 sulfic。与此类似， $\text{H}_3\text{PO}_4$  叫 phosphoric acid 而不是 phosphic。

The less common negative ions are not included in the Valence Table 3. For example,  $\text{BO}_3^{3-}$  is the borate ion and  $\text{H}_3\text{BO}_3$  is boric acid;  $\text{TeO}_4^{2-}$  is the tellurate ion and  $\text{H}_2\text{TeO}_4$  is telluric acid, and so on.

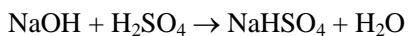
比较不常见的负离子不包括在价键表3中。例如， $\text{BO}_3^{3-}$  叫 borate ion， $\text{H}_3\text{BO}_3$  叫 boric acid； $\text{TeO}_4^{2-}$  叫 tellurate ion（碲酸根离子）， $\text{H}_2\text{TeO}_4$  叫 telluric acid（碲酸）等等。

### Acid and Basic Salts (酸和碱式盐)

It is conceivable that in the neutralization of an acid by a base, only a part of the hydrogen might be neutralized; thus



可以想象得到，在酸被碱中和的反应中，可能只有部分氢被中和，因此



The compound  $\text{NaHSO}_4$  has acid properties, since it contains hydrogen, and is also a salt, since it contains both a metal and an acid radical. Such a salt containing acidic hydrogen is termed (称为，把...叫做) an acid salt. Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) might be progressively (日益增多地) neutralized to form the salts,  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{Na}_3\text{PO}_4$ . The first two are acid salts, since they contain replaceable hydrogen. A way of naming these salts is to call  $\text{Na}_2\text{HPO}_4$  disodium hydrogen phosphate and  $\text{NaH}_2\text{PO}_4$  sodium di- hydrogen phosphate. These acid phosphate are important in controlling the alkalinity (碱度) of the blood. The third compound, sodium phosphate

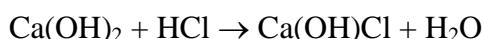
$\text{Na}_3\text{PO}_4$ , which contains no replaceable hydrogen, is often referred to as normal (正常的, 正规的) sodium phosphate, or trisodium phosphate to differentiate it from the two acid salts.

化合物  $\text{NaHSO}_4$  有酸性, 因为她含有氢, 同时它也是一种盐, 因为她既含有金属也含有酸根。这种含有酸性氢的盐叫做酸式盐。磷酸  $\text{H}_3\text{PO}_4$  可以被分步中和而形成盐  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$  和  $\text{Na}_3\text{PO}_4$ 。前两种是酸式盐, 因为它们含有可以被置换的氢。命名这些盐的一种方法是把  $\text{Na}_2\text{HPO}_4$  叫做磷酸氢二钠, 而  $\text{NaH}_2\text{PO}_4$  叫做磷酸二氢钠, 这些酸式磷酸盐在控制血液碱度方面非常重要。第三种化合物, 不含有可以被取代的氢  $\text{Na}_3\text{PO}_4$ , 通常被叫做正磷酸钠, 或者与前两种酸式盐区分开叫做磷酸三钠。

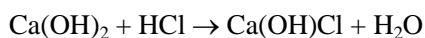
Historically, the prefix bi- has been used in naming some acid salts; in industry, for example,  $\text{NaHCO}_3$  is called sodium bicarbonate and  $\text{Ca}(\text{HSO}_3)_2$  calcium bisulfite. Since the bi- is somewhat misleading, the system of naming discussed above is preferable.

历史上, 前缀 bi-曾经用来命名某些酸式盐; 例如, 在工业上,  $\text{NaHCO}_3$  叫做 sodium bicarbonate (碳酸氢钠),  $\text{Ca}(\text{HSO}_3)_2$  叫做 calcium bisulfite (亚硫酸氢钙)。因为 bi-在某些程度上容易误解, 所以用上面讨论的命名系统更优越些 (更好)。

If the hydroxyl (羟基, 氢氧基) radicals of a base are progressively neutralized by an acid, basic salts may be formed:



如果碱的氢氧根被酸分步中和, 也可以形成碱式盐。



Basic salts have properties of a base and will react with acids to form a normal

salt and water. The OH group in a basic salt is called an hydroxy group. The name of  $\text{Bi(OH)}_2\text{NO}_3$  would be bismuth dihydroxynitrate.

碱式盐具有碱的性质，将与酸反应形成正盐和水。碱式盐中的 OH 基团叫做羟基。

$\text{Bi(OH)}_2\text{NO}_3$  的名字是二羟基硝酸铋 (bismuth dihydroxynitrate)。

### Mixed Salts (混合盐)

If the hydrogen atoms in an acid are replaced by two or more different metals, a mixed salt results. Thus the two hydrogen atoms in  $\text{H}_2\text{SO}_4$  may be replaced with sodium and potassium to yield the mixed salt  $\text{NaKSO}_4$ , sodium potassium sulfate.  $\text{NaNH}_4\text{HPO}_4$  is a mixed acid salt that may be crystallized from urine.

如果酸中的氢原子被两种或两种以上的不同的金属取代，就形成了混合盐。因此， $\text{H}_2\text{SO}_4$  中的两个氢原子可以被钠和钾产生混合盐  $\text{NaKSO}_4$ ，硫酸钾钠。 $\text{NaNH}_4\text{HPO}_4$  是可以从尿液中结晶出来的混合酸式盐。

## 8. Bronsted's and Lewis' Acid-Base Concepts

Bronsted-Lowry Concept (1923), According to this concept, an acid is a substance that releases protons (a proton donor) and a base is a substance that combines with protons (a proton acceptor). Neutralization reactions involve the transfer of protons. Salts are merely aggregates (集合体) of ions that are produced in some but not all neutralization reactions.

Bronsted-Lowry 概念 (1923)，按照这个概念，酸是释放质子的物质（质子给予体）而碱是与质子结合的物质（质子接受体）。中和反应涉及到的是质子的转移反应。盐仅仅是部分而不是全部酸碱反应所产生的离子的集合体。

Upon loss of a proton, an acid forms a base, since by the reverse reaction the substance formed can gain a proton. **In the same way** (同样地) a base forms an acid upon gaining a proton. These relationships can be represented (表现, 描绘) by equations, and the sum is an equation for a neutralization reaction.

酸失去质子后就形成了碱，因为通过逆反应所形成的物质可接受一个质子。同样地，碱得到一个质子后可形成酸。这些关系可以用方程式表现出来。总的方程式是中和反应的方程式。

We see, then, that a neutralization reaction is a competition for protons between two bases. The acid and base represented in Equation 1 (and Equation 2) are a conjugate pair; that is, an acid forms its conjugate base upon loss of a proton and a base forms its conjugate acid when it gains proton. Substances with the same subscript (写在下方的; 下标) in Equation 3 are conjugate pairs. This concept can be illustrated (举例说明, 图解; 加插图于, 阐明) by some examples.

我们可以看出，中和反应是两个碱竞争质子的反应。方程式 1 (或方程式 2 中) 中描绘的

酸和碱是共轭酸碱对；即酸失去质子后形成了它的共轭碱而碱得到质子后形成的是它的共轭酸。方程式 3 中带有同样下标的物质是共轭酸碱对。这个概念可以用一些例子来说明。

The first equation is a neutralization reaction according to the Arrhenius concept as well as Bronsted-Lowry but, since Arrhenius recognized only the base OH<sup>-</sup>, the other reactions are excluded according to his concept. Note that in the second and third reactions that water acts as a base and an acid, respectively. Water, like many other substances that can both donate and accept protons, is amphoteric (两性的) according to this concept. It functions as an acid in the presence of bases stronger than itself (NH<sub>3</sub>, for example) and as a base in the presence of an acid stronger than itself (HCl, for example). The positions of the equilibria given above depend upon the relative proton-donating ability of the two acids in each case (or the relative proton-accepting ability of the two bases).

无论是按照 Arrhenius 概念还是按照 Bronsted-Lowry 概念，第一个方程式都是中和反应，但是因为 Arrhenius 概念只承认 OH<sup>-</sup> 是碱，所以按照他的概念，其它的反应就不是中和反应了（都被排斥在中和反应之外）。要注意的是在第二个和第三个反应中，水分别是碱和酸。水，象许多其它物质一样，既可以给出质子，也可以接受质子。按照这个概念，它是两性物质。当存在比它强的碱时（例如 NH<sub>3</sub>），水就作为（是）酸存在（扮演酸的角色），当存在比它强的酸时（例如 HCl），它就作为（是）碱存在。上面所给的平衡状态（位置）取决于在每一个例子中两种酸给出质子的能力的相对大小（或两种碱接受质子的能力的相对大小）。

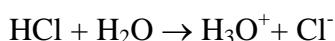
These relationships allow (允许, 准许; 使得以发生) the establishment (建立, 成立, 确定) of scales (天平, 台秤, 秤; 衡量; 标度, 刻度) of acid and base strength.

Relative acid strength of proton donors is measured (测量, 权衡) by the extent to

which reactions with a common (共同的, 共通的, 联合的, 公共的; 常见的, 常有的) base proceed (进行, 继续下去, 发生) at equilibrium (平衡). Relative base strength of proton acceptors is established in similar fashion (方式). Table 8. lists several familiar substances arranged in the order of decreasing (减少, 降低) acid strength. Since the conjugate base of a weak acid is strong, and vice versa, the bases formed in the reactions given are in the reverse order by strength; that is, the strongest base is at the bottom of the table.

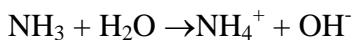
这些关系就使得建立衡量酸碱强度的标准成为可能。质子给予体的相对酸强度是通过它们与同一碱反应进行到平衡的程度来衡量(测量)的。质子接受体的相对碱强度通过同样的方式来建立标准。表 8 所列出的物质是按照酸度逐渐降低的顺序排列的。因为弱酸的共轭碱是强碱, 反之亦然, 所以所给出的反应中形成的碱的强度顺序与酸相反, 即最强的碱在表的底部。

The relative strength of a base, according to the Bronsted concept, is a measure of its ability to accept a proton. Between any two substances that compete for protons, the one that gains protons over the other is more basic. For example, water may compete with the chloride ion for a proton, but  $\text{Cl}^-$  is so weak as a base that water easily accepts a proton and forms  $\text{H}_3\text{O}^+$  in this reaction:



按照 Bronsted 概念, 碱的相对强度是衡量它接受质子能力的量度。在任意两种竞争质子的物质之间, 超过另一个而获得质子的这种碱是较强的碱。例如, 水和氯离子竞争质子, 而  $\text{Cl}^-$  作为一种碱是如此之弱(是一种非常弱的碱), 以至于水在这个反应中容易接受质子而形成  $\text{H}_3\text{O}^+$ 。

On the other hand, water **loses out** (损失, 失败, 输) in the competition for protons when water competes with ammonia for protons. Ammonia takes protons from the water, forcing the water to act as an acid in the reaction



另外一方面, 当水和氨竞争质子时, 水就失去了质子。氨从水上拿走了质子, 迫使水在反应中作为酸而存在。

The relative strength of the competitors for protons can be derived (获得, 导出, 推论, 推导) from Table 8. The strongest proton acceptors are the bases at the bottom of the list, while the strongest acids or proton donors are acids at the top of the list.

质子竞争者的相对强度可以从表 8 中导出。最强的质子接受体是处于表最底部的碱, 而最强的酸或者最强的质子给予体是处于表最顶端的酸。

Lewis Concept (1923). G. N. Lewis proposed another acid-base concept in the same year that the Bronsted-Lowry concept appeared. Lewis defined an acid as a molecule or ion that can accept an electron pair from another molecule or ion, and a base as a substance that can share its electron pair with an acid. Thus, an acid is an electron-pair acceptor and a base is an electron-pair donor. When a Lewis acid reacts with a Lewis base, consequently, a coordinate covalent bond is formed. This is essentially (本质上, 本来) the neutralization reaction.

Lewis 概念 (1923) G. N. Lewis 在 Bronsted-Lowry 酸碱理论提出的同一年建议了另外一种酸碱理论 (概念)。Lewis 定义酸是可以从另外一个分子或离子接受电子对的分子或离子, 而碱是和酸共用电子对的物质。因此, 酸是电子对的接受体, 而碱是电子对的给予体。因此, 当 Lewis 酸和 Lewis 碱反应的时候, 配位共价键就形成了。这就是中和反应的本质。

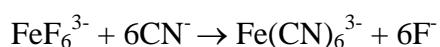
Electron dot formulas (公式、方程式) clarify (解释、澄清、阐明) the mechanism of forming a coordinate bond in the neutralization of a Lewis acid. Neutralization of a proton by an ammonia molecule is

电子点方程式解释说明了 Lewis 酸在中和反应中形成配位键的机理。质子被氨分子中和的反应是

The acid-base pair  $\text{Al}^{3+}$  and  $\text{H}_2\text{O}$  undergoes (经历, 经受, 忍受) Lewis neutralization by forming six coordinate bonds.

$\text{Al}^{3+}$  和  $\text{H}_2\text{O}$  酸碱对通过形成六个配位键进行 Lewis 中和反应。

Many displacement reactions illustrate (举例说明, 图解; 加插图于, 阐明) the relative strength of the Lewis acid or base. For example, the cyanide ion is a stronger base than the fluoride ion by **virtue of** (有...优点) its ability to displace the fluoride ion from the hexafluoroferrate(III) ion:



许多取代反应可以说明 Lewis 酸或碱的相对强度。例如,  $\text{CN}^-$  具有能够从  $\text{FeF}_6^{3-}$  离子中取代 F 的优点, 所以  $\text{CN}^-$  是比 F 更强的碱。

There are many reactions that fit the Lewis acid-base concept. In contrast to proton loss or gain in the Bronsted-Lowry concept, the Lewis concept emphasizes the electron pair-a Lewis acid lacks an electron pair in an empty orbital, or has an orbital that can be vacated (腾出, 空出) and a Lewis base has a nonbonding electron pair and can supply this pair to another substance lacking an electron pair.

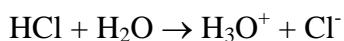
有很多符合 Lewis 酸碱概念的反应。与 Bronsted-Lowry 理论中得失质子相反, Lewis 理论强调的是电子对- Lewis 酸具有空轨道而缺少电子对填充在空轨道上, 或者具有能够腾

出的轨道；Lewis 碱具有非键电子对，能够把此电子对提供给缺少电子对的物质。

It is evident that the Lewis concept applies(适用,应用) **not only to the chemical behavior** correlated by the Bronsted-Lowry concept, **but also to many chemical reactions** that do not involve proton transfer, and for this reason it is most useful. Its generality (一般性, 普遍性, 通性; 大多数, 大部分; 概论, 通论, 通则; 普遍有效 (适用) 性, 普遍性, 通则; 概括, 概要, 笼统, 梗概) precludes (避免, 排除, 阻止, 防碍) the establishment of a scale of acid and base strengths for all Lewis acids and bases, but comparisons can be made between selected substances.

很明显 Lewis 酸碱理论不仅仅适用于和 Bronsted-Lowry 理论相关的化学反应，而且适用于不涉及质子转移的许多化学反应（根据两个并列成分 **not only to the chemical behavior** 和 **but also to many chemical reactions**, 可以判断出 **the chemical behavior** 和 **chemical reactions** 的含义一样，正因为如此，它是最有用的理论。Lewis 酸碱理论的普遍适用性防碍了对所有的 Lewis 酸碱建立酸碱强度的量度标准，但是在所选择的物质之间可以进行比较相对强度。

The terms nucleophilic, and electrophilic are sometimes applied to bases and acids. Lewis acids that accept an electron pair are electrophilic, and the strength of Lewis bases is measured by their tendencies to supply electrons. For example, H<sub>2</sub>O is a stronger base than Cl<sup>-</sup> because H<sub>2</sub>O displaces Cl<sup>-</sup> in supplying an electron pair for the proton:



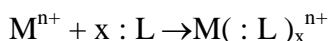
Consequently, H<sub>2</sub>O is a stronger nucleophilic agent than Cl<sup>-</sup>.

术语亲质子性和亲电子性有时也适用于碱和酸。接受电子对的 Lewis 酸是亲电子性的，而 Lewis 碱的强度可以通过它们提供电子趋势的大小来衡量。例如，在向质子提供电子对方面，

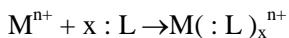
$\text{H}_2\text{O}$  比  $\text{Cl}^-$  强，因此  $\text{H}_2\text{O}$  的碱性比  $\text{Cl}^-$  强。因此， $\text{H}_2\text{O}$  是比  $\text{Cl}^-$  更强的亲质子试剂。

## 9. The Coordination Complex (配位化合物)

The chemical basis for the formation of a coordination complex is the coordinate bond. There must be an electron-pair acceptor and an electron-pair donor. Thus, coordination reactions are examples of Lewis acid—base neutralization. The central ion is the Lewis acid, or electron-pair acceptor, and the surrounding groups, called ligands, are Lewis bases or electron-pair donors. In general, this reaction may be described as



配位化合物形成的化学基础是配位键。配位化合物的形成过程必须存在电子对接受体和电子对给予体。因此，配位反应是 Lewis 酸碱反应的例子。中心离子是 Lewis 酸，或者叫电子对接受体，中心离子周围的叫配体的基团是 Lewis 碱或者电子对给予体。一般，这类反应可以描述如下：



The forward (前进的，向前地) reaction is coordination and the reverse reaction is dissociation. Both coordination and dissociation usually occur in stepwise (楼梯式的，逐步的) fashion when  $x$  is greater than 1, so that the general equation above may be the sum of several stepwise equations.

正向的反应是配位反应，逆反应是配合物的解离反应。当  $x$  大于 1 时，配位反应和解离反应通常都是逐步进行的，因此上面的总方程式是几个分步反应方程式的和。

The nature of the coordinate bond varies from essentially covalent, including double bond character in some cases, to essentially ionic. (配位键的性质从以实质上的共价键，某些情况下包括双键性质变化到实质上的离子键。) In the case of complexes

such as  $\text{Na}(\text{H}_2\text{O})_x^+$  in aqueous solution, the sodium ion interacts (互相作用, 互相影响) with the coordinated water molecules much as a sodium ion in crystalline sodium chloride interacts with neighboring chloride ions. (在象水溶液中存在的  $\text{Na}(\text{H}_2\text{O})_x^+$  这样的例子中, 钠离子与配位水分子的互相作用非常类似处于结晶状态的氯化钠中钠离子与相邻氯离子的互相作用。) The bonding forces can be treated as electrostatic interactions. (结合力可以作为静电引力处理。) At the other extreme, complexes like  $\text{Fe}(\text{CN})_6^{4-}$  involve primarily covalent bonding. (另外一个极端, 象  $\text{Fe}(\text{CN})_6^{4-}$  这样的配合物主要涉及的是共价键。) This (应该 These) variation (应该为 variations) in behavior is (应该是 are) further illustrated by compounds listed in Table 9. (这种性质的变化可以进一步用表 9 中所列出的化合物说明。)(The first four compounds listed are saltlike substances in which either the cation or anion is complex. (所列的前四个化合物是类似盐的物质, 其中或者阳离子, 或者阴离子是配合物。) This is apparent from their composition in aqueous solution. However, these same ions exist in the solids, although their formulas may be written as double salts as in the table. (这一点从它们在水溶液中的组成上明显可以看出来。在固体中仍然存在同样的离子, 尽管它们的分子式可以写成表中两种盐的形式。) In each of these cases the complex ion survives through the solution process and there is little evidence of free ligand or hydrated monatomic cation in solution. (在每一个例子中, 配离子通过溶液作用而存在, 溶液中几乎没有游离配体或者水合的单原子阳离子存在。) Note that the ligands may be molecular, as  $\text{NH}_3$ , or anionic, as  $\text{CN}^-$ ,  $\text{NO}_2^-$ , or  $\text{F}^-$ . (要注意的是配体可以是分子, 如  $\text{NH}_3$ , 或阴离子, 如  $\text{CN}^-$ ,  $\text{NO}_2^-$ , 或  $\text{F}^-$ 。) In the case of  $\text{VF}_4(\text{H}_2\text{O})_2^-$ , vanadium is coordinated with both anionic and molecular ligands. (在  $\text{VF}_4(\text{H}_2\text{O})_2^-$  这个例子中, 钒同时与阴离子配体和分子配体配)

位。) The fifth compound,  $\text{Pt}_2\text{Cl}_4 \cdot 4\text{NH}_3$ , contains both complex cation and complex anion in solution and in the solid. (第五个化合物  $\text{Pt}_2\text{Cl}_4 \cdot 4\text{NH}_3$ , 在溶液和固体中都存在配阳离子和配阴离子。) The last compound has a crystal structure indicating the presence of  $\text{CuCl}_4^{2-}$  complex ions. (最后一种化合物的晶体结构表明存在  $\text{CuCl}_4^{2-}$  配阴离子。) However, when the substance is dissolved in water, a mixture of hydrated monatomic ions results. (但是, 当此物质溶解在水中时, 形成的是单原子离子的水合离子的混合物。) This simply indicates that Cu(II) forms a more stable complex with water ligands than with chloride ligands, and that a high degree of ionic character allows rapid conversion to hydrated Cu(II) upon solution. (这只是表明了 Cu(II)与配体水形成的配合物比与 Cl<sup>-</sup>形成的配合物稳定, 高度的离子性使得在水溶液的作用下, 能够快速转化为水合的 Cu(II)离子。) The absence of  $\text{CuCl}_4^{2-}$  in solution does not prove that it is not present in the solid. (在溶液中不存在  $\text{CuCl}_4^{2-}$  并不能证明在固体中也不存在  $\text{CuCl}_4^{2-}$ 。)

表 9 见 P<sub>45</sub>

#### Ligand field theory. 配体场理论

A recent theory which has proven useful **in connection with** (关于, 与...有关) coordination compounds is the crystal field or ligand field theory, which states that ligands are held to the central ion of a coordination compound by electrostatic attractive forces due primarily to the charge of the central ion and the polar nature of the ligands. (已经证明近来的晶体场理论或配体场理论是关于配位化合物的有用的理论, 这个理论说明在配合物中, 配体和中心离子的结合, 主要是因为中心离子的电荷和配体的极性而产生的静电吸引力。) The extent of the attractive forces determines the stability of the complex, and is dependent on the charge and size of the central ion and ligands.

(引力的大小决定了配合物的稳定性,而引力本身的大小由中心离子和配体的电荷和尺寸所决定。)

Using this theory, it is possible to calculate the energy effects for many of the charge and size factors and finally to obtain values (价值, 估价, 评价, 价格; (数) 值, 确切含义) for bond energies. The latter are useful in predicting properties and types of configurations for a large number of compounds.

利用这个理论,能够计算许多因电荷和尺寸效应引起的能量效应,最终获得键能的数值。后者在预测大量化合物的性质和构型种类方面非常有用。

### Ligand Groups (配体基团)

Ligands must be polar or polarizable (nonpolar molecules are poor coordinating groups), and they usually have unshared electron pairs that may form coordinate bonds with the central ion. Ligands may be classified (Table 10.) on the basis of their ability to form one bond with the metal ion (unidentate 单齿的) or their ability to form two bonds (bidentate 双齿的). Ligands that are divalent(二价的) or contain two donor (给体, 供体, 施主) atoms, like ethylenediamine ( $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ), are bidentate because they contain two points or sites that enter into bonds with the central ion.

配体必须是极性的或可以极化的(非极性分子配位能力差),通常具有可以和中心离子形成配位键的孤对电子。配体可以按照能够和中心离子形成一个键(单齿配体)还是两个键(双齿配体)进行分类。二价的或含有两个给予体原子的象乙二胺这样的配体叫做双齿配体,因为它们含有两个和中心离子结合成键的位置(配位点)。

Ligands may be still more complex and many tridentate, tetradeinate, and even hexadentate ligands are known. (有的配体更复杂,已经知道三齿,四齿甚至六齿的配

体。) Polydentate ligands may have both neutral and anionic sites that coordinate with the central ion, such as the glycinate (甘氨酸盐(酯)) ion: (多齿配体可能同时含有和中心离子配位的中性的和阴离子性的配位点, 如甘氨酸根离子:

Table 10. Some Ligand Groups

Unidentate			
	Ions	Molecules	
CN-	Cyano 氰合, 氰基	H <sub>2</sub> O	Aquo 水合
OH-	Hydroxo 羟基合	NH <sub>3</sub>	Ammine 氨合
CH <sub>3</sub> COO-	Acetato 醋酸合	CO	Carbonyl 羰基合, 羰基
NO <sub>3</sub> <sup>-</sup>	Nitrate 硝酸合	CH <sub>3</sub> NH <sub>2</sub>	Methylamine 甲胺合, 甲胺
NO <sub>2</sub> <sup>-</sup>	Nitro 硝基		
F	Fluoro 氟合, 氟代		
Cl <sup>-</sup>	Chloro 氯合, 氯代		
Br <sup>-</sup>	Bromo 溴合, 溴代		
Bidentate			
-OOC-COO-	Oxalato 草酸合	H <sub>2</sub> N-CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub>	Ethylenediamine 乙二胺
CO <sub>3</sub> <sup>2-</sup>	Carbonato 碳酸合(根)		

Here both the anionic oxygen and the nonionic nitrogen have unshared electron pairs and may coordinate with a given cation. (此处阴离子性的氧和非离子性的氮都有孤对电子, 可以和给定的阳离子配位。) An example is the complex [Co(H<sub>2</sub>NCH<sub>2</sub>CO<sub>2</sub>)<sub>3</sub>], in which the Cobalt is coordinated with the nitrogen and one of the oxygens of each

glycinate. (例如 $[\text{Co}(\text{H}_2\text{NCH}_2\text{CO}_2)_3]$ , 其中 Co 同时和每一个甘氨酸根离子的氮原子和氧原子配位。) A polydentate ligand, when coordinated at two or more points to a central ion, forms a ring structure such as illustrated by the ethylenediamine complex of cobalt above. (当多齿配体在两个或多个配位点同时与中心离子配位时, 就形成了如上面所示的钴的乙二胺配合物的环状结构。) This type of complex is called a chelate, and the polydentate ligand is a chelating group. (这种类型的配合物叫做螯合物, 对应的多齿配体叫做螯合配体。)

#### Naming and Examples of coordination compounds (配位化合物的命名和例子)

1. Cations are named first, anions last. 先命名阳离子, 后命名阴离子。
  2. The names of negative ion ligands end in o. Examples from Table 10. are cyano-, hydroxo-, chloro-, carbonato-. The order of ligands is alphabetic.
- 阴离子配体的命名以 o 结尾。表 10 中的例子是 cyano-(CN<sup>-</sup>), hydroxo-(OH<sup>-</sup>), chloro-(Cl<sup>-</sup>), carbonato-(CO<sub>3</sub><sup>2-</sup>)。配体的顺序是按照字母排列的。
3. Neutral units have historical endings, such as ammine, aqua- (formerly aquo-), carbonyl, nitroso-. 中性单元具有历史性的结尾, 如 ammine (氨, 氨配合物), aqua- (水, 溶液, 水剂, 水合的, ) (formerly aquo-以前是 aquo-水合的, 含水的, 水合离子), carbonyl (羰基), nitroso- (亚硝基) .

4. The oxidation number of the central atom in the complex is **specified by** (用...说明) Roman numerals in parentheses following the name of the element. When a complex ion is negative, the name of the central element has -ate appended (附加, 添加, 悬挂) .

配合物中中心原子的氧化数用元素名字后面括号中的罗马数字说明。当配位离子是阴离子时, 中心元素的名字加上 (-ate) 酸。

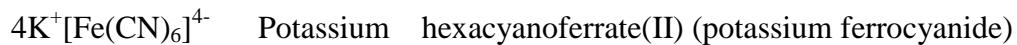
5. Neutral complexes are named as if they were cations.

中性配合物的命名和阳离子相同。

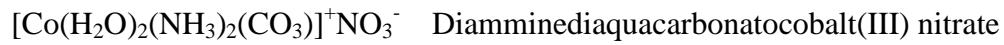
6. If a complex is a positive ion, the names of the acid radicals not in the complex complete the name for the compound.

当配位离子是阳离子时，  
命名化合物时，酸根的名字不包含在配离子中。

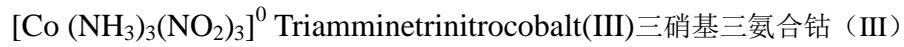
These rules will be clarified by the examples below. 下面的例子可以解释说明这些规则。



六氰合铁(II)酸钾 (亚铁氰化钾)



硝酸化碳酸合二氨二水合钴(III)



## 10. ALKANES (烷烃)

Number of Isomers 异构体的数目

The compounds now assigned (分配, 指派, 赋值, 确定, 选定) the **generic name** (总名称, 属名) alkane are also referred to as saturated (饱和, 浸透) hydrocarbons (烃, 碳氢化合物) and as paraffin (石蜡, 链烷烃) hydrocarbons. The word paraffin, from the Latin *parum affinis* (近缘的) (slight affinity (密切关系, 媚亲关系, 吸引力, 亲合力) refers to (涉及、提到, 针对、有关, 认为与...有关, 认为起源于...) the inert chemical nature of the substances and is applied also to the wax (蜡, 蜡状物) obtainable (能得到的, 可到手的) from petroleum (石油) and consisting of a mixture of higher (高级的, 高等的) alkanes.

1. refer to sb. [sth.] as 称某人 (某物) 为
2. paraffin oil: 石蜡油
3. paraffin wax: 石蜡

现在确定总名称为烷烃的化合物也叫做饱和碳氢化合物和 (石蜡) 链状碳氢化合物。词语 paraffin (石蜡) 来源于希腊语 *parum* (?) *affinis* (意思是有些密切关系的), 它指的是物质具有的化学惰性, 也应用于从石油中可以得到的由高级烷烃组成的蜡状物。

Derivation (衍生, 派生) of the formulas of the pentanes (戊烷) (3 isomers), hexanes (己烷) (5), and heptanes (庚烷) (9) has already demonstrated the sharp rise in diversity (差异, 不同, 千变万化, 差异性, 多样性) with increasing carbon content (含量).

与戊烷、己烷、庚烷分子式相同的异构体分别有 3 种, 5 种, 9 种衍生物, 这一点证明了随着碳含量的增加, 衍生物的种类陡然上升。

Normal Alkanes (正烷烃)

Successive (继承的, 连续的) members of the series differ in composition (组成, 构成) by the increment (增加, 增量)  $\text{CH}_2$  and form a homologous (相应的, 类似的, 一致的, 同源的) series. Thus heptane (庚烷) and octane (辛烷) are homologous hydrocarbon; icosane (“icosa” 表示二十) is a higher homolog (同系物) of methane (甲烷, 沼气).

这个系列的连续成员随着  $\text{CH}_2$  数目的增加组成发生变化, 形成了类似的系列。因此, 庚烷和辛烷是类似的碳氢化合物; 二十烷是甲烷的高级同系物。

### Saturated Unbranched—Chain Compounds and [Univalent Radicals](#)

#### [饱和的直链化合物和单价基团 \(原子团\)](#)

The first four saturated unbranched (无支链的) acyclic (无环的, 非环状的) hydrocarbons are called methane (甲烷), ethane (乙烷), propane (丙烷) and butane (丁烷). Names of the higher members of this series consist of a numerical term, followed by “-ane” with elision (省略) of terminal “a” from the numerical term. Examples of these names are shown in the table below. The generic name of saturated acyclic hydrocarbons (branched or unbranched) is “alkane.”

前四个饱和无支链的非环状的碳氢化合物叫做甲烷, 乙烷, 丙烷和丁烷。高级直链烷烃同系物的名字由数字项后根“ane”组成, 命名时省略了数字项终端的“a”。有关例子见下表。饱和的非环状碳氢化合物 (包括有支链的和无支链的) 的总名字叫烷烃 “alkane”。

Examples of names: (n=total number of carbon atoms)

n	n	n
1 Methane	15 Pentadecane	29 Nonacosane
2 Ethane	16 Hexadecane	30 Triacontane

3 Propane	17 Heptadecane	31 Hentriacontane
4 Butane	18 Octadecane	32 Dotriacontane
5 Pentane	19 Nonadecane	33 Tritriacontane
6 Hexane	20 Icosane	40 Tetracontane
7 Heptane	21 Henicosane	50 Pentacontane
8 Octane	22 Docosane	60 Hexacontane
9 Nonane	23 Tricosane	70 Heptacontane
10 Decane	24 Tetracosane	80 Octacontane
11 Undecane	25 Pentacosane	90 Nonacontane
12 Dodecane	26 Hexacosane	100 Hectane
13 Tridecane	27 Heptacosane	132 Dotriacontahectane
14 Tetradecane	28 Octacosane	

Saturated branched acyclic hydrocarbon is named by prefixing the designations  
 (指示、指定、选派、名称; 指出, 指明; 称呼, 名称) of the side chains to (在...之前)  
 the name of the longest chain which is numbered from one end to the other by Arabic  
 (阿拉伯的) numerals, the direction being so chosen as to give the lowest numbers  
 possible to the side chains. When series of **locants** (位次) containing the same number  
 of terms are compared term by term, that series is “lowest” which contains the lowest  
 number **on the occasion of** (在...的时候, 值此之际) the first difference. This principle  
 (原则, 法则, 原理) is applied irrespective (不顾的, 不考虑的, 无关的) of the nature  
 of the substituents.

Examples (见书) :                  2, 3, 5-Trimethylhexane

饱和的有支链的、非环状的碳氢化合物的命名是通过在最长链的名字之前给支链的名字加前缀来命名的，最长的链用阿拉伯数字从一端到另一端标号，所选择的最长链的方向应该是使支链的编号最可能地小。当逐一比较包含着相同（碳）原子数目的词语的许多位次时（当包含同一数字项的一系列位次进行比较时），根据第一个位次差值的理由（在出现的第一个有差别的位次时），含最低数字的是最低者。不管取代基是什么，这个原则都适用。

例如：2, 3, 5-三甲基己烷

The presence of identical **unsubstituted** radicals is indicated by the appropriate multiplying (增加) prefix di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, deca, etc.

Example (见书) :            3, 3-Dimethylpentane

如果存在同样的未取代基团，应该适当地增加 di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, deca 等前缀来指出。

例如：3, 3-二甲基戊烷

Univalent radicals derived from saturated acyclic hydrocarbons by removal (移动, 免职, 切除) of hydrogen from a terminal carbon atom are named by replacing the ending “-ane” of the hydrocarbon by “-yl”. The carbon atom with the **free valence (自由价)** is numbered (给... 编号) as class, these radicals are called normal, or unbranched chain, alkyls (烷基) .

单价基团是通过从饱和的非环状的碳氢化合物的端基碳原子上去掉氢原子形成的，它的命名是通过把碳氢化合物的词尾“ane”用“yl”来取代而进行的。自由价碳原子可以进行分类编号，这些基团叫做正链烷基或直链烷基。

### Examples

Pentyl (戊(烷)基)        1 — Methylpentyl (1-甲基戊基)        2 — Methylpentyl  
(2-甲基戊基)        5 — Methylhexyl (5-甲基己基)

Isobutyl (异丁基)

sec-Butyl (仲丁基)

tert-Butyl (叔丁基)

Neopentyl (新戊(烷)基)

**Stability.** (稳定性) Alkanes are relatively inert, chemically, since they are indifferent (无关紧要的; 漠不关心的; 惰性的) to reagent which react readily with alkenes (链烃、链烯、烯烃) or with alkynes (炔). N-Hexane (正己烷), for example, is not attacked by concentrated sulfuric acid, boiling nitric acid, molten sodium hydroxide, potassium permanganate, or **chromic acid** (铬酸); With the exception of sodium hydroxide, these reagents all attack alkenes at room temperature. The few reactions of which alkanes are capable require a high temperature or special catalysis.

烷烃的化学性质相对比较惰性，因为它们对很容易和烯烃、炔烃反应的试剂呈现出惰性。

例如，浓硫酸，沸腾的硝酸，熔融的氢氧化钠，高锰酸钾或铬酸都不能进攻正己烷（或者都不和正己烷反应）。而除了氢氧化钠，这些试剂在室温下都可以进攻烯烃。烷烃能够进行的寥寥无几的（为数不多的）反应都需要高温或特殊的催化。

**Halogenation** (卤化反应(作用)). If a test tube containing n-hexane is put in a dark place and treated with a drop of bromine, the original color will remain undiminished in intensity for days. If the solution is exposed to sunlight, the color fades (褪色) in a few minutes, and breathing across the mouth of the tube produces a cloud (烟雾) of condensate (冷凝物) revealing (展现, 显示, 揭示, 暴露) hydrogen bromide as one reaction product. The reaction is a photochemical substitution:



如果把装有正己烷的试管放在黑暗的地方，然后用一滴溴处理，溶液的颜色可以保持几天不变暗。如果把此溶液暴露在阳光下，溶液几分钟就褪色了，在试管口呼一口气会产生

冷凝的雾，说明反应产物之一是 HBr。这个反应是一个光化学取代反应：C<sub>6</sub>H<sub>14</sub> + Br<sub>2</sub> Light



Chlorination (氯化, 用氯处理) of alkanes is more general and more useful than bromination (溴化作用) and can be effected (招致、实现、达到(目的)等) not only photochemically but also by other methods.

烷烃的氯化作用比溴化作用更普遍，也更有用，它不仅可以通过光催化进行，通过其它方法也可以进行。

Light initiates (引发, 发动) chlorination of an alkane by converting (使转变, 转换) chlorine molecules into chlorine atoms by a process of homolysis (均裂), in which a covalent bond is severed (断裂, 裂开) and one electron is retained (保持, 保留) by each of the atoms forming the bond: C<sub>1</sub>:C<sub>1</sub> → C<sub>1</sub>· + C<sub>1</sub>·。烷烃的光引发氯化作用是通过均裂过程把氯分子转变成氯原子进行的，在这个过程中，氯分子中的共价键断裂，形成氯分子的每个氯原子保留一个电子。C<sub>1</sub>:C<sub>1</sub> → C<sub>1</sub>· + C<sub>1</sub>·

A chlorine atom has an odd, or unpaired electron and is a free radical. Because of the tendency of atoms to attain (达到, 获得) their normal valence shells, any free radical is a highly reactive species. Photochemical chlorination proceeds (进行, 继续下去, 发生) through a succession (连续, 继承, 传递) of free radicals; it is a free radical **chain reaction** (链(锁)反应)。氯原子具有奇数个电子，或者说具有未成对电子，是自由基。因为原子具有达到正常价电子层的趋势，所以任何自由基都是高度活泼的物种。光化学氯化作用是通过自由基的传递作用进行的，是自由基的链反应。

The chain initiating step (1), **homolytic fission** (均裂) of chlorine molecules, produces chlorine free radicals; in chain propagating (传播, 传送) steps, a chlorine radical

attacks a molecule of alkane to produce hydrogen chloride and an alkyl radical (2), which in turn attacks a chlorine molecule to produce a chloroalkane (氯代烷) and a chlorine radical (3).

氯分子的均裂反应，即链引发步骤 1，产生了自由基氯；在链反应传播过程中，自由基氯进攻烷烃分子而产生 HCl 和烷基自由基 (2)，烷基反过来又进攻氯分子而形成氯代烷和自由基氯 (3)。

Since chlorine radicals required in step (2) are regenerated in step (3), the two reactions together constitute (组成, 构成) a chain which, if both reactions proceeded with perfect (完美的, 理想的) efficiency (效率, 功效), would be self-propagating without further requirement of light energy,

因为步骤 (2) 所需要的自由基氯在步骤 (3) 中又重新产生，这两个反应在一起就构成了链反应，如果这两个反应都以理想的效率进行的话，这个链反应将是不需要进一步的光能的自发传播反应。

The efficiency, however, is not perfect, for chlorine radicals can recombine (4), combine with alkyl radicals (5), or dissipate (驱散, 消散, 浪费; 散逸) energy by collision (碰撞) with the flask (长颈瓶, 烧瓶, 瓶) walls (墙壁). Hence continued radiation is required to maintain an adequate (适当的, 足够的) supply of initiating radicals. The chain initiating step requires input of light energy amounting to +242·8kJ/mole.

但是，反应效率并不理想，因为自由基氯在步骤 (4) 中重新结合，在步骤 (5) 中和烷基结合，或者在和烧瓶壁碰撞的过程中浪费了能量。因此需要持续的辐射来维持供应足够的引发基团。链引发步骤需要输入+242·8kJ/mole 的光能量。

Step (2), however, is exothermic (放热的), since the energy required to break the C-H bond is less than the bond energy of H-C1. The second chain propagating step (3) is likewise (同样地, 照样地) exothermic, and indeed chlorination of an alkane can proceed explosively (爆炸式地).

但是, 步骤 (2) 是放热反应, 因为断裂 C-H 键所需要的能量比 H-C1 的键能小。第二个链传播步骤 (3) 同样是放热的, 实际上烷烃的氯化作用是爆炸式地进行的。

烷烃的光引发氯化作用是通过均裂过程把氯分子转变成氯原子进行的, 在这个过程中, 氯分子中的共价键断裂, 形成氯分子的每个氯原子保留一个电子。 $\text{Cl}_2 \rightarrow \text{Cl}\cdot + \text{Cl}\cdot$  氯原子具有奇数个电子, 或者说具有未成对电子, 是自由基。因为原子具有达到正常价电子层的趋势, 所以任何自由基都是高度活泼的物种。光化学氯化作用是通过自由基的传递作用进行的, 是自由基的链反应。氯分子的均裂反应, 即链引发步骤 1, 产生了自由基氯; 在链反应传播过程中, 自由基氯进攻烷烃分子而产生 HCl 和烷基自由基 (2), 烷基反过来又进攻氯分子而形成氯代烷和自由基氯 (3)。因为步骤 (2) 所需要的自由基氯在步骤 (3) 中又重新产生, 这两个反应在一起就构成了链反应, 如果这两个反应都以理想的效率进行的话, 这个链反应将是不需要进一步的光能的自发传播反应。但是, 反应效率并不理想, 因为自由基氯在步骤 (4) 中重新结合, 在步骤 (5) 中和烷基结合, 或者在和烧瓶壁碰撞的过程中浪费了能量。因此需要持续的辐射来维持供应足够的引发基团。链引发步骤需要输入+242.8kJ/mole 的光能量。但是, 步骤 (2) 是放热反应, 因为断裂 C-H 键所需要的能量比 H-C1 的键能小。第二个链传播步骤 (3) 同样是放热的, 实际上烷烃的氯化作用是爆炸式地进行的。

Cracking (列解, 断裂). -Heated to temperatures in the range 500~700°C, higher alkanes undergo pyrolytic (热解的, 高温分解的) rupture (裂开, 断裂) or cracking to mixtures of smaller molecules, some saturated and some unsaturated. **Unsaturated**

hydrocarbons produced by selective cracking of specific petroleum (石油) fractions are useful in chemical synthesis. Cracking ruptures (破裂) carbon-carbon rather than carbon-hydrogen bonds because the energy required to break the C-C bond is 247kJ./mole, whereas the C-H bond energy is 364 kJ./mole.

裂解：当加热到 500~700°C 时，高级烷烃就会进行高温分解或裂解成一些饱和烃和不饱和烃的小分子混合物。由特殊石油馏分的选择性裂解所产生的碳氢化合物在化学合成中是很有用的。在裂解过程中断裂的是碳-碳键而不是碳氢键断裂因为断裂 C-C 键所需要的能量是 247kJ./mole，而断裂 C-H 键所需要的能量是 364 kJ./mole。

Oxidation (氧化). -The reaction of hydrocarbons with oxygen with the output (产量, 输出, 输出量) of energy is the basis for use of gasoline (汽油) as fuel in **internal (内在的, 国内的) combustion engines (内燃机)**. The energy release on burning a given hydrocarbon is expressed as the heat of combustion **in terms of** (以...的观点, 就...而说, 依..., 据..., 从...角度来讲, 换算, 折合, 以...为单位, 关于, 在...方面) kJ./mole.

氧化：碳氢化合物和氧反应放出能量的过程是汽油作为内燃机的燃料应用的基础。燃烧给定的碳氢化合物所释放的能量可以以 kJ./mole 为单位，用燃烧热来表示（表达）。

**Incomplete combustion (不完全燃烧)** of gaseous (气体的, 气态的) hydrocarbons is important in the manufacture (加工, 制造) of **carbon blacks (炭黑)**, particularly lampblack (灯烟, 灯黑), a pigment (色素, 颜料, 色料) for ink, and **channel black (槽法炭黑)**, used as a filler in **rubber (橡胶) compounding (配料, 配方)**. Natural gas is used because of its cheapness and availability (可用性, 有效性, 实用性); the yield of black (黑色, 黑颜料) **varies with (随...而变化)** the type of gas and the manufacturing process but usually is **in the range of (在...范围之内)** 2—6% of the

theoretical amount.

气体碳氢化合物的不完全燃烧在加工炭黑，尤其是灯黑、墨水颜料、以及在橡胶配方中用做填充剂的槽法炭黑方面非常重要。因为便宜和容易开采，所以天然气得到了使用，黑色颜料的产率随着气体的种类和加工过程而改变，但是理论值通常在 2—6% 范围内。

Partial air oxidation of a more limited extent is a means (手段, 方法) for production of specific oxygenated (以氧处理, 氧化) substances. air oxidation of high-boiling mineral oils and waxes (蜡) from petroleum affords (提供, 给予, 供应得起) mixtures of higher **carboxylic acid** (羧酸) similar to those derived from fats (脂肪) and suitable for use in making soaps (肥皂) .

如果要对某种物质进行更有限程度的氧化，局部空气氧化是生产特殊氧化产物的方法。从石油中提取的高沸点矿物油和蜡的空气氧化可以提供类似于那些脂肪衍生物的高级羧酸的混合物，**这些混合物**适合于用来制造肥皂。

## 课 文 注 释

1. When series of locants containing the same number of terms are compared term by term, that series is “lowest” which contains the lowest number on the occasion of the first difference. 系主从复合句，“When series…term by term”是时间状语从句，其中分词短语“containing the same number of terms”作主语 series of locants 的定语，term by term 作状语，其中的 by 在此表示连续性，该复合句主句是“that series…first difference”，其中“which contains…difference”是定语从句，修饰 that series。本句译文：“当逐一比较包含着相同(碳原子)数目的词语的许多位次时，根据第一个位次差值的理由，含最低数字的是最低者”。

2. 温度和压力的表达方法：温度和压力一般使用介词短语结构来表达，如

Heated to temperatures in the range 500—700°C,

Cool the mixture to room temperature

At

The beaker of water is maintained at a temperature of 90—95°C.

Zinc may be rolled into sheets at between 120° to 150°C.

CuI undergo similar phase changes at high pressures,

Diamond changes at a pressure of 600000 atm and 1000°C from the four-neighbor diamond crystal to...

above

Above 160°C the S<sub>8</sub> rings break open.

about

It becomes brittle again about 200°C

under

under high pressures it is possible to convert many nonconductors to conductors.

## 11. Unsaturated Compounds (不饱和化合物)

### Unsaturated Compounds and Univalent Radicals (不饱和化合物和自由基)

Unsaturated unbranched acyclic hydrocarbons having one double or triple bond are named by replacing the ending “-ane” of the name of the corresponding saturated hydrocarbon with the ending “-ene” or “-yne.” If there are two or more double or triple bonds, the ending will be “-adiene”, “-atriene” or “-adiyne”, “-atriyne”, etc. The generic names of these hydrocarbons (branched or unbranched) are “alkene”, “alkadiene”, “alkatriene” or “alkyne”, “alkadiyne”, “alkatriyne”, etc. The chain is so numbered as to give the lowest possible numbers to the double or triple bonds.

Examples: 2-Hexene  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH=CH-CH}_3$  2-己烯

1, 4—Hexadiene  $\text{CH}_3\text{-CH=CH-CH}_2\text{-CH=CH}_2$  1, 4—己二烯

The following non-systematic names are retained: 以下的例子保留了非系统的命名:

Ethylene  $\text{CH}_2=\text{CH}_2$  (乙烯) Allene (丙二烯)  $\text{CH}_2=\text{C}=\text{CH}_2$  Acetylene (乙炔)  $\text{HC}\equiv\text{CH}$  Isoprene (异戊二烯)  $\text{CH}_2=\text{CH-C(CH}_3\text{)=CH}_2$

So as to: 使得, 以致, 如此, 以致于

具有一个双键或叁键的不饱和直链非环状碳氢化合物是通过把对应的饱和碳氢化合物的名字的词尾“ane”用“ene”或“yne”来取代而命名的。如果存在两个或更多的双键或叁键, 词尾就是“-adiene”, “-atriene”或“-adiyne”, “-atriyne”等。这些碳氢化合物的总名称(或一般的名字)(包括带有支链的和直链的)叫烯烃, 二烯, 三烯或炔烃, 链二炔, 链三炔等。链的选取要使双键或叁键的编号(位次)最低。

Examples: 2-Hexene  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH=CH-CH}_3$  2-己烯

1, 4—Hexadiene     $\text{CH}_3\text{-CH=CH-CH}_2\text{-CH=CH}_2$    1, 4—己二烯

The following non-systematic names are retained: 以下的例子保留了非系统的命名:

Ethylene  $\text{CH}_2=\text{CH}_2$  (乙烯)   Allene (丙二烯)    $\text{CH}_2=\text{C=CH}_2$    Acetylene (乙炔)    $\text{HC}\equiv\text{CH}$

Isoprene (异戊二烯))    $\text{CH}_2=\text{CH-C(CH}_3\text{)=CH}_2$

The names of univalent radicals derived from unsaturated acyclic hydrocarbons have the endings “-enyl”, “-ynyl”, “-dienyl”, etc., the positions of the double and triple bonds being indicated where necessary.

The carbon atom with the free valence is numbered as 1.

不饱和链状碳氢化合物的衍生的自由价基团的名字具有“-enyl”，“-ynyl”，“-dienyl”等词尾。在必要的地方要指出双键和叁键的位置。自由基碳原子的标号如1。

Examples:      Ethynyl       $\text{CH}\equiv\text{C}-$       2-propynyl       $\text{CH}\equiv\text{C-CH}_2-$   
1-Propenyl       $\text{CH}_3-\text{CH=CH}-$       2-Butenyl       $\text{CH}_3-\text{CH=CH-CH}_2-$   
1, 3-Butadienyl       $\text{CH}_2=\text{CH-CH=CH-}$

Exceptions: 例外:

The following names are retained: 下列名称仍然保留。

Vinyl (for ethenyl)  $\text{CH}_2=\text{CH-}$  乙烯基   Allyl (for 2-propenyl)  $\text{CH}_2=\text{CH-CH}_2-$  丙烯基

Isopropenyl 异丙烯基(for 1-methylvinyl)  $\text{CH}_2=\text{C(CH}_3\text{)-}$  1-甲基乙烯基

Physical Properties. Alkenes (烯烃, 链烯) are known also as ethylenic (烯的, 乙烯的) hydrocarbons and as olefins (烯烃, 石蜡). The term olefin, meaning oil-forming (生成石油, 成油), was applied by early chemists because the gaseous members of the series combine with chlorine and bromine to form oily (油的, 油状的,

含油的) addition (加成, 加合) products.

物理性质：烯烃也作为烯的碳氢化合物和烯烃为我们所知道。早期的化学家用术语 olefin，意思是生成石油，因为气态的烯烃和氯、溴结合形成油状的加合产物。

Alkenes are hardly distinguishable (可区别的, 可辨别的) from the corresponding saturated hydrocarbons. The boiling points are **no more than** (只是) a few degrees below those of alkanes of slightly higher molecular weight, and the densities (密度, 比重) are a few percent higher; in the first few members of the two series there is even a marked correspondence in the melting points. Cycloalkanes (环烷烃) differ more from alkanes (链烷烃) than alkenes do, and hence ring formation influences physical properties more than introduction of an ethylene linkage (键合). The heat of combustion of 1-hexene is practically the same as that of n-hexane on either a weight or volume basis.

烯烃与对应的饱和碳氢化合物几乎不可区分。因为它们的沸点仅仅比分子量稍微高点的烷烃低几度，密度高几个百分点，甚至在烯烃和烷烃这两个系列的前几个成员中，它们的熔点明显的一致。环烷烃与链烷烃的差异比链烯烃和链烷烃的差异大，因此，环的形成比乙烯基的引入对物理性质的影响大。无论是基于重量还是体积，1-己烯的燃烧热实际上都和正己烷的燃烧热相同。

Pyrolytic (热解的, 高温分解的) Dehydration (脱水). -Elimination (消去, 去除) of water from alcohols (酒精, 酒, 乙醇) is a useful method for the preparation of alkenes; thus on elimination of OH from one carbon atom and of H from another, ethanol yields ethylene.

从乙醇中消去水是制备乙烯的一种有效的方法；因此，从一个碳原子上去除 OH，从另

外一个碳原子上去掉一个 H, 乙醇就变成了乙烯。

One of several experimental procedures (程序, 手续, 过程, 步骤) is catalytic dehydration. The alcohol is distilled (蒸馏) through a tube packed (充满...的, 塞满了...) with granules (颗粒) of alumina (氧化铝) and maintained at a temperature of 350~400° in an electrically heated furnace (炉子, 熔炉). The reaction resembles (象, 类似) pyrolysis (热解, 高温分解) of an alkane, since it involves production of an unsaturated product from a saturated one at an elevated (提高的) temperature, but the pyrolysis temperature for an alcohol is distinctly (清楚地, 显然) lower, and the process is simpler and more uniform (统一的, 相同的, 一致的, 均衡的, 始终如一的).

脱水是几个实验步骤中的一步。乙醇在塞满了氧化铝颗粒的管子中进行蒸馏，蒸馏的温度用电热炉维持在 350~400°。这个反应与烷烃的高温分解类似，因为升高温度时，饱和的化合物生成了不饱和的产物，但是，乙醇的热分解温度显然要低得多，反应过程更简单，更均衡。

Sulfuric Acid Method. -Sulfuric acid is a dihydroxy acid represented (表现, 描绘) for simplicity by formula I. The substance may have one semipolar bond as in II, in which case sulfur has expanded its shell to accommodate (供应, 供给, 容纳) twelve electrons, or it may have two double bonds(III).

硫酸法。硫酸是一个二羟基酸，可以用分子式 I 简单地表示。这种物质有一个如 II 中的半（不完全的）极性键，在这两种情况中，硫都电子壳层扩展到容纳 12 个电子，或者说它含有两个双键（见 III）。图 见书。

When concentrated sulfuric acid is added gradually (逐渐地) to ethanol with ice cooling, water is eliminated from the two components (成分, 元件) and ethylsulfuric acid is formed. The reaction proceeds to completion because the water formed is

absorbed by the concentrated acid; the process, however, is an equilibrium, and can be reversed by treatment of the product with a large excess of water. Ethylsulfuric acid is the mono ester (酯) of the inorganic diacid; it is a strong acid soluble in sulfuric acid as well as in water. It is stable at a low temperature but decomposes when heated. This chief organic product of the decomposition is ethylene, formed by loss of  $\text{OSO}_2\text{OH}$  from one carbon atom and of hydrogen from the adjacent position to produce sulfuric acid. A **side reaction** (副反应) **consists in** (存在于) formation of diethyl ether (ordinary ether) by the action of alcohol on ethylsulfuric acid. This reaction can be operated for preparation of ether by adjusting the proportions of reagents and maintaining a temperature of  $140^\circ$ . The difference in the optimum (最适宜的) temperatures for ethylene and ether formation is so slight that each product is a **by-product** (副产物, 副产品) of the production of the other. A third product, diethyl sulfate, can be prepared by heating ethylsulfuric acid at a temperature below  $140^\circ$  at a pressure sufficiently reduced to cause diethyl sulfate to distill from the nonvolatile (非挥发性) acids. Diethyl sulfate is the normal ester, or di-ester, of sulfuric acid. It is useful as an ethylating (乙基化) reagent, sometimes as an alternative to an ethyl halide. Dimethyl sulfate (b.p.  $188.5^\circ$ ) is used similarly.

当在冰的冷却下, 把浓硫酸逐渐地加入到乙醇中时, 这两种成分就通过消去反应除去了水, 形成了乙基硫酸。因为形成的水被浓硫酸吸收, 所以这个反应进行得比较完全。但是, 这个反应是一个可逆反应, 可以通过加大量的水处理产物而使反应逆转。乙基硫酸是无机二元酸的单酯, 具有强酸性, 象溶解在水中一样, 可以溶于硫酸。它在低温下稳定, 加热时分解。分解的主要有机产物是乙烯, 它是通过在一个碳原子上失去  $\text{OSO}_2\text{OH}$  和在相邻的碳原

子上失去氢原子产生硫酸后形成的。一个副反应是乙醇与乙基硫酸作用生成二乙醚（普通醚）。这个醚的制备反应可以通过调整反应物的比例和维持反应温度在 140° 条件下进行。乙烯和二乙基醚的最适宜的形成温度差异非常小，因此每一种产物都是另外一种产物的副产物。第三种产物，硫酸二乙酯，可以通过在低于 140°、足够低的压力条件下加热乙基硫酸而使硫酸二乙酯从非挥发性酸中蒸馏出来而制备。硫酸二乙酯是硫酸的正（中性）酯，或者说二酯。它是一个非常有用的乙基化试剂。有时作为制备氯乙烷的一个选择。硫酸二甲酯(b.p. 188.5°) 的用途与硫酸二乙酯相似。

Acid-Catalyzed Dehydration. -Dehydration can be effected also with hydrochloric acid, phosphoric acid, potassium bisulfate, or oxalic acid (草酸)， $(COOH)_2$ . These are strong acids capable of effecting elimination in catalytic amounts, and some are incapable of forming intermediate (中间的) esters.

酸催化的脱水作用。脱水作用也可以用盐酸，磷酸，硫酸氢钾或草酸来实现。这些都在微量时就能够实现消除作用的强酸。有些酸不能形成中间体酯。

Ease of Dehydration. -Among alcohols having no activating group, the ease of dehydration depends upon the alcohol type and is in the following order: tertiary > secondary > primary. The differences are illustrated in the accompanying examples. The case of ethanol, a primary alcohol, has been cited (引用, 引证) ; the acid strength is 96% and the temperature 170°. The secondary alcohol is dehydrated by 62% acid at the temperature of the steam bath, whereas the tertiary alcohol affords an alkene at the same temperature on reaction with acid of only 46% strength.

脱水作用的容易程度：在没有活性基团的醇中，脱水作用的容易程度取决于水的类型，而且按照以下顺序：叔醇>仲醇>伯醇。差异可以用附随的例子来说明。乙醇，是一种仲醇，

已经被引证过。它脱水所需要的酸强度是 96%，温度是 170°。仲醇脱水需要 62% 的酸和蒸气浴般的温度，然而，叔醇在同样的温度下反应只需要 46% 的酸就可以形成烯烃。

Direction of Dehydration. -The structure of an alcohol may be such that two routes of dehydration are open (公开的, 坦率的, 未决定的). 2-Pentanol offers the possibility for elimination of hydrogen from either the 1- or the 3-position, along with the adjacent hydroxyl group, but the 3- hydrogen is utilized almost exclusively (排除地, 专有地) and the product is 2-pentene.

脱水作用的方向：醇的结构具有两种不确定的脱水路线。2-戊醇在 1-位或 3-位和邻位的羟基一起提供了脱氢的可能性，但是 3-氢的利用具有很高的选择性，因此产物为 2-戊烯。

## 16. The structure of Covalent Compounds

Most of us realize from our earlier chemical training that each covalent chemical compound has a structure—that is, a definite arrangement of its constituent atoms in space. The concept of covalent compounds as three-dimensional objects was developed in the latter part of the last century. Chemists who lived before that time regarded covalent compounds as shapeless groups of atoms held together in a rather undefined way by poorly understood electrical forces. Although the currently (普遍地, 通常地, 当前, 现在) accepted structural characteristics of organic compounds were first suggested in 1874, these postulates (假定, 基本条件, 基本原理) were based on indirect (间接的, 迂回的) chemical and physical evidence. Until the early twentieth century no one knew whether they had any physical reality, since scientists had no techniques for viewing (注视, 检视, 观察) molecules at the atomic level of resolution. Thus, as recently as the second decade (十年) of the twentieth century investigators (调查人) could ask two questions: (1) Do organic molecules have specific (详细而精确的, 明确的) geometries and, if so, what are they? (2) Can we develop simple principles to predict molecular geometry?

经过初步的学习后，我们大部分人都知道每一种化合物都有它的结构。也就是，组成化合物的原子在空间上有确定的排列顺序。三维的共价化合物的概念在上个世纪后期得到了发展。上个世纪末期以前的化学家把共价化合物认为是由原子间按照一种非常不确定的方式、由人们了解极少的电性引力结合在一起的不定形的化合物。尽管现在已经接受的有机化合物的特征是在 1874 年首先提出来的，但是这些基本原理（假定）都是建立在间接的化学和物理学的证据之上的。直到 20 世纪早期，仍然无人知道他们是否具有物理（物质）上的真实

性，因为科学家缺少在原子水平的分辨率上来观察分子的技术。因此，在最近的二十世纪的第二个十年期间，调查者就可以提出两个问题：(1)有机分子有明确的结构吗？如果有，是什么样的？(2)我们能够发展简单的原理来预测分子的几何结构吗？

#### A. Methods for Determining Molecular Structure (测定分子结构的方法)

Among the greatest developments of chemical physics in the early twentieth century were the discoveries of ways to peer (凝视，盯着看) into molecules and deduce the arrangement in space of their constituent atoms. Most information of this type today comes from three sources; X-ray crystallography (晶体学，结晶学), electron diffraction, and microwave spectroscopy. The arrangement of atoms in the crystalline solid state can be determined by X-ray crystallography. This technique, discovered in 1915 and revolutionized (使彻底改革，使革命化) in recent years by the availability of high-speed computers, uses the fact that X rays are diffracted from the atoms of a crystal in precise (精确的，准确的) patterns that can be translated into a molecular structure. In 1930 another technique, electron diffraction, was developed from the observation that electrons are scattered by the atoms in molecules of gaseous substances. The diffraction patterns resulting from this scattering can also be used to deduce the arrangements of atoms in molecules. Following (在...之后，跟踪) the development of radar in World War II came microwave spectroscopy, in which the absorption of microwave radiation by gaseous molecules provides structural information.

在二十世纪早期物理化学的最伟大的发展是 发现了注视分子和推论出组成分子的原子在空间的排列情况的方法。今天，这方面的大量信息来源于三个方面：X-射线晶体学，电

子衍射和微波光谱学。在结晶的固体中，原子的排列情况可以用 X-射线晶体学来测定。这种技术，发现于 1915 年，近年来由于高速计算机的使用，又得到了彻底的改革，利用了 X-射线在晶体中能够以精确的方式进行衍射，然后可以翻译成分子结构的事实。1930 年，另外一种技术，电子衍射，从观察电子能够被气态物质的分子中原子散射开始得到了发展。导致这种散射的衍射方式也能够用来推断分子中原子的排列方式。第二次世界大战发展雷达之后，迎来了微波光谱学的发展。其中，微波射线可以被气体分子吸收，从而提供结构信息。

Most of the details of atomic structure in this book are derived from gas-phase methods-electron diffraction and microwave spectroscopy. For molecules that are not readily studied in the gas phase, X-ray crystallography is the most important source of structural information. There is no comparable (可比较的，比得上的；类似的) method that allows the study of structure in solution, a fact that is unfortunate because most chemical reactions take place in solution. The consistency of gas-phase and crystalline structures suggests. However, that molecular structures in solution probably differ little from those of molecules in the solid or gaseous state.

这本书中原子结构的大部分详细信息来源于气相法-电子衍射和微波光谱。对于不容易在气相中研究的分子来说，X-射线晶体学是结构信息的最重要来源。在溶液中，却没有可相比的研究结构的方法，因为一个不幸的事实是大部分化学反应都在溶液中进行。但是，气相和晶体结构的一致性表明溶液中分子的结构可能有些与固相和气相的分子结构不同。

## B. Prediction of Molecular Geometry (分子结构的预测)

The geometry of a simple covalent molecule is defined by two quantities (参量，程

度), bond length and bond angle. The bond length is defined as the distance between the centers of bonded nuclei. Bond length is usually measured in angstroms;  $1\text{\AA}=10^{-10}$  meter= $10^{-8}$  centimeter. Bond angle is the angle between two bonds to the same atom.

**Consider** (假定; 思考, 考虑, 认为), for example, the compound methane,  $\text{CH}_4$ . When the C-H bond length and H-C-H bond angles are known, we know the structure of methane.

简单的共价分子的几何结构由两个参量来确定, 即键长和键角。键长定义为两个成键原子核中心之间的距离。键长通常用 Å 来衡量;  $1\text{\AA}=10^{-10}\text{m}=10^{-8}\text{cm}$ 。键角是同一个原子所成的两个化学键之间的夹角。例如, 假定甲烷,  $\text{CH}_4$ ; 当知道 C-H 键长和 H-C-H 键角时, 我们就知道了甲烷的结构。

Molecular structure is important because the way a molecule reacts chemically is closely linked to its structure. From the many structures that have been determined, we can now make several generalizations about the structures of covalent compounds.

分子结构非常重要因为分子的化学反应机理与它的结构紧密相关。从大量已经测定的结构中, 我们现在能够对共价化合物的结构做几点总结 (概括)。

**Bond length** The following generalization can be made about bond length:  
键长: 下列所做的总结是关于键长的。

1. Bond lengths between atoms of a given type decrease with the amount of multiple bonding. Thus, bond lengths for carbon-carbon bonds are in the order  $\text{C}-\text{C} >> \text{C}=\text{C} > \text{C}\equiv\text{C}$ .

1. 给定类型的原子间的键长随着多重键的增加而递减。因此, 碳-碳键之间的键长具有以下顺序:  $\text{C}-\text{C} >> \text{C}=\text{C} > \text{C}\equiv\text{C}$

2. Bond lengths tend to increase with the size of the bonded atoms. This effect is most dramatic (戏剧性的, 生动的; 引人注目的, 显著的) as we proceed down the periodic table. Thus, a C-H bond is shorter than a C-F bond, which is shorter than a C-Cl bond. Since bond length is the distance between the centers of bonded atoms, it is reasonable that larger atoms should form longer bonds.

2. 键长倾向于随着成键原子的体积的增加而增大。如果我们沿着元素周期表来看，这个效应是非常显著的。

3 . When we make comparisons within a given row (排, 行) of the periodic table, bonds of a certain type(single, double, or triple) between a given atom and a series of other atoms become shorter with increasing electronegativity. Thus, the C-F bond in H<sub>3</sub>C-F is shorter than the C-C bond in H<sub>3</sub>C-CH<sub>3</sub>. This effect occurs because a more electronegative atom has a greater attraction for the electrons of the bonding partner, and therefore “pulls it closer,” than a less electronegative atom.

3. 当我们对元素周期表中某一周期进行比较时，给定原子和一系列其它原子之间的确定类型的键的键长（单键，双键或叁键）随着原子电负性的增加而变短。因此，H<sub>3</sub>C-F 中 C-F 键的键长要比 H<sub>3</sub>C-CH<sub>3</sub> 中 C-C 键的键长短。出现这种结果是因为电负性大的原子对和其成键的原子的电子具有较大的吸引力，从而要比电负性较小的原子把和其成键的原子拉得更近一些。

**Bond Angle** The bond angles within a molecule determine its shape-whether it is bent or linear. Two generalizations (概括, 归纳; 一般的法则) allow us to predict the approximate (近似的, 大约的) bond angles, and therefore the general shapes, of many simple molecules. The first is that the groups bound to a central atom are arranged so

that they are as far apart as possible. For methane, CH<sub>4</sub>, the central atom is carbon and the groups are the four hydrogens. The hydrogens of methane are farthest apart when they occupy the vertices (至高点, 头顶) of a tetrahedron centered on the carbon atom. Because the four C-H bonds of methane are identical, the hydrogen atoms of methane lie at the vertices of a regular tetrahedron (a tetrahedron with equal sides). The tetrahedral shape of methane requires an H-C-H bond angle of 109.5°.

键角：分子内的键角决定了分子的形状，即分子是弯曲型的还是线形的。有两点基本原则可以让我们预测许多简单分子的近似键角，因而得出她们的形状。第一点是与中心原子结合的基团在空间的排列要尽可能分开。例如，CH<sub>4</sub>，中心原子是碳原子，与其结合的基团是四个氢原子。当这四个氢原子占据以碳原子为中心的四面体的顶点时，他们之间的距离是最远的。因为在 CH<sub>4</sub> 中，四个 C-H 键是等同的，甲烷中的氢原子位于正四面体的顶点（边长相等的四面体）。甲烷的四面体形状需要 H-C-H 键角是 109.5°。

In applying this rule for the purpose of predicting bond angles we regard all groups as identical. Thus the groups that surround carbon in H<sub>3</sub>CCl (methyl chloride) are treated as identical, even though in reality the C-Cl bond is considerably (相当地, 相当多地) longer than the C-H bonds. Although the bond angles show minor deviations from the exact (精确的) tetrahedral bond angle of 109.5° , methyl chloride in fact has the general tetrahedral shape.

在应用这个规则来预测键角的时候，我们把所有的基团都看成是等同的。因此在预测 H<sub>3</sub>CCl (氯甲烷) 的结构中，围绕碳原子的基团作等同处理，即使实际上 C-Cl 键键长比 C-H 键长得多。尽管键角与正四面体的键角 109.5° 表现出微小的差别，氯甲烷实际上仍然具有一

般的四面体形状。

The tetrahedral structure, then, is assumed (假定, 假设; 担任, 承担, 接受; 表现为..., 呈) by molecules when four groups are arranged about (在...附近, 在...周围) a central atom. Since carbon is tetravalent, this is an extremely important geometry for many organic compounds. Since we shall see this geometry repeatedly (重复地, 再三地), it is worth the effort to become familiar with it. Tetrahedral carbon is often represented, as shown below in the structure of methylene(亚甲基) chloride,  $\text{CH}_2\text{Cl}_2$ , with two of its bound groups in the plane of the page. One of the remaining groups, indicated with a dashed line, is behind the page, and the other, indicated with a wedge-shaped heavy line, is in front of the page.

然后, 当四个基团在中心原子周围排列的时候, 分子采用了四面体结构。因为碳原子是四价的, 这是许多有机化合物的非常重要的一个几何结构。因为我们将不断地看到这种几何结构, 因此有必要努力地去熟悉它。四面体结构经常为如下面的二氯甲烷的结构, 其中两个结合基团在页面上, 剩下的两个基团, 一个用虚线指出的基团在页面后, 另外一个用楔形粗虚线指出的在页面前。

You should make a molecular model of a simple tetrahedral molecule such as  $\text{CH}_2\text{Cl}_2$  and relate the three-dimensional model to its two-dimensional representation (图象) above.

你可以制作一个简单的四面体分子如  $\text{CH}_2\text{Cl}_2$  的分子模型, 把三维模型与上面的二维图象联系起来。

When three groups surround central atom, the groups are as far apart as possible when all bonds lie in the same plane with bond angles of  $120^\circ$  in boron trichloride, the central atom (in this case boron) is said to have trigonal geometry.

在  $\text{BCl}_3$  中，当三个基团围绕着中心原子的时候，所有键位于同一平面，键角为  $120^\circ$  的时候，他们之间分开得最远，我们说中心原子（在这种情况下是硼）具有三角形的几何结构。

When a central atom is surrounded by two groups, maximum separation of the groups demands a bond angle of  $180^\circ$ . This is the situation with each carbon in acetylene,  $\text{H-C}\equiv\text{C-H}$ . Each carbon is surrounded by two groups, a hydrogen and another carbon. (it **makes no difference** (对...没有关系) that the carbon has a triple bond.) Because of the  $180^\circ$  bond angle at each carbon, acetylene is a linear molecule.

当中心原子被两个基团所围绕时，基团的最大的分离需要  $180^\circ$  的键角。这就是乙炔  $\text{H-C}\equiv\text{C-H}$  中每一个碳原子的情况。在乙炔中，每一个碳原子被两个基团围绕着，一个是氢，另外一个是碳原子。(碳原子具有三重键对分子构型没有什么影响。) 因为每一个碳原子的键角都是  $180^\circ$ ，乙炔是个线形分子。

The second generalization about molecular structure applies to molecules with unshared electron pairs. In predicting the geometry of a molecule, an unshared electron pair can be considered as a bond without a nucleus at one end. This rule allows us to handle, for example, the geometry of ammonia, In view of (考虑到, 由于) this rule , ammonia,  $:\text{NH}_3$ , has four groups about the central nitrogen, three hydrogens and an electron pair. **To a first approximation** (接近, 走近, 近似值), these groups adopt the tetrahedral geometry with the electron pair occupying one corner of the tetrahedron. (This geometry is sometimes called pyramidal, or pyramid-like, geometry.) We can refine (改善, 改进) our prediction of geometry even more if we recognize that an electron pair without a nucleus at-one end has an especially repulsive interaction with electrons in adjacent bonds. As a result, the bond angle

between the electron pair and the N-H bond is a little larger than tetrahedral, leaving the H-N-H angle a little smaller than tetrahedral; in fact, the H-N-H angle is 107.3°.

第二个关于分子结构的一般原则应用在含有孤对电子的分子上。在预测分子的几何结构中，孤对电子可以当成一端没有原子核的一个化学键来处理。这种原则就使我们可以处理象氨分子这样的结构。按照这个原则，氨，:NH3，在中心原子氮周围，有四个基团，三个氢原子和一队孤对电子。第一点近似，这些基团采取四面体构型，孤电子对占据四面体的一个顶点。(这种几何结构有时叫做锥形，或类锥形的几何结构。)如果承认一端没有原子核的孤对电子和相邻的化学键之间存在特殊的排斥作用，那么我们在预测分子几何结构方面将得到进一步的改进。结果，孤对电子与 N-H 键之间的键角比四面体的键角大一些，因此 H-N-H 键角比四面体的键角小一些。实际上，H-N-H 键角是 107.3°。

If we examine the structure of a molecule that is somewhat more complex than those we have just discussed, we discover one [further aspect](#) of structure. Consider, for example, the structure of ethylene, H2C=CH2. Each carbon of ethylene is bound to three groups: two hydrogens and the other carbon. Our rules for predicting bond angle require, then, that the geometry at each carbon should be trigonal. The structure of ethylene shows that the H-C-H bond angle, 117°, indeed approaches the idealized trigonal value of 120° quite closely, and that the three groups bonded to either of the carbons lie in the same plane. However, ethylene poses (形成, 引起, 造成; 提出, 陈述) a new problem of geometry. Imagine sighting along the carbon-carbon double bond from one end of the molecule. The resulting angle between the C-H bonds on adjacent carbons is called the dihedral angle. The value of the dihedral angle determines the conformation of ethylene: the spatial (空间的) relationship of the

groups on one carbon to those on the other.

如果我们检验那些比我们刚才讨论过的更为复杂一些的分子的结构，就会发现结构的更深层次的（另外）一面。例如，我们来考虑乙烯的结构。在乙烯中，每一个碳原子与三个基团结合，两个氢和另外一个碳原子。然后，我们预测键角的规则要求每一个碳原子的几何结构应该是三角形的。乙烯的结构表明 H-C-H 键角是  $117^\circ$ ，实际上非常接近正三角形的数值  $120^\circ$ ，与任何一个碳原子结合的三个基团都处于同一个平面。但是，乙烯提出了一个几何结构的新问题。假设从碳-碳双键的一端来看这个分子，相邻碳原子之间的 C-H 键之间的夹角叫做二面角。二面角的数值决定了乙烯的空间构型。一个碳原子上的基团和另外一个碳原子上的基团间的空间关系。

In summary, then, the structure of a molecule is completely determined by three elements: its bond lengths, its bond angles, and its conformation. There are simple molecules whose structures are completely determined by bond lengths and bond angles. We have learned [what trends in bond lengths to expect](#) and how to predict the shapes of molecules from bond angles. Conformation enters the [picture](#) for more complex molecules. We shall learn at various stages of our study some of the principles that determine molecular conformation.

总之，分子的结构完全由三个因素决定：键长、键角和空间构型。也有一些简单的分子的结构完全由：键长和键角来决定。我们已经学会？以及如何从键角来预测分子的形状。构型进入了更复杂分子的图象中。我们将在学习的不同阶段学会一些决定分子构型的原则。

## 17. OXIDATION AND REDUCTION IN ORGANIC CHEMISTRY

### 有机化学中的氧化还原反应

The conversion( (变换, 转化) ) of alcohols into carbonyl compounds is an important reaction of primary and secondary alcohols, and is one of many examples in organic chemistry of oxidation.

(乙) 醇转换成羰基化合物是伯醇和仲醇的一类重要反应, 也是有机化学中大量氧化反应的一个例子。

How do we know when an organic compound has been oxidized? In the last section, we recognized that conversion of an alcohol to a ketone (酮) is an oxidation because it is brought about by the reduction of Cr(VI). But there are other oxidations in which the oxidizing agent is less obvious. Our goal in this section is to be able to recognize an oxidation or reduction merely by examining the transformation of the organic compound itself. The procedure for doing this involves three steps:

我们如何知道有机化合物什么时候被氧化? 在最后一部分, 我们承认醇转变成酮是一个氧化反应, 因为它是因 Cr(VI)的还原而产生的。但是, 另外一部分氧化反应中, 氧化剂不是明显能够看出来的。在此部分, 我们的目标就是仅仅通过有机化合物本身的变化来辨别氧化反应或还原反应。

Step 1. **Assign** an oxidation level **to** each carbon atom in reactant and product. (It is only necessary to assign an oxidation level to carbons that undergo some chemical change during the transformation; other carbons maybe ignored.) The oxidation level of a particular carbon is assigned by considering the relative electronegativities of the groups bound to the carbon, as follows:

注: assign…to… 把…指认为……

第一步: 确定反应物和产物中每一个碳原子的氧化水平。(只对在转换过程中, 进行化学变化的碳原子有必要确定氧化级数, 其它碳原子可以忽略。) 特殊碳原子的氧化级数可以通过和它结合的基团的电负性来确定, 如下:

(a) For every bond to an element less electronegative than carbon (including hydrogen), and for every negative charge on the carbon, assign a -1.

对于和比碳原子电负性小的元素(包括氢)所成的每一个化学键, 以及碳原子上的每一个负电荷, 确定为-1。

(b) For every bond to another carbon atom, and for every unpaired electron on the carbon, assign a zero.

对于和另外一个碳原子上所成的每一个化学键以及碳原子上的每一对孤对电子, 确定为0。

(c) For every bond to an element more electronegative than carbon, and for every positive charge on the carbon, assign a +1.

对于和每一个电负性比碳大的元素所成的每一个化学键, 以及碳原子上的每一个正电荷, 确定为+1。

(d) Add the numbers assigned in (a), (b), and (c) to obtain the oxidation level for the carbon atom **under consideration** (在考虑中) .

把(a)、(b)和(c)中所确定的数字加起来就得到所考虑的碳原子的氧化级数。

Let us apply this first step to the transformation of isopropyl(异丙基)alcohol to acetone. (见书)

让我们把第一步应用到异丙基醇转变到丙酮的变化上去。

Since the carbon atoms of the two methyl groups do not change, we do not need to assign oxidation levels to these carbons. Notice in the treatment of acetone that the C=O double bond is **counted as** (算做) two bonds; +1 for each bond gives a total of +2 for the double bond.

Reactant: product:

$$\text{Sum: } 0 + 0 + (+1) + (-1) = 0 \quad \text{Sum: } 0 + 0 + (+2) = +2$$

因为两个甲基上的碳原子没有发生什么变化，我们不需要确定这些碳原子的氧化水平。要注意的是，在处理丙酮时，C=O 双键算作两个化学键；每一个碳是+1，所以双键就是+2。

反应物: 产物:

$$\text{和: } 0 + 0 + (+1) + (-1) = 0 \quad \text{和: } 0 + 0 + (+2) = +2$$

Step 2. The oxidation number  $N_{ox}$  for each compound is computed by adding the oxidation levels of all carbons. In the structures above, only one carbon has changed its oxidation level, so the  $N_{ox}$  values of the reactant and product are simply equal to the respective oxidation levels of this carbon. Therefore, the oxidation level of the reactant is 0 and that of the product is +2. In other reactions involving more than one carbon atom,  $N_{ox}$  is computed by summing the oxidation levels of all carbon atoms that undergo a chemical change.

第二步：每一个合乎的氧化数  $N_{ox}$  可以通过所有碳原子的氧化级加起来计算。在上面的结构中，只有碳原子的氧化级发生了改变，因此反应物和产物的氧化数值仅仅等于这个碳原子的各自的氧化级。因此，反应物的氧化级是 0，而产物的氧化级是+2。在其它涉及多于一个碳原子的反应中， $N_{ox}$  通过把所有进行化学反

应的碳原子的氧化级加起来来计算。

Step 3. Compute the difference.

$$N_{ox}(\text{product}) - N_{ox}(\text{reactant})$$

If this difference is positive, the transformation is an oxidation. If this difference is negative, the transformation is a reduction. If the difference is zero, neither an oxidation nor a reduction has taken place. For the reaction of Eq. 17-1 this difference is  $+2-0=+2$ . This transformation is thus an oxidation.

第三步：计算差值： $N_{ox}$  (产物) -  $N_{ox}$  (反应物)

如果这个差值是正值，那么这个变化就是氧化反应。如果差值是负值，变化就是还原反应。如果差值是零，氧化反应和还原反应都没有发生。对反应方程式 17-1，这个差值是 $+2-0=+2$ 。因此，这个转变是氧化反应。

Although the oxidation-number formalism (形式, 拘泥形式, 形式主义) is very useful, we should not **lose sight of** (不再看见, 忽略, 忘记) the following two general characteristics of organic oxidations and reductions. These two points can enable us to spot (认出, 发现, 找到, 认准) an oxidation or reduction at a glance.

尽管形式氧化数非常有用，我们仍然不应该忽略关于有机氧化反应和还原反应的下面两个总特征。这两点能够让我们一眼（立即）就可以看出一个反应是氧化反应还是还原反应。

1. In most oxidations of organic compounds, either hydrogen in a C-H bond or carbon in a C-C bond is replaced by a more electronegative element, such as halogen or oxygen. The converse is true for reductions.

1. 在有机化合物的大部分氧化反应中，C-H 键中的 H 和 C-C 键中的碳都被

电负性更大的元素所取代，例如卤素或氧。[反过来对还原反应也是如此。](#)

2. The oxidation state of a molecule is determined from the oxidation states of its individual carbon atoms.

2. 一个分子的氧化态由组成它的各个碳原子的氧化态决定。

The oxidation number concept can be simply (简单地，完全，简直，仅仅，只不过，朴素地，只是) related to a definition of oxidation that is often used in inorganic chemistry. According to this definition, oxidation is the loss of electrons and reduction is the gain of electrons. To see how this definition applies to organic compounds, let us consider as an example the oxidation of ethanol to acetic acid: (见书)

氧化数的概念完全与无机化学中经常用的氧化反应的定义相关。按照这个定义，氧化反应是失去电子，而还原反应是得到电子。来看看这个定义在有机化合物中是如何应用的。让我们考虑乙醇氧化变成乙酸的例子。

We can write this oxidation as a balanced half-reaction using H<sub>2</sub>O to balance missing oxygens, protons to balance missing hydrogens, and “dummy (虚拟的，假的，虚构的) electrons” to balance charges. (见书)

我们可以把氧化反应写成一个配平的半反应，用水来平衡失去的氧，用质子来平衡失去的氢，用[虚构](#)的电子来平衡电荷。(课后翻译：我们能利用水平衡失去的氧，用质子平衡失去的氢和用设定的电子平衡电荷，从而把该氧化反应写成一个平衡的半反应。)

According to this half-reaction, four electrons are lost from the ethanol molecule when acetic acid is formed. (Since this is only a half-reaction, a

corresponding number of electrons must be gained by the species that brings about the oxidation.) It can be said that the oxidation of ethanol to acetic acid is a four-electron oxidation. This type of terminology (术语), which is frequently used in biochemistry, comes from the half-reaction formalism.

按照这个半反应，当乙酸形成后，乙醇失去了 4 个电子。（因为这仅仅是一个半反应，对应数目的电子肯定被使这个氧化反应发生的物种得到了。）可以说乙醇氧化成乙酸的反应是 4 电子的氧化反应。这个经常用在生物化学中的术语，来源于形式上的半反应。

If we compute the oxidation numbers of ethanol and acetic acid, we can see that the change in oxidation number for Eq. 17-2 is +4 (verify this statement). This example illustrates the following point: the change in oxidation number is equal to the number of electrons lost. If the change in oxidation number is negative, the reaction is a reduction, and the number corresponds to electrons gained.

如果我们计算乙醇和乙酸的氧化数，我们就可以看出方程式 17-2 的氧化数变化值是+4（证明了这个状况）。这个例子证明了下面的一点。氧化数的变化等于失去的电子数。如果氧化数的变化值是负值，这个反应就是还原反应，氧化数的变化值与得到的电子一致。

Oxidations and reductions, like acid-base reactions, always occur in pairs. Therefore, whenever something is oxidized, something else is reduced. When an organic compound is oxidized, the reagent that brings about the transformation is called an **oxidizing agent** (氧化剂) .

象酸碱反应一样，氧化反应和还原反应总是成对出现的。因此，当某种物质

被氧化时，就有其它物质被还原。当有机化合物被氧化的时候，使转变发生的试剂就叫做氧化剂。

Likewise, when an organic compound is reduced, the reagent that effects the transformation is called a reducing agent. For example, **suppose that** (假如) chromate ion ( $\text{CrO}_4^{2-}$ ) is used to bring about the oxidation of ethanol to acetic acid in Eq. 17-2 in this reaction, chromate ion is reduced to  $\text{Cr}^{3+}$ .

见书。

同样地，当有机化合物被还原时，使这个转变作用实现的试剂（反应物）就叫做还原剂。例如，在方程式 17-2 的反应中，铬酸根离子  $\text{CrO}_4^{2-}$  是用来使乙醇转变为乙酸的反应发生的试剂，铬酸根离子就被还原为  $\text{Cr}^{3+}$ 。

Three electrons are gained in the reduction of chromate to  $\text{Cr}^{3+}$ . Since four electrons are lost in the oxidation (Eq. 17-3), stoichiometry (化学计量(学)) requires that for every three ethanol molecules oxidized to acetic acid (twelve electrons lost), four  $\text{CrO}_4^{2-}$  are reduced (twelve electrons gained).

铬酸根离子在被还原为  $\text{Cr}^{3+}$  的反应中获得了三个电子。因为方程式 17-3 中失去了四个电子，化学计量学要求每三个乙醇分子被氧化为乙酸(失去 12 个电子)，就有四个  $\text{CrO}_4^{2-}$  被还原 (得到 12 个电子)。

By considering the change in oxidation number for a transformation, we can tell whether an oxidizing or reducing agent is required to bring about the reaction. For example, the following transformation is neither an oxidation nor a reduction (verify this statement): 见书 Although one carbon is oxidized, another is, reduced. Even though we might know nothing else about the reaction, it is clear that an oxidizing or

reducing agent alone would not effect this transformation. (In fact, the reaction is the pinacol rearrangement, which is brought about by **mineral acid** (无机酸) .)

通过考虑转变过程中氧化数的变化，我们能够判断出是否需要氧化剂或还原剂来使反应发生。例如下面的转变中，尽管一个碳原子被氧化，而另一个碳原子被还原，它却既不是氧化反应，也不是还原反应。（验证了这种状况。）甚至我们对这个反应一无所知。很明显单独的氧化剂或还原剂都不能使这个转变实现。（实际上，这个反应是无机酸引起的？呐醇的重排反应。）

The oxidation-number concept can be used to organize organic compounds into functional groups with the same oxidation level. [Compounds within a given box](#) are generally interconverted by reagents that are neither oxidizing nor reducing agents. For example, we know that alcohols can be converted into alkyl (烷基) halides with HBr, which is neither an oxidizing nor a reducing agent. On the other hand, conversion of an alcohol into a carboxylic acid involves a change in oxidation level, and indeed this transformation requires an oxidizing agent. There are a greater number of possible oxidation states for carbons with larger numbers of hydrogens. Thus, a tertiary alcohol cannot be oxidized at the  $\alpha$ -carbon (without breaking carbon-carbon bonds) because this carbon **bears** (携带) no hydrogens. Methane, on the other hand, can be oxidized to  $\text{CO}_2$  (Of course, any hydrocarbon can be oxidized to  $\text{CO}_2$  if carbon-carbon bonds are broken.)

氧化数的概念能够用来使有机化合物组成同一氧化级数的功能基团。在同一空间存在的化合物因为既非氧化剂也非还原剂的存在而通常发生互变。例如，我们知道乙醇在 HBr 的存在下能够转化为卤代烷，而 HBr 既不是氧化剂也不是还

原剂。另外一方面，乙醇转化为乙酸的反应涉及到氧化级数的改变，实际上这个反应需要氧化剂。带有大量氢原子的碳存在大量可能的氧化状态。因此，叔醇不能在  $\alpha$ -碳（没有断裂碳-碳键）上被氧化，因为这个碳原子没有相连的氢原子。另外一方面，甲烷能够被氧化成二氧化碳（当然，如果碳-碳键断裂，任何碳氢化合物都可以被氧化成二氧化碳。）

ignore: 忽视 oxidation level n. 氧化水平, 氧化级(数) isopropyl 异丙基  
count 算为 oxidation number 氧化值 formalism 拘泥形式, 形式主义  
spot 找到, 认准 verify 证明 stoichiometry 化学计量学 pinacol 呐醇  
rearrangement 重排 bear 携带 transformation 转化  
-metry(名词词尾), 测定, 度量的方法 stoichiometry, geometry, spectrophotometry  
-ism(名词词尾)表示“特性、状态、主义, 体系”之义。formalism, mechanism,  
alcoholism(酒中毒)

### 短语

assign…to… 把…指认为……	under consideration 所考虑的
neither…nor 既不…又不	at a glance 一看就
either…or… 要么…或者…	relate to… 关联于
oxidation of … to … 氧化为…	be equal to 等于
in pairs 成对地	be converted into… 被转变为…
(be) characteristic of 有…特色的	

## 19. Organometallics-Metal $\pi$ Complexes

Metal  $\pi$  complexes are characterized by (突出的表现为) a type of direct carbon-to-metal bonding that is not a classical ionic,  $\sigma$ , or  $\pi$  bond. Numerous molecules and ions, eg, mono- and di-olefins, polyenes, arenes, cyclopentadienyl (环戊二烯基) ions, tropylium ions, and  $\pi$ -allylic (烯丙基) ions, can form metal  $\pi$  complexes with transition-metal atoms or ions. These are classified as organometallic complexes, because of their direct carbon-metal bond, and as coordination complexes, because the nature and characteristics of the  $\pi$  ligands are similar to those in coordination complexes. In 1827, **Zeise** reported that ethylene reacts with platinum(II) chloride to form a salt  $K(C_2H_4)PtCl_3$  (1), but it was not until after the elucidation (说明, 阐明) of the structure of ferrocene (2) in 1953 that attention was redirected (使改道, 使改变方向; 查问) to Ziese's Salt, which was the first metal  $\pi$  complex. (见书)

### 有机金属的- $\pi$ 配合物

金属 $\pi$ 配合物用一类直接的碳-金属键来表征，这种键不是传统的 $\sigma$ 或 $\pi$ 键。许多分子和离子，例如，单烯烃和二烯烃，多烯烃，芳烃，环戊二烯基离子，草<sup>?</sup>离子，以及 $\pi$ -烯丙基离子，都能够和过度金属原子或离子形成金属 $\pi$ 配合物。因为其中存在直接的碳-金属键，这一类配合物归类为金属有机配合物，同时因为 $\pi$ 配体的性质和特征类似于配合物中的配体，所以又可以归类为配合物。1827年，Zeise 做了乙烯与  $PtCl_2$  反应形成盐  $K(C_2H_4)PtCl_3$  (1)的报导，但是直到 1953 年，二茂铁的结构阐明之后，Ziese's 盐才引起人们的注意，(人们才把注意力转向 Ziese's 盐)，它是第一个金属- $\pi$ 配合物。

Generally, metal  $\pi$  complexes can be classified into three main groups: olefin-, cyclopentadienyl-, and arene-metal  $\pi$  complexes; mixed complexes are categorized (分类) according to structural or chemical analogies (类似物, 相似体) within these groups. Allyl  $\pi$  complexes are designated as (被叫做) olefin  $\pi$  complexes in this review. Study of metal  $\pi$  complexes has contributed to the elucidation of the mechanisms of Ziegler-Natta polymerization, the **oxo reaction** (羰基合成), and catalytic hydrogenation (加氢), and to the development of the Wacker process which is used for the oxidation of olefins.

一般, 金属- $\pi$ 配合物主要分为三大类: 烯烃配合物, 环戊二烯基配合物, 芳烃-金属 $\pi$ 配合物; 混合型配合物可以按照在结构或化学性质方面的相似性在这三类内进行归类。按照这种意见, 烯丙基- $\pi$ 配合物被叫做烯烃- $\pi$ 配合物。金属 $\pi$ 配合物的研究对阐明 Ziegler-Natta 聚合反应机理, 羰基合成, 催化加氢, 以及用于烯烃氧化的 Wacker 反应的发展做出了贡献。

The following nomenclature (命名法) for metal  $\pi$  complexes is used: (1) organic  $\pi$  ligands precede (领先于..., 在...之前) the metal atom. (2) Organic  $\pi$  ligands precede inorganic  $\pi$  ligands. (3) Inorganic  $\pi$  ligands, eg, carbonyl or nitrosyls, generally follow the metal atom; halides also follow the metal but precede carbonyls or nitrosyls. (4) A prefix, eg, di, is preferred rather than bis in describing sandwich-type  $\pi$  complexes, eg, dibenzenechromium. (5) The symbol  $\pi$  can be used preceding a ligand in order to distinguish  $\pi$ -complex bonding from  $\sigma$ , ionic, or other bonding. The symbol  $\eta$  (eta (希腊语字母的第七字) or haptic (络合点)) precedes a ligand and indicates the number of C-M bonds in the ligand.

金属 $\pi$ 配合物使用了下列命名方法：(1) 先命名有机 $\pi$ 配体，后命名金属原子。(2) 先命名有机 $\pi$ 配体，后命名无机 $\pi$ 配体。(3) 无机 $\pi$ 配体，例如，羰基或亚硝酰基一般放在金属原子后，卤素离子也放在金属后，但是放在羰基或亚硝酰基之前。(4) 在描述三明治型 $\pi$ 配合物时，首选的前缀是 di，而不是 bis，例如二苯铬。(5) 符号 $\pi$ 放在配体之前，目的是区分 $\pi$ 配合物和 $\sigma$ 配合物，离子型化合物以及其它键合类型的化合物。符号 $\eta$ (eta or haptic)放在配体之前，用来指出配体中 C-M 键的数目。

Monoolefins, dienes, polyolefins, and acetylenes serve as ligands to transition metals and form olefin  $\pi$  complexes. Typical examples of olefin  $\pi$  complexes are monoolefin ligands, eg, potassium  $\eta^2$ -ethyleneplatinum trichloride (1); and cyclopentadienylum.  $\eta^3$ -cycloheptatrienylum (环庚三烯基) molybdenum dicarbonyl (3); diene ligands, eg,  $\eta^4$ -butadieneiron tricarbonyl (4).

单烯烃、二烯烃、多烯烃以及乙炔都可以作为配体与过度金属配位，形成烯烃 $\pi$ 配合物。烯烃 $\pi$ 配合物的典型例子是单烯烃配体化合物，例如三氯 $\eta^2$ -乙烯合铂(II)酸钾(1)；以及环戊二烯基配体化合物，环戊二烯基合一 $\eta^3$ -环庚三烯基合二羰基合钼(3)；二烯烃配合物，例如 $\eta^4$ -丁二烯合三羰基合铁。

Certain of the delocalized,  $\pi$ -electron ring systems of aromatic molecules overlap with  $d_{xy}$  and  $d_{yz}$  metal orbitals as the  $\pi$  electrons do of alkenes with metal d orbitals. The following aromatic rings can form  $\pi$  complexes.

某些芳香分子的离域的， $\pi$ 电子环状系统与金属的  $d_{xy}$  和  $d_{yz}$  轨道的重叠和烯烃的 $\pi$ 电子与金属的 d 轨道重叠一样（类似）。下面的芳香环可以形成 $\pi$ 配合物。（芳香性（环）： $\pi$ 电子数符合  $4n + 2$  规则 ( $n=0, 1, 2\dots$ )）

The  $C_5H_5^-$ ,  $C_6H_6$ , and  $C_8H_8$  (环辛四烯) arenes are the most common in arene  $\pi$  complexes that are characterized by  $\pi$ -bonded rings alone or  $\pi$ -bonded rings that are associated with one ring and other ligands, eg, halogens, CO, RNC, and  $R_3P$ . Typical examples are the di- $\eta^5$ -cyclopentadienyl complexes, i.e. (也就是), metallocenes, eg, di- $\eta^5$ -cyclopentadienyliron (2). In di- $\eta^5$ -cyclopentadienyliron, i.e. (也就是), ferrocene, the 6- $\pi$ -electron system of the  $C_5H_5^-$  ion is bonded to the metal. Other aromatic ring systems are mono- $\eta^5$ -cyclopentadienylmetal nitrosyl and carbonyl complexes.

芳烃  $C_5H_5^-$ 、 $C_6H_6$  和  $C_8H_8$  (环辛四烯) 在单独的  $\pi$ -键合的环状或与一个环和其它配体如卤素, CO, RNC, a 和  $R_3P$  相连的  $\pi$ -键合的环状芳烃- $\pi$ 配合物中最常见。典型的例子是二- $\eta^5$ -环戊二烯基配合物, 也就是, 二茂金属化合物, 例如: 二茂铁 (2)。在二茂铁中,  $C_5H_5^-$  离子的六  $\pi$  电子系统与金属键合。其它的芳环系统是单- $\eta^5$ -环戊二烯基金属的羰基或亚硝酰基配合物。

## Properties

The  $\pi$ -complex bond. Metal  $\pi$  complexes are among those that are least satisfactorily (满意地) described by crystal-field theory (CFT) or valence-bond theory (VBT). The nature of the bonding can be treated more completely and quantitatively by molecular-orbital theory (MOT) or ligand-field theory (LFT). The ligand-field theory originally (最初, 原先) was advanced (发展) as a corrected (修正的) CFT. The LFT relies on the use of molecular orbitals and often is used interchangeably (可交地, 可替交地) with the MOT. The usual approach is to use the linear combination of atomic orbitals (LCAO 原子轨道的线性组合) method. It is

assumed that when an electron in a molecule is near a **particular** (个别的) nucleus, the molecular wave function (函数) is approximately an atomic orbital that is centered at the nucleus. The molecular orbitals are formed by adding or subtracting the appropriate atomic orbitals. For transition metals, the 3d, 4s, and 4p orbitals are the atomic orbitals of interest. The ligands may have  $\sigma$ - and  $\pi$ -valence orbitals. Once the appropriate atomic orbitals have been selected for the metal and ligands, the proper linear combination of valence atomic orbitals is determined for the molecular orbitals. The determination of orbital overlaps that are possible, i.e. (也就是), meet inherent (固有的, 内在的) symmetry requirements, is done by application of the principles of **group theory** (群论). At this point, the procedure becomes arbitrary in that approximate wave functions must be selected for use in the calculations of the **overlap integrals** (重叠积分) and **coulomb integrals** (库仑积分). Finally, an arbitrary charge distribution is chosen and the orbital energies and interaction energies are calculated, and a solution (解答, 解决方法, 解决方案) of the **secular** (长期的) **equation** (久期方程) for the energies and coefficients (系数) of the atomic wave functions can be determined. A new initial (最初的, 初始的) charge distribution is repeated until consistent values are obtained.

**π配位键:** 金属 $\pi$ 配合物是一类很难用晶体场理论 (CFT) 或价键理论 (VBT) 进行满意地描述的配合物之一。成键的性质可以用分子轨道理论 (MOT) 或配体场理论 (LFT) 进行更彻底地、定量地处理。配体场理论最初是在改进 CFT (晶体场理论) 的基础上发展起来的。配体场理论建立在分子轨道的基础之上, 经常与 MOT 交替使用。配体场理论通常的途径是利用原子轨道的线性组合法。假设当分子中的一个电子靠近某个原子核时, 分子的波

函数近似为中心在原子核的原子轨道。分子轨道是通过适当的原子轨道相加或相减得到的。对过度金属来说，3d、4s 和 4p 轨道是我们感兴趣的原子轨道。配体可能具有 $\sigma$ - 和  $\pi$ -价轨道。一旦选择了金属和配体的合适的轨道后，形成分子轨道的适当的原子价轨道的线性组合就确定了。原子轨道可能的组合，也就是符合内在的对称需要（要求）的组合，是应用群论的基本原理确定的。（课后翻译）在（使用群论）这一点上，使用近似波函数来计算重叠积分和库仑积分的方法便成为专用的方法。最后，选择一个专有的电荷分布，计算轨道能量和（轨道间）相互作用能量，关于能量的久期方程和原子波函数的系数就确定了。重新选择初始的电荷分布，进行反复计算，直到得到一致的数值。（反复修正）（类似回归计算）

## Reactions

Metal  $\pi$  complexes react with a wide range of chemical reagents. However, the reactions of the  $\pi$ -olefin-,  $\pi$ -cyclopentadienyl-, and  $\pi$ -arene-metal complexes are distinctly characteristic of each group.  $\pi$  Cyclopentadienyl complexes, i.e., metallocenes, exhibit a high degree of aromaticity（芳香性，芳香族化合物的结构特性） and undergo many typical aromatic substitution reactions. However, the  $\pi$  arene complexes do not exhibit a discernible（可辨别的） degree of aromaticity.

金属 $\pi$ 配合物与很多化学试剂反应。但是， $\pi$ -烯烃-， $\pi$ -环戊二烯基和 $\pi$ 芳烃-金属配合物各有自己明显的特征。例如， $\pi$ -环戊二烯基配合物，即二茂金属化合物，表现出高度的芳香性，可以进行许多典型的芳环取代反应。但是，芳烃 $\pi$ 配合物并不表现出能够辨别出的芳香性（很难看出芳香性）。

Although most physical properties, particularly the structure of metal  $\pi$  complexes, are interpreted by use of the basic principles of coordination chemistry, these established principles do not explain suitably some reaction anomalies（不规则，异

常的人或物) of the different groups of metal  $\pi$  complexes.

尽管大部分物理性质，尤其是金属 $\pi$ 配合物的结构，能够利用配位化学的基本原理来解释，但是，这些已经建立的原则却不能恰当地解释金属 $\pi$ 配合物上的不同基团在反应上表现出的一些反常性。

Olefin  $\pi$  Complexes. Reactions involving olefin  $\pi$  complexes similarly are characteristic of uncomplexed and complexed olefin functions. Generally, reactions involving the former are not very different from those observed for free olefins. However, reactions of the latter are altered significantly by  $\pi$ -complex formation. Among the reactions of interest are addition, elimination, and substitution.

注：be characteristic of... 所独有的特征，有...的特色

烯烃 $\pi$ 配合物：未配位的和配位的烯烃的功能类似，涉及烯烃 $\pi$ 配合物的反应是它们所独有的特征。一般，涉及前者的反应与在游离烯烃中的反应并没有多少区别。但是，后者的反应却因 $\pi$ 配合物的形成而改变很大。人们最感兴趣的反应是加成、消去、和取代反应。

Cyclopentadienyl  $\pi$  Complexes. The most significant feature of the reactions of  $\pi$ -cyclopentadienyl complexes in general and ferrocene in particular involves their aromatic nature. The resonance (共振) stabilization energy for ferrocene is 210 kJ/mol (50 kcal/mol). Ferrocene undergoes a large number of typical ionic aromatic substitution reactions, eg, Fiedel-Crafts acylation (酰基化作用), alkylation (烷基化作用), metalation (金属化作用), sulfonation (磺化作用), and aminomethylation (氨基甲基化作用).

环戊二烯基 $\pi$ 配合物：一般，环戊二烯基 $\pi$ 配合物尤其是二茂铁最明显的反应特征是它们的芳香性质。二茂铁的共振稳定化能是 210 kJ/mol(50 kcal/mol)。二

茂铁可以进行大量的典型的离子性的芳环取代反应。例如，Fiedel-Crafts 酰基化作用，烷基化作用，金属化作用，磺化作用以及氨基甲基化作用。

Fiedel-Crafts Acylation. (傅-克酰基化作用) The acylation of metallocenes proceeds easily. The equimolar (等摩尔的) reaction of ferrocene and acetyl chloride (乙酰氯) in the presence of aluminum chloride yields monoacetylferrocene almost exclusively. When an excess of acetyl chloride and aluminum chloride is used, a mixture of two isomeric diacetylferrocenes is produced. The heteroannular (杂环的) disubstituted derivative 1, 1'-diacetylferrocene and the homoannular (均环的) isomer 1, 2-diacetylferrocene are obtained in a ratio of 60:1. The first acetyl group deactivates (使失活) the  $\pi$ -cyclopentadienyl ligand toward further **electrophilic substitution** (亲电子取代作用). Thus, the second acetyl group enters the other ring.

Fiedel-Crafts 酰基化作用：金属茂合物的酰基化作用很容易进行。二茂铁和乙酰氯在氯化铝的存在下进行等摩尔反应，几乎是爆炸性地产生单乙酰基二茂铁。当乙酰氯和氯化铝过量时，就得到了二乙酰基二茂铁的两种同分异构体的混合物。所得到的杂环二取代衍生物 1, 1'-二乙酰基二茂铁和均环异构体 1, 2-二乙酰基二茂铁的比例是 60:1。第一个乙酰基基团使 $\pi$ -环戊二烯基配体在亲电子取代作用方面失去活性（不能进一步进行亲电子取代作用）。因此，第二个乙酰基基团结合到了另外一个环。

Sulfonation. Ferrocene can be sulfonated readily by sulfuric acid or chlorosulfonic (氯磺酸的) acid in **acetic anhydride** (乙酸酐) to form ferrocenesulfonic (二茂铁磺酸) acid and heteroannular (杂环的) disulfonic acid,  $\pi$ -cyclopentadienylrhenium tricarbonyl (环戊二烯基合三羰基合铑) can be

sulfonated with concentrated sulfuric acid in acetic anhydride; the product is isolated as the p-toluidine (对甲苯胺) salt.

碘化作用：在乙酸酐中存在硫酸或氯碘酸的情况下，二茂铁很轻易碘化而形成二茂铁碘酸和杂环的二碘酸，在乙酸酐中浓硫酸很轻易使环戊二烯基合铑碘化，分离出的产物是对甲苯胺盐。

Formylation (甲酰化). Ferrocene is formylated (甲酰化) with N-methylformanilide (N-甲基甲酰苯胺) in the presence of **phosphorus oxychloride** (三氯氧化磷). This reaction also is characteristic of highly reactive aromatic rings.

在三氯氧化磷的存在下，二茂铁可以用 N-甲基甲酰苯胺来实现甲酰化。这个反应也是高度活泼的芳环的特征。

Arylation (芳基化作用). The most significant radical substitution reaction of ferrocene is its reaction with aryl (芳基的) diazonium (重氮盐) salts giving an arylation product.

二茂铁最显著的基团取代反应是和芳基重氮盐作用，产生芳基化产物。

Arene-Metal  $\pi$  Complexes. Generally, arene  $\pi$  complexes do not undergo the reactions that are characteristic of benzene and its derivatives. However, arene  $\pi$  complexes do undergo a limited number of substitution, addition, **expansion** (扩展, 膨胀), and condensation (缩合) reactions.

芳烃-金属 $\pi$ 配合物：一般，芳烃 $\pi$ 配合物并不发生苯以及其衍生物的特征反应。但是，芳烃 $\pi$ 配合物确实能够进行一定数目的取代、加成、扩展、缩合反应。

### Catalysis Involving Metal $\pi$ -Complex Intermediates

Many metal-catalyzed reactions proceed by way of (经由, 为了, 作为) a substrate (酶作用物) metal  $\pi$ -complex intermediate. Commercially, the most significant of these include the polymerization of ethylene, the hydroformylation (加氢甲酰基化作用) of olefins yielding aldehydes(醛, 乙醛), i.e., the oxo process(qv), and the air oxidation of ethylene-producing acetaldehyde(qv), ie, the Wacker process.

### 涉及金属 $\pi$ 配合物中间体的催化作用

许多金属催化反应是通过酶作用物的金属 $\pi$ 配合物中间体进行的。在商业上, 最重要的反应包括乙烯的聚合反应, 烯烃加氢甲酰基化作用生成醛的反应, 即氧化 (羰基化) 反应; 和乙烯的空气氧化产生乙醛的 Wacker 反应。

#### Polymerization of Olefins. Ziegler-Natta Process.

During the 1950s, ethylene was polymerized using a Ziegler-Natta catalyst, i.e. (也就是), a mixture of transition metal halides, eg, titanium halides, and trialkylaluminum (三烷基铝) (triethylaluminum commonly is used). The use of triethylaluminum stimulated research into the use of organometallic compounds in general. It has been determined that the Ziegler-Natta process involves a metal  $\pi$ -complex intermediate. A plausible (似是而非的; 似乎合理的, 似乎可能的) mechanism for the polymerization can be formulated (明确地表达, 做简洁陈述) by applying typical organometallic and coordination reactions.

#### 烯烃的聚合作用: Ziegler-Natta 反应

在二十世纪五十年代, 乙烯聚合使用的是 Ziegler-Natta 催化剂, 即过度金属卤化物的混合物, 例如: 卤化钛, 三烷基铝 (通常使用的是三乙基铝)。三乙基铝的使用促进了人们在有机金属化合物应用方面的总体研究。已经确定,

Ziegler-Natta 反应涉及到金属 $\pi$ -配合物中间体。聚合反应的一个似乎可能的机理是可以通过应用典型的有机金属和配位反应来简单地说明。

#### Oxidation of Olefins. Wacker Process.

The oxidation of ethylene exclusively to acetaldehyde (乙醛) and of other straight-chain olefins to ketones is achieved by the catalytic reaction of ethylene in an aqueous solution by palladium(II) or by oxygen in the presence of palladium(II) chloride, copper(II) chloride, or iron(III) chloride. Generally, the oxidation of olefins by other metal ions, eg, Hg(II), Th(III), and Pb(IV), yields glycol (乙二醇) derivatives as well as carbonyl products. The mechanism for the oxidation is postulated (假定, 假设) to include  $\pi$ - $\sigma$  rearrangements. (为什么会有乙二醇衍生物? )

#### 烯烃的氧化: Wacker 反应

乙烯的快速氧化为乙醛以及其它直链烯烃氧化为酮可以通过在水溶液中用 Pd(II)催化或在  $PdCl_2$ 、 $CuCl_2$  或  $FeCl_3$  的存在下用氧氧化来实现。一般, 烯烃可以用其它金属离子, 如 Hg(II)、Th(III) 和 Pb(IV) 氧化产生乙二醇衍生物和羰基产物。假定氧化反应机理包括 $\pi$ - $\sigma$ 重排反应。

Addition of Carbon Monoxide. Oxo Reaction. The **oxo process** has been developed extensively (广阔地, 广泛地) to produce primary alcohols by the reduction of the aldehydes (醛, 乙醛) which are formed in the process.

#### 一氧化碳的加成反应: 羰基化反应

羰基合成反应已经通过在此过程中醛的还原反应而广泛地用来生产伯醇。

#### Health and Safety Factors (健康和安全因素)

Some metal  $\pi$  complexes are air-sensitive and, therefore, their preparation

requires an air-free reaction system. Their toxicity (毒性) usually is based on the metal; however, organometallic compounds generally exhibit greater toxicities than their corresponding inorganic salts. The alkyl derivatives tend to be more toxic than the aryl (芳基) complexes, which exhibit toxicities similar to those of the corresponding inorganic compounds.

有些金属 $\pi$ -配合物对空气敏感，因此，它们的制备需要隔绝空气的反应系统。毒性的产生通常是因为金属的存在，但是，一般，有机金属化合物比对应的无机盐表现出更大的毒性。烷基衍生物通常表现出比芳基配合物更大的毒性，而芳基配合物表现出的毒性与对应的无机化合物相似。

## 20. The Role of Protective Groups in Organic Synthesis

### 有机合成中保护基的作用

#### Properties Of a Protective Group (保护基的性质)

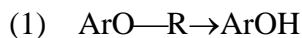
When a chemical reaction is to be carried out selectively at one **reactive site** (反应活性部位) in a multifunctional (多功能的) compound, other reactive sites must be temporarily (临时地) blocked (防碍, 阻塞, 阻止). Many protective groups have been, and are being, developed for this purpose. A protective group must fulfill (履行、实现、完成、达到...目的) a number of requirements. It must react selectively in good yield to give a protected substrate (底物, 基质) that is stable to the projected (计划, 设计, 突出, 使突出) reactions. The protective group must be selectively moved in good yield by readily available, preferably (更适宜) nontoxic (无毒的) reagents that do not attack the regenerated functional group. The protective group should form a crystalline derivative (without the generation of new chiral centers) that can be easily separated from side products associated with its formation or cleavage (分解、裂解). The protective group should have a minimum of additional functionality to avoid further (更多的) sites of reaction.

当一个化学反应将要在多功能化合物中的一个反应活性部位有选择的进行时, 其它的活性部位必须是暂时地受阻 (不反应)。许多活性基团已经以及正在因此而发展起来。一个保护性基团必须能够实现大量的需要。它必须能够以较高的产率进行选择性反应而给出一个被保护的底物, 这个底物对于所计划的反应表现稳定。保护性基团必须能够以较高的产率通过有效的, 更适宜的、无毒的、不进攻重新产生的功能基团的试剂而进行选择性转移 (能上能下)。保护性基团应该能够结晶 (没有产生新的手性中心), 以便于

与与其形成或分解相关的副产物分离。保护性基团应该具有最低的附加功能以避免更多的部位（结合点）反应。

### Historical Development (发展历史)

Since a few protective groups cannot satisfy all these criteria (标准) for elaborate (精心制作的, 详细阐述的; 精致的, 精巧的) substrates, a large number of mutually (互相地, 互助) complementary (补充的, 补足的) protective groups are needed and, indeed, are becoming available. In early syntheses the chemist chose a standard derivative known to be stable to the subsequent reactions. Other classical methods of cleavage include acidic hydrolysis (eq. 1), reduction (eq. 2), and oxidation (eq. 3):



Some of the original work in the carbohydrate (碳水化合物, 糖类) area **in particular** (特别地) reveals extensive protection of carbonyl and hydroxyl groups. For example, a cyclic (环的, 环状的) diacetonide (二丙酮化物) of glucose (葡萄糖) was selectively cleaved to the monoacetonide (单丙酮化物). A more recent summary describes the selective protection of primary and secondary hydroxyl groups in a synthesis of gentiobiose (龙胆二糖), carried out in the 1870s, **as triphenylmethyl (三苯甲基) ethers.**

因为一些保护性基团不能满足所有精致的底物的标准, 因此需要大量互相补充的保护性基团, 实际上, 这些保护性基团是有效的。在早期的合成中, 化学家

选择一个已知的对随后的反应稳定的标准衍生物。其它的传统分解方法包括酸解（方程式 1），还原反应（方程式 2），和氧化反应（方程式 3）。特别是碳水化合物方面的一些原始性（独创性）工作展现了对羰基和羟基基团的广泛保护作用。例如，葡萄糖的一种环状二丙酮化物可以选择性裂解成单丙酮化物。最近的一篇文章概括地描述了在 19 世纪七十年代进行的合成长胆二糖过程中以及在合成三苯甲基醚过程中，对伯羟基和仲羟基基团的选择性保护作用。

### Development of New Protective Groups

As chemists proceeded to synthesize more complicated structures, they developed more satisfactory protective groups and more effective methods for the formation and cleavage of protected compounds. At first a tetrahydropyranyl (四氢吡喃基) acetal (乙缩醛，乙醛缩二乙醇) was prepared, by an acid-catalyzed reaction with dihydropyran, to protect a hydroxyl group. The acetal is readily cleaved by mild acid hydrolysis, but formation of this acetal introduces a new chiral center. Formation of the 4-methoxytetrahydropyranyl acetal eliminates this problem.

### 新保护基的发展

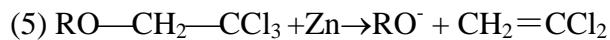
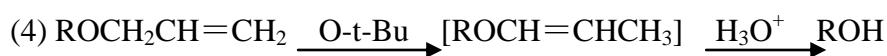
在进行合成更复杂结构的同时，化学家发展了更令人满意的保护基和更有效的形成和分解被保护化合物的方法。首先，通过二氢吡喃的酸催化反应制备了四氢吡喃基乙缩醛来保护羟基。乙缩醛很容易被中等强度的酸水解，但是乙缩醛的形成引进了一个新的手性中心。4-甲氧基四氢吡喃基乙缩醛的形成消除了这个问题。

Catalytic hydrogenolysis (氢解作用，破坏加氢作用) of an *O*-benzyl (邻苯甲基) protective group is a mild, selective method introduced by Bergmann and Zervas to cleave a benzyl carbamate (氨基甲酸盐) ( $>\text{NCO}-\text{OCH}_2\text{C}_6\text{H}_5 \rightarrow >\text{NH}$ ) prepared to protect an amino group during peptide syntheses. The method also has

been used to cleave alkyl benzyl ethers, stable compounds prepared to protect alkyl alcohols; benzyl esters are cleaved by catalytic hydrogenolysis under neutral conditions.

邻苯甲基保护基的催化氢解作用是 Bergmann 和 Zervas 引入的一种在制备肽的过程中, 分解所制备的苯甲基氨基甲酸盐来保护氨基基团的温和的和选择性的方法。这种方法也已经用来分解所制备的稳定的化合物烷基苯甲基醚来保护烷基醇。苯甲基醚在中性条件下被催化氢解作用所分解。

Three selective methods to remove protective groups are receiving much attention: “assisted,” electrolytic, and photolytic removal. Four examples illustrate “**assisted removal**” of a protective group. A stable allyl (烯丙基) group can be converted to a labile (不安定的, 易发生变化的) vinyl (乙烯基) ether group (eq. 4);  $\alpha\beta$ -haloethoxy (卤代乙氧基) (eq. 5) or  $\beta$ -silylethoxy (甲硅烷基乙氧基) (eq. 6) derivative is cleaved by attack at the  $\beta$ -substituent; and a stable *o*-nitrophenyl (硝基苯基) derivative can be reduced to the *o*-amino compound, which undergoes cleavage by nucleophilic (亲核的, 亲质子的) displacement:



R=alkyl, aryl, R'CO—, or R'NHCO—

The design of new protective groups that are cleaved by “**assisted removal**” is a challenging and rewarding (报答的, 有益的, 值得的) undertaking (事业, 工作).

有三种除去保护基的选择性方法引起了关注: “**assisted,**” 电解消除法, 光解

消除法。有四个例子证明了保护基的辅助性消除。一个稳定的烯丙基可以转变成不稳定的乙烯基醚（方程式 4）。 $\alpha$ -卤代乙氧基（方程式 5）或  $\beta$ -甲硅烷基乙氧基（方程式 6）的衍生物因为  $\beta$  取代基被进攻而分解。一个稳定的邻硝基苯基衍生物可以被还原成在亲核取代反应的作用下而分解的邻氨基化合物。因“assisted removal”而分解的新的保护基的设计是一项挑战性和值得一做的事业（充满了挑战和机遇的工作）。

Removal of a protective group by electrolytic oxidation or reduction can be very satisfactory. The equipment required ranges from a minimum of two electrodes, a potentiostat (恒电势器, 稳压器), and a source of DC current to quite sophisticated (高度发展的, 精密复杂的) systems. A suitable electrolyte (电解、电解液)/solvent (溶剂) system is needed, and the deprotected product must not undergo further electrochemistry under the experimental conditions. The use and subsequent removal of chemical oxidants or reductants (e.g., Cr or Pb salts; Pt-C or Pd-C) are eliminated. Reductive cleavages have been carried out in high yield at -1 to -3 V (vs. SCE) depending on the group; Oxidative cleavages in good yield have been realized at 1.5-2 V (vs. SCE). For systems possessing two or more electrochemically labile protective groups, selective cleavage is possible when the half wave potentials,  $E_{1/2}$ , are sufficiently different; excellent selectivity can be obtained with potential differences on the order of (属于...一类的, 与...相似的) 0.25 V. Protective groups that have been removed by electrolytic oxidation or reduction are described at the appropriate places in this book; a review article by Mairanovsky discusses electrochemical removal of protective groups.

用电解氧化或还原除去保护基是非常令人满意的。所需要的设备从最低限度的两个电极，稳压器和直流电源到非常精密复杂的系统。同时需要合适的电解液/溶剂系统，而且去质子化的产物在实验条件下必须不能发生进一步的电化学反应。化学氧化剂或还原剂(例如 Cr 或 Pb salts; Pt-C 或 Pd-C)的使用和随后的去除被消除。还原分解已经在-1 到 -3 V 范围内依赖于基团以高产率进行。在 1.5-2 V 的氧化分解也已经以高产率实现。对于拥有两个或更多电化学上不稳定的保护基来说，当半波电位  $E_{1/2}$  差异较大时，可能发生选择性分解。在电势差接近 0.25V 时，可以得到良好的选择性分解。这本书在合适（一定）的位置对用电解氧化或电解还原可以去除的保护基进行了介绍。Mairanovsky 所写的一篇综述性文章保护基的电化学去除方法。

Photolytic cleavage reactions (e.g., of *o*-nitrobenzyl, phenacyl, and nitrophenyl-sulfonyl derivatives) take place in high yield on irradiation of the protected compound for a few hours at 254-350 nm. For example, the *o*-nitrobenzyl group, used to protect alcohols, amines, and carboxylic acids, has been removed by irradiation. Protective groups that have been removed by photolysis are described at the appropriate places in this book; in addition, [the reader may wish to consult three review articles.](#)

在 254-350 nm 范围对所保护的化合物进行辐射，光分解作用（例如：邻硝基苯甲基、苯甲酰甲基、硝基苯基亚磺酰基的衍生物的光解作用）可以以高产率发生。例如，用来保护醇、胺和羧酸的邻硝基苯甲基可以利用辐射去除。已经用光解作用去除的保护基将在这本书的适当的地方进行介绍。另外，读者可能希望参考三篇综述。

## Selection of a Protective Group from This Book

To select a specific protective group, the chemist must consider in detail all the reactants, reaction conditions, and functionalities involved in the proposed synthetic scheme. First he or she must evaluate all functional groups in the reactant to determine those that will be unstable to the desired reaction conditions and require protection. The chemist should then examine reactivities of possible protective groups, listed in the Reactivity Charts (图没, 表), to determine compatibility (兼容性) of protective group and reaction conditions. The protective groups listed in the Reactivity Charts have been used most widely; **consequently**, considerable experimental information is available for them. He or she should consult the complete list of protective groups in the relevant chapter and consider their properties. It will frequently(往往) be advisable to examine the use of one protective group for several functional groups (i.e., a 2, 2, 2-trichloroethyl group to protect a hydroxyl group as an ether, a carboxylic acid as an ester, and an amino group as a carbamate). When several protective groups are to be removed simultaneously (同时地), it may be advantageous to use the same protective group to protect different functional groups (e.g., benzyl group, removed by hydrogenolysis, to protect an alcohol and a carboxylic acid). When selective removal is required, different classes of protection must be used (e.g., a benzyl ether, cleaved by hydrogenolysis but stable to **basic hydrolysis**, to protect an alcohol, and an alkyl ester, cleaved by basic hydrolysis but stable to hydrogenolysis, to protect a carboxylic acid).

从这本书中选择保护基

为了选择特效的保护基，化学家必须对所提出的合成系统中涉及到的所有反应物，反应条件以及功能进行详细的考虑。首先，他或她必须对反应物的所有功能基团进行评价，来决定哪些基团对于所期望的反应条件不稳定和需要保护。然后，化学家应该对列在反应图中的可能的保护基进行检测来确定保护基和反应条件的兼容性。列在反应图中的保护基已经得到了最广泛的使用，因此化学家就可以获得大量的实验信息。他或她必须对在相关章节中列出保护基的整个表格进行考虑，考虑它们的性质。检测具有几种功能的一个保护基的用途往往是明智的。（也就是 2, 2, 2-三氯乙基可以作为醚来保护羟基，作为酯来保护羧基，作为氨基甲酸盐来保护氨基）。当几个保护基要同时去除时，用同一个保护基来保护不同的基团是有利的（方便的）。（例如，用可以由氢解作用去除的苯甲基来保护醇和羧酸）。当需要选择性去除时，必须使用不同种类的保护（例如，可以被氢解作用分解而对碱性水解稳定的苯甲基醚可以用来保护醇，而可以被碱性水解分解却对氢解稳定的烷基醚可以用来保护羧酸。）

If a satisfactory protective group has not been located, the chemist has a number of alternatives: rearrange the order of some of the steps in the synthetic scheme so that a functional group no longer requires protection or a protective group that was reactive in the original scheme is now stable; redesign the synthesis, possibly (可能地，或者) making use of latent (潜在的，潜伏的) functionality (i. e., a functional group in a precursor form; e.g., anisole (茴香醚，苯甲醚) as a precursor of cyclohexanone (环己酮)). Or, it may be necessary to include the synthesis of a new protective group in the overall plan.

如果找不到符合要求的保护基，化学家仍然具有大量可供选择的方法：重新

安排合成系统中一些步骤的顺序，保证官能团不再需要保护或者在原来的系统中的活性保护基现在变得稳定；可能利用潜在的功能重新设计合成（也就是功能性基团以前驱体形式出现；例如：茴香醚作为环己酮的前驱体）。或者，有必要在总体计划中包括新保护基的合成。

A number of standard synthetic reference books are available. A review article by Kosssell and Seliger discusses protective groups used in oligonucleotide (低聚核苷酸) syntheses, including protection for the phosphate group, which is not included in this book; and a series of articles describe various aspects of protective group chemistry.

目前存在大量的标准合成文献书。Kosssell 和 Seliger 写的一篇综述性文章对在低聚核苷酸合成中所用的保护基进行了讨论，包括这本书中没有的磷酸根的保护作用，还有一系列文章对保护基化学的各方面进行了介绍。

## 20. The Role of Protective Groups in Organic Synthesis

### 有机合成中保护基的作用

#### Properties Of a Protective Group (保护基的性质)

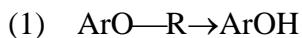
When a chemical reaction is to be carried out selectively at one **reactive site** (反应活性部位) in a multifunctional (多功能的) compound, other reactive sites must be temporarily (临时地) blocked (防碍, 阻塞, 阻止). Many protective groups have been, and are being, developed for this purpose. A protective group must fulfill (履行、实现、完成、达到...目的) a number of requirements. It must react selectively in good yield to give a protected substrate (底物, 基质) that is stable to the projected (计划, 设计, 突出, 使突出) reactions. The protective group must be selectively moved in good yield by readily available, preferably (更适宜) nontoxic (无毒的) reagents that do not attack the regenerated functional group. The protective group should form a crystalline derivative (without the generation of new chiral centers) that can be easily separated from side products associated with its formation or cleavage (分解、裂解). The protective group should have a minimum of additional functionality to avoid further (更多的) sites of reaction.

当一个化学反应将要在多功能化合物中的一个反应活性部位有选择的进行时, 其它的活性部位必须是暂时地受阻 (不反应)。许多活性基团已经以及正在因此而发展起来。一个保护性基团必须能够实现大量的需要。它必须能够以较高的产率进行选择性反应而给出一个被保护的底物, 这个底物对于所计划的反应表现稳定。保护性基团必须能够以较高的产率通过有效的, 更适宜的、无毒的、不进攻重新产生的功能基团的试剂而进行选择性转移 (能上能下)。保护性基团应该能够结晶 (没有产生新的手性中心), 以便于

与与其形成或分解相关的副产物分离。保护性基团应该具有最低的附加功能以避免更多的部位（结合点）反应。

### Historical Development (发展历史)

Since a few protective groups cannot satisfy all these criteria (标准) for elaborate (精心制作的, 详细阐述的; 精致的, 精巧的) substrates, a large number of mutually (互相地, 互助) complementary (补充的, 补足的) protective groups are needed and, indeed, are becoming available. In early syntheses the chemist chose a standard derivative known to be stable to the subsequent reactions. Other classical methods of cleavage include acidic hydrolysis (eq. 1), reduction (eq. 2), and oxidation (eq. 3):



Some of the original work in the carbohydrate (碳水化合物, 糖类) area **in particular** (特别地) reveals extensive protection of carbonyl and hydroxyl groups. For example, a cyclic (环的, 环状的) diacetonide (二丙酮化物) of glucose (葡萄糖) was selectively cleaved to the monoacetonide (单丙酮化物). A more recent summary describes the selective protection of primary and secondary hydroxyl groups in a synthesis of gentiobiose (龙胆二糖), carried out in the 1870s, **as triphenylmethyl (三苯甲基) ethers.**

因为一些保护性基团不能满足所有精致的底物的标准, 因此需要大量互相补充的保护性基团, 实际上, 这些保护性基团是有效的。在早期的合成中, 化学家

选择一个已知的对随后的反应稳定的标准衍生物。其它的传统分解方法包括酸解（方程式 1），还原反应（方程式 2），和氧化反应（方程式 3）。特别是碳水化合物方面的一些原始性（独创性）工作展现了对羰基和羟基基团的广泛保护作用。例如，葡萄糖的一种环状二丙酮化物可以选择性裂解成单丙酮化物。最近的一篇文章概括地描述了在 19 世纪七十年代进行的合成长胆二糖过程中以及在合成三苯甲基醚过程中，对伯羟基和仲羟基基团的选择性保护作用。

### Development of New Protective Groups

As chemists proceeded to synthesize more complicated structures, they developed more satisfactory protective groups and more effective methods for the formation and cleavage of protected compounds. At first a tetrahydropyranyl (四氢吡喃基) acetal (乙缩醛，乙醛缩二乙醇) was prepared, by an acid-catalyzed reaction with dihydropyran, to protect a hydroxyl group. The acetal is readily cleaved by mild acid hydrolysis, but formation of this acetal introduces a new chiral center. Formation of the 4-methoxytetrahydropyranyl acetal eliminates this problem.

### 新保护基的发展

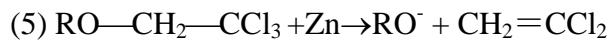
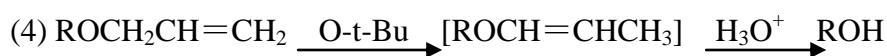
在进行合成更复杂结构的同时，化学家发展了更令人满意的保护基和更有效的形成和分解被保护化合物的方法。首先，通过二氢吡喃的酸催化反应制备了四氢吡喃基乙缩醛来保护羟基。乙缩醛很容易被中等强度的酸水解，但是乙缩醛的形成引进了一个新的手性中心。4-甲氧基四氢吡喃基乙缩醛的形成消除了这个问题。

Catalytic hydrogenolysis (氢解作用，破坏加氢作用) of an *O*-benzyl (邻苯甲基) protective group is a mild, selective method introduced by Bergmann and Zervas to cleave a benzyl carbamate (氨基甲酸盐) ( $>\text{NCO}-\text{OCH}_2\text{C}_6\text{H}_5 \rightarrow >\text{NH}$ ) prepared to protect an amino group during peptide syntheses. The method also has

been used to cleave alkyl benzyl ethers, stable compounds prepared to protect alkyl alcohols; benzyl esters are cleaved by catalytic hydrogenolysis under neutral conditions.

邻苯甲基保护基的催化氢解作用是 Bergmann 和 Zervas 引入的一种在制备肽的过程中, 分解所制备的苯甲基氨基甲酸盐来保护氨基基团的温和的和选择性的方法。这种方法也已经用来分解所制备的稳定的化合物烷基苯甲基醚来保护烷基醇。苯甲基酯在中性条件下被催化氢解作用所分解。

Three selective methods to remove protective groups are receiving much attention: “assisted,” electrolytic, and photolytic removal. Four examples illustrate “**assisted removal**” of a protective group. A stable allyl (烯丙基) group can be converted to a labile (不安定的, 易发生变化的) vinyl (乙烯基) ether group (eq. 4);  $\alpha\beta$ -haloethoxy (卤代乙氧基) (eq. 5) or  $\beta$ -silylethoxy (甲硅烷基乙氧基) (eq. 6) derivative is cleaved by attack at the  $\beta$ -substituent; and a stable *o*-nitrophenyl (硝基苯基) derivative can be reduced to the *o*-amino compound, which undergoes cleavage by nucleophilic (亲核的, 亲质子的) displacement:



R=alkyl, aryl, R'CO—, or R'NHCO—

The design of new protective groups that are cleaved by “**assisted removal**” is a challenging and rewarding (报答的, 有益的, 值得的) undertaking (事业, 工作).

有三种除去保护基的选择性方法引起了关注: “**assisted,**” 电解消除法, 光解

消除法。有四个例子证明了保护基的辅助性消除。一个稳定的烯丙基可以转变成不稳定的乙烯基醚（方程式 4）。 $\alpha$ -卤代乙氧基（方程式 5）或  $\beta$ -甲硅烷基乙氧基（方程式 6）的衍生物因为  $\beta$  取代基被进攻而分解。一个稳定的邻硝基苯基衍生物可以被还原成在亲核取代反应的作用下而分解的邻氨基化合物。因“assisted removal”而分解的新的保护基的设计是一项挑战性和值得一做的事业（充满了挑战和机遇的工作）。

Removal of a protective group by electrolytic oxidation or reduction can be very satisfactory. The equipment required ranges from a minimum of two electrodes, a potentiostat (恒电势器, 稳压器), and a source of DC current to quite sophisticated (高度发展的, 精密复杂的) systems. A suitable electrolyte (电解、电解液)/solvent (溶剂) system is needed, and the deprotected product must not undergo further electrochemistry under the experimental conditions. The use and subsequent removal of chemical oxidants or reductants (e.g., Cr or Pb salts; Pt-C or Pd-C) are eliminated. Reductive cleavages have been carried out in high yield at -1 to -3 V (vs. SCE) depending on the group; Oxidative cleavages in good yield have been realized at 1.5-2 V (vs. SCE). For systems possessing two or more electrochemically labile protective groups, selective cleavage is possible when the half wave potentials,  $E_{1/2}$ , are sufficiently different; excellent selectivity can be obtained with potential differences on the order of (属于...一类的, 与...相似的) 0.25 V. Protective groups that have been removed by electrolytic oxidation or reduction are described at the appropriate places in this book; a review article by Mairanovsky discusses electrochemical removal of protective groups.

用电解氧化或还原除去保护基是非常令人满意的。所需要的设备从最低限度的两个电极，稳压器和直流电源到非常精密复杂的系统。同时需要合适的电解液/溶剂系统，而且去质子化的产物在实验条件下必须不能发生进一步的电化学反应。化学氧化剂或还原剂(例如 Cr 或 Pb salts; Pt-C 或 Pd-C)的使用和随后的去除被消除。还原分解已经在-1 到 -3 V 范围内依赖于基团以高产率进行。在 1.5-2 V 的氧化分解也已经以高产率实现。对于拥有两个或更多电化学上不稳定的保护基来说，当半波电位  $E_{1/2}$  差异较大时，可能发生选择性分解。在电势差接近 0.25V 时，可以得到良好的选择性分解。这本书在合适（一定）的位置对用电解氧化或电解还原可以去除的保护基进行了介绍。Mairanovsky 所写的一篇综述性文章讨论了保护基的电化学去除方法。

Photolytic cleavage reactions (e.g., of *o*-nitrobenzyl, phenacyl, and nitrophenyl-sulfonyl derivatives) take place in high yield on irradiation of the protected compound for a few hours at 254-350 nm. For example, the *o*-nitrobenzyl group, used to protect alcohols, amines, and carboxylic acids, has been removed by irradiation. Protective groups that have been removed by photolysis are described at the appropriate places in this book; in addition, [the reader may wish to consult three review articles.](#)

在 254-350 nm 范围对所保护的化合物进行辐射，光分解作用（例如：邻硝基苯甲基、苯甲酰甲基、硝基苯基亚磺酰基的衍生物的光解作用）可以以高产率发生。例如，用来保护醇、胺和羧酸的邻硝基苯甲基可以利用辐射去除。已经用光解作用去除的保护基将在这本书的适当的地方进行介绍。另外，读者可能希望参考三篇综述。

## Selection of a Protective Group from This Book

To select a specific protective group, the chemist must consider in detail all the reactants, reaction conditions, and functionalities involved in the proposed synthetic scheme. First he or she must evaluate all functional groups in the reactant to determine those that will be unstable to the desired reaction conditions and require protection. The chemist should then examine reactivities of possible protective groups, listed in the Reactivity Charts (图没, 表), to determine compatibility (兼容性) of protective group and reaction conditions. The protective groups listed in the Reactivity Charts have been used most widely; **consequently**, considerable experimental information is available for them. He or she should consult the complete list of protective groups in the relevant chapter and consider their properties. It will frequently(往往) be advisable to examine the use of one protective group for several functional groups (i.e., a 2, 2, 2-trichloroethyl group to protect a hydroxyl group as an ether, a carboxylic acid as an ester, and an amino group as a carbamate). When several protective groups are to be removed simultaneously (同时地), it may be advantageous to use the same protective group to protect different functional groups (e.g., benzyl group, removed by hydrogenolysis, to protect an alcohol and a carboxylic acid). When selective removal is required, different classes of protection must be used (e.g., a benzyl ether, cleaved by hydrogenolysis but stable to **basic hydrolysis**, to protect an alcohol, and an alkyl ester, cleaved by basic hydrolysis but stable to hydrogenolysis, to protect a carboxylic acid).

从这本书中选择保护基

为了选择特效的保护基，化学家必须对所提出的合成系统中涉及到的所有反应物，反应条件以及功能进行详细的考虑。首先，他或她必须对反应物的所有功能基团进行评价，来决定哪些基团对于所期望的反应条件不稳定和需要保护。然后，化学家应该对列在反应图中的可能的保护基进行检测来确定保护基和反应条件的兼容性。列在反应图中的保护基已经得到了最广泛的使用，因此化学家就可以获得大量的实验信息。他或她必须对在相关章节中列出保护基的整个表格进行考虑，考虑它们的性质。检测具有几种功能的一个保护基的用途往往是明智的。（也就是 2, 2, 2-三氯乙基可以作为醚来保护羟基，作为酯来保护羧基，作为氨基甲酸盐来保护氨基）。当几个保护基要同时去除时，用同一个保护基来保护不同的基团是有利的（方便的）。（例如，用可以由氢解作用去除的苯甲基来保护醇和羧酸）。当需要选择性去除时，必须使用不同种类的保护（例如，可以被氢解作用分解而对碱性水解稳定的苯甲基醚可以用来保护醇，而可以被碱性水解分解却对氢解稳定的烷基醚可以用来保护羧酸。）

If a satisfactory protective group has not been located, the chemist has a number of alternatives: rearrange the order of some of the steps in the synthetic scheme so that a functional group no longer requires protection or a protective group that was reactive in the original scheme is now stable; redesign the synthesis, possibly (可能地，或者) making use of latent (潜在的，潜伏的) functionality (i. e., a functional group in a precursor form; e.g., anisole (茴香醚，苯甲醚) as a precursor of cyclohexanone (环己酮)). Or, it may be necessary to include the synthesis of a new protective group in the overall plan.

如果找不到符合要求的保护基，化学家仍然具有大量可供选择的方法：重新

安排合成系统中一些步骤的顺序，保证官能团不再需要保护或者在原来的系统中的活性保护基现在变得稳定；可能利用潜在的功能重新设计合成（也就是功能性基团以前驱体形式出现；例如：茴香醚作为环己酮的前驱体）。或者，有必要在总体计划中包括新保护基的合成。

A number of standard synthetic reference books are available. A review article by Kosssell and Seliger discusses protective groups used in oligonucleotide (低聚核苷酸) syntheses, including protection for the phosphate group, which is not included in this book; and a series of articles describe various aspects of protective group chemistry.

目前存在大量的标准合成文献书。Kosssell 和 Seliger 写的一篇综述性文章对在低聚核苷酸合成中所用的保护基进行了讨论，包括这本书中没有的磷酸根的保护作用，还有一系列文章对保护基化学的各方面进行了介绍。

## 22. Polymers (聚合物, 聚合体)

The term **macromolecule** (大分子), or polymer, is **applied to** (关系到, 牵涉到; 适用于, 应用于; 将...应用于) substances of high molecular weight that are composed of a large number (usually at least 100) of units of low **molecular** weight joined by covalent bonds. If the low molecular weight units making up the macromolecule are bonded **end-to-end** (头尾相接) in a long chain and no covalent chemical bonds exist between the chains, the macromolecules are called linear polymers. Such polymers, unless of extremely high molecular weight(1000000), can usually be dissolved and, when heated, they soften or melt so that they can be extruded (使...喷出, 挤压成) into fibers (纤维, 光纤) or molded (浇铸, 塑造) into desired (渴望的, 想得到的) shapes. These polymers are said to be **thermoplastic** (热塑性塑料, 热塑性的). On the other hand, if the polymer chains are linked together at numerous points, the polymer is one large three-dimensional molecule, infusible(不熔化的, 不熔化性的) and insoluble. Such polymers are called **cross-linked** (交联, 交联键) polymers (交联聚合物), and the bonds connecting the chains are cross-links. Certain linear polymers, referred to as **thermosetting** (热固性的, 热成型的, 热凝性的, 热硬性的), contain groups, which, when heated, react to (与...起反应) give cross-linked polymers.

术语大分子或聚合物, 适用于共价键连接大量 (通常最少 100 个) 低分子量单元组成的高分子量物质。(适用于大量低分子量单元组成的高分子量物质, 这些低分子单元之间由共价键相连。) 如果组成聚合物的低分子量单元在一个长链中是按照头尾相连成键的方式结合的, 而且在链之间没有共价化学键存在, 这个

聚合物就叫做线形聚合物。这类聚合物，除了分子量极高的（1000000）之外，通常都可以溶解，当加热时，易软化或融化，因此，可以压制或铸塑成想得到的形状。因此说这类聚合物具有热塑性。另外一方面，如果聚合物链在很多点连接在一起，聚合物就是一个大的三维的分子，很难熔化和溶解。这样的聚合物叫做交联（交叉链接）聚合物。连接链的化学键叫做交联键。某些称为热固性的线形聚合物，含有一些在加热时可以互相起反应给出（形成）交联（交叉链接）聚合物的基团。

The process by which small molecules undergo **multiple combination** to form macromolecules is polymerization. Small molecules from which a macromolecule or polymer can be made are called monomers (单体). Two types of polymerization are recognized (公认的, 经过验证的; 普遍接受的): (1) **condensation polymerization** (缩聚) and (2) addition polymerization. A **polymer-forming** (形成聚合物) reaction involving elimination of a small molecule such as water or alcohol between monomer units is described as condensation polymerization. In addition polymerization, unsaturated or cyclic molecules **add to** each other without elimination of any portion of the monomer molecule. The **empirical formula** (实验式) of the polymer is then, of course, the same as that of the monomer.

小分子进行多重结合形成大分子的过程叫做聚合反应。组成大分子或聚合物的小分子叫单体。现在有两类公认的聚合反应：(1) 缩合聚合(缩聚)反应和(2) 加成聚合(加聚)反应。如果形成聚合物的反应涉及到在单体间消去小分子如水或醇，这样的反应就叫做缩合聚合(缩聚)反应。在加聚反应中，不饱和的或环状的分子互相反应，彼此增长，而且没有消去单体分子的任何一部分。那么，当

然，聚合物的实验式与单体的相同。

Reactions capable of forming macromolecules by either addition or condensation polymerization must be functionally (就其功能作用，功能上；机能上地，官能地) capable of proceeding indefinitely (不确定地，无限期地，无限制地). Whenever (无论何时，只要) two monomer molecules react, the product must contain a functional group capable of reacting with another molecule of monomer. In condensation polymerization, each monomer unit must have at least two functional groups. In addition polymerization, the monomer need have only one functional group—the presence of two or more functional groups usually leads to the production of cross-linked addition polymers. Examples of some of the more important synthetic polymers formed by condensation polymerization are listed in Table 15.

通过加聚或缩聚反应能够形成聚合物的反应在功能上，必须能够无限制地进行。只要两个分子反应，产物必须含有能够和另外一个单体分子结合的官能团。在缩聚反应中，每个单体单元至少必须有两个官能团。在加聚反应中，单体只需要有一个官能团—两个或更多官能团的存在通常导致交联加成聚合物的产生。一些由缩聚反应形成的比较重要的合成聚合物已经列在表 15。

#### Condensation Polymers (由缩聚反应形成的聚合物)

Typical of condensation polymers are the polyamides (聚酰胺) or “nylons” formed by condensation reaction of a diacid with a diamine (二胺). Nylon 66, poly(hexamethyleneadipamide) (聚亚乙基己二酰胺，聚己撑己二酰胺), is formed by heating an equimolar mixture of **adipic acid** (脂肪酸) and hexamethylenediamine at a temperature of 215° for several hours and then at 270° under vacuum for about

one hour.

典型的缩聚反应形成的聚合物是由二酸和二胺进行缩聚反应形成的聚酰胺或尼龙。尼龙 66，即聚己撑己二酰胺是通过在 215°C 下把等摩尔的脂肪酸和己二胺的混合物加热数小时，然后在 270°C 下进行真空反应大约一小时形成的。

In the laboratory, nylons are more conveniently (便利地) prepared by a polymer-forming reaction called interfacial (界面的) polymerization. The reaction is between a diacid chloride dissolved in a water-immiscible (不混溶的, 难溶的) organic solvent and a water solution of a diamine. Reaction apparently occurs at the interface of two solutions.

在实验室，通过界面聚合反应，比较容易制备尼龙。这个反应是在溶解于难和水混溶的有机溶剂中的氯代二元酸和二胺的水溶液之间进行的。显然，反应是在两种溶液的界面进行的。

Place a solution of 2.0 mL. of sebacoyl (癸二酰) chloride in 100 mL. of carbon tetrachloride in a 200-mL. **tall-form beaker** (高形烧杯). Over the acid chloride solution carefully pour a solution of 2.2 g. of hexamethylenediamine and 1.5 g. of sodium hydroxide in 50 mL. of water. The addition of the diamine-sodium hydroxide solution is best done by pouring the solution through a funnel (漏斗, 烟窗) placed so that its outlet (出口, 出路; 排水口) is just **over** the surface of the diacid solution. Grasp the polymeric film which forms at the interface of the two solutions with forceps (镊子, 钳子) and raise it from the beaker **as continuously forming rope**. If a mechanical windup (装有发条的) device is placed above the beaker, the polymer may be **wound up** (缠绕, 卷起) continuously until one of the reactants is exhausted.

把 2.0mL 的氯代癸二酰溶解在 100mL 的四氯化碳中，然后放在 200mL 的高

形烧杯中。(在 200mL 的高形烧杯中，加入 2.0mL 的氯代癸二酰和 100mL 的四氯化碳)在氯代酸溶液上小心地倒入 2.2 克己二胺和 1.5 克氢氧化钠溶解于 50mL 水形成的溶液。己二胺和氢氧化钠的加入最好通过(容器上)放置的漏斗来进行，这样它的出口就正好在二元酸溶液的上方。用镊子抓住两种溶液界面的聚合物膜，**作为连续形成的绳索状从烧杯中提出**。如果在烧杯上装上机械上有发条的设备，聚合物就会被连续卷起，直到其中的一种反应物耗尽。

Wash the polymer thoroughly (十分地，彻底地) with water and finally with a 50% acetone solution. Allow the washed polymer to air dry. Place about 0.1g. of the dried polymer on a **metal spatula** (金属刮刀、钢刮刀) or spoon (匙、调羹、勺子) and melt it carefully over a **low flame** (低温火焰) care being taken not to char (烧焦) the polymer. Touch a glass rod (杆、棒) or a matchstick (火柴杆) to the molten polymer and pull it slowly away to form a fiber.

先用水彻底地洗涤聚合物，最后用 50% 的丙酮溶液洗涤。然后把洗涤后的聚合物置于空气中干燥。把 0.1 克干燥的聚合物放在金属刮刀或金属勺上，在低温火焰上小心地使其熔化，当心不要使聚合物烧焦。用一根玻璃棒或火柴杆接触熔化的聚合物，然后慢慢地拉起来使其形成纤维。

## 2. Addition Polymers (由加聚反应形成的聚合物)

### Introduction (前言、导言)

Addition polymerization usually must be catalyzed by a base, by an acid, or by free radicals. Three stages are involved in all addition polymerization reactions, no matter what the catalyst: these are initiation, propagation, and termination. In the initiation step, the catalyst molecules attack the monomers to give

intermediates which, during the propagation stage, are capable of attacking other molecules of monomer with lengthening of the chain. In the termination step, chain growth is stopped by elimination of a group from the reacting end of the chain or by addition of a group to the end of the chain to form a molecule which is no longer a chain carrier.

加聚反应通常必须用碱、酸或自由基进行催化。无论催化剂是什么，所有的加聚反应中都包括三个阶段：即引发（开始）步骤，链传递步骤，和终止（结束）步骤。在引发步骤中，催化剂分子进攻单体产生能够在链传递步骤中进攻其它的单体分子而使链延长的中间体。在终止步骤中，因为链的反应末端的基团的消去或因为链的末端的加成反应形成了不再是链的传递者的分子而导致链增长结束。

Free radical-initiated polymerizations follow a similar course (过程, 经过) but with radical, rather than ionic, intermediates. If two or more monomers undergo addition polymerization together, the process is called copolymerization, and the product is a copolymer. Should one of the monomers (even though present in only minor amounts) from which a copolymer is formed contain two or more groups capable of undergoing addition polymerization (这一部分是虚拟条件从句), the copolymer will be insoluble as a result of cross-linking (主句不用虚拟语气, 表示该事物实现的可能性虽较小, 但仍然是可能的).

自由基引发的聚合反应遵循相似的过程，涉及到的是自由基而不是离子性中间体。如果两个或更多的单体在一起进行加聚反应，这个过程就叫做共聚作用，产物叫共聚物（共聚体）。如果形成共聚物的一种单体（即使仅仅存在少量的）含有两个或更多的能够进行加聚反应的基团，交联形成的共聚物将是难溶解于水

的交联型聚合物。

Examples of some of the more important synthetic polymers formed by addition polymerization are listed in Table 16.

表 16 列出了由加聚反应形成的一些比较重要的合成聚合物。

#### Preparation of Polystyrene (聚苯乙烯)

(1) Polymerization of Styrene (苯乙烯) with Benzoyl (苯甲酰) Peroxide (过氧化物). To a large test tube add 20 ml. of toluene (甲苯) and 5 ml. of styrene. Then add 0.3g. of benzoyl peroxide and place the test tube in a beaker (大口杯, 有倾口的烧杯) of water which is maintained at a temperature of 90°~95°. After 60 minutes, remove the test tube, allow the contents to cool for 5 minutes, and note the viscosity of the solution. Pour the solution into 200ml. of **methyl alcohol** (甲醇) contained in a 400-ml. beaker. Collect the white precipitate of polystyrene by filtration, using a Buchner funnel, and wash the precipitate on the funnel with 50 ml. of methyl alcohol. Remove the precipitate from the funnel and **spread it out** to dry on a large, clean sheet of filter paper.

##### (1) 苯乙烯和苯甲酰过氧化物形成的聚合物

在一个大试管中加入 20mL 甲苯和 5mL 苯乙烯。然后加入 0.3 克苯甲酰过氧化物，把试管放在温度维持在 90°C~95°C 装有水的烧杯中。60 分钟后，移去试管，并且使其冷却 5 分钟，注意溶液的黏度。把溶液倒入含有 200mL 甲醇的 400mL 烧杯中。用布氏漏斗过滤后，收集白色的聚苯乙烯沉淀，然后在布氏漏斗上用 50mL 的甲醇洗涤沉淀。从布氏漏斗上转移沉淀后，把它在一个大的、干净滤纸上铺成一层进行干燥。

Place 3 mL. Of acetone in a clean test tube, add 0.2g. of the dried polymer, and stir the mixture for several minutes. Is the polymer soluble? Use this same procedure to determine the solubility of polystyrene in water, ethyl alcohol, benzene, carbon tetrachloride, and **petroleum ether** (石油醚). Place approximately 0.1g of the polymer on a metal spatula or spoon and warm it gently over a flame until the polymer melts. To the molten polymer touch a glass stirring rod or a matchstick and pull away gently to **draw out** (抽出, 拉长) a fiber. How would you describe the properties of the fibers **as to** (关于, 至于) brittleness, color, and strength? Compare the properties of this polystyrene fiber with those of the Nylon fiber. Allow the molten polymer on the spatula to cool. Describe the appearance of the cooled polymer. Scrape (刮, 擦) this material from the spatula, place it in a test tube, and determine its solubility in acetone. Did melting change the solubility of the polystyrene?

把 3mL 的丙酮放在一个干净的试管中，然后加入 0.2 克干燥的聚合物，把混合物搅拌几分钟。聚合物能溶解了吗？用同样的过程确定聚苯乙烯在水、乙醇、苯、四氯化碳和石油醚中的溶解性。把大约 0.1 克的聚合物放在金属刮刀或金属勺上，在火焰上轻轻地（小火）加热直到聚合物熔化。用一根玻璃搅拌棒或火柴杆一样的东西接触聚合物，然后从聚合物上轻轻地拉开，抽出纤维。你如何描述关于纤维的脆性、颜色和强度等性质？比较聚苯乙烯纤维的性质和尼龙纤维的性质。让熔化的聚合物在刮刀上冷却。描述一下冷却后的聚合物的外观。把这个材料从刮刀上刮起来放在试管里，确定它在丙酮中的溶解性。熔化改变了聚苯乙烯的溶解性了吗？

Table 15. Condensation Polymers

Name	Monomers	Repeating Unit	Principal Use
Dacron Mylar Terylene (商品名) 的确凉, 涤纶, 聚对苯二甲酸乙二醇酯	Dimethyl terephthalate(对苯二甲酸或酯) and ethylene glycol (乙二醇)		Fiber, film
Nylon 66 尼龙 66	Adipic acid (脂肪酸) and hexamethylene diamine (己二胺)		Fiber, <b>molded articles</b> (模型制品)
Epoxy resins 环氧树脂	Bisphenol-A (双酚 A) and epichlorohydrin (3-氯-1, 2-环氧丙烷, 环氧氯丙烷)		Protective coatings, adhesives(黏合剂, 胶粘剂), potting(陶品制造的) resins
Urethans 聚氨酯(橡胶)	Toluene diisocyanate (甲苯二异氰酸酯 and poly(propylene (丙烯) glycol)		Rigid (刚性的) and elastic (有弹性的) foams (泡沫)
Thiokols (聚硫橡胶) (poly sulfide rubbers)	Ethylene chloride (1, 2-二氯乙烷, 氯化乙烯) and sodium polysulfide 多硫化钠		Oil-resistant rubber (耐油橡胶)
Silicones 聚硅氧烷, (聚)硅酮	Methyl dichlorosilanes (硅烷) and/or trichlorosilanes		Oils, rubbers coatings, resins
Phenol (苯 酚)-formaldehyde (甲醛)	Phenol and formaldehyde	Ortho (邻位的) or para linkages	Molded articles, adhesives, laminating resins (层压树脂)

Table 16. Addition Polymers

Name (名称)	Monomer (单体)	Repeating Unit (重复单元)	Principal Use (基本用途)
Polyethylene 聚乙烯			Film, molded articles 薄膜, 模型制品
Poly(vinyl chloride)聚氯乙烯			Coatings(油漆,涂层,衣料), sheet (被单, 褥单, 薄片)
Polyacrylonitrile (聚丙烯腈), Orlon (腈纶, 聚丙烯腈纤维), Acrilan 腈纶, 聚丙烯腈纤维)			Fiber
Polystryrene (聚苯乙烯), Lustron(商品名) 聚苯乙烯 (塑料), Styron (商品名) 肉桂塑料, 聚苯乙烯(塑料)			Molded articles, Rigid foams 刚性泡沫 (塑料), 硬泡沫 (塑料)
Poly(methyl methacrylate) 聚甲基丙烯酸甲酯 Lucite (商品名) 有机玻璃聚甲基丙烯酸甲酯, , Plexiglass (商品名) 有机玻璃聚甲基丙烯酸甲酯			Coatings, Molded articles , sheet
Polyformaldehyde (聚甲醛), Delrin (商品名) 聚甲醛塑料			Molded articles
Polyethylene oxide 聚环 氧 乙 烷 , Polyethyleneglycol 聚乙二醇, Carbowax(商品名) 聚乙二醇			Waxes 蜡, 蜡状物
Polycaprolactam 聚己内酰胺, Nylon 6			Fiber

## 前缀

1. macro-大， 常量， 宏观

macromolecule, macrocyclic (大环的) ; macroanalysis (常量分析)

2. poly-聚， 多 polymer, polyamide (聚酰胺) ; polyatomic (多原子的), polycyclic

(多轮的， 多环的， 多相的)

3. thermo-热 thermoplastic (热塑性塑料), thermometer (温度计), thermostatic

(恒温的)

4. ep(i) 环 epoxide (环氧化物), epichlorohydrin 表氯醇 (用于橡胶制造)

## 词组

end-to-end 头尾相接

wind up 缠绕， 卷起

low flame 低温火焰

no matter what 无论什么， 不管是什么

no longer

spread...out...把...摊开 (铺开)

draw out 抽出， 拉长