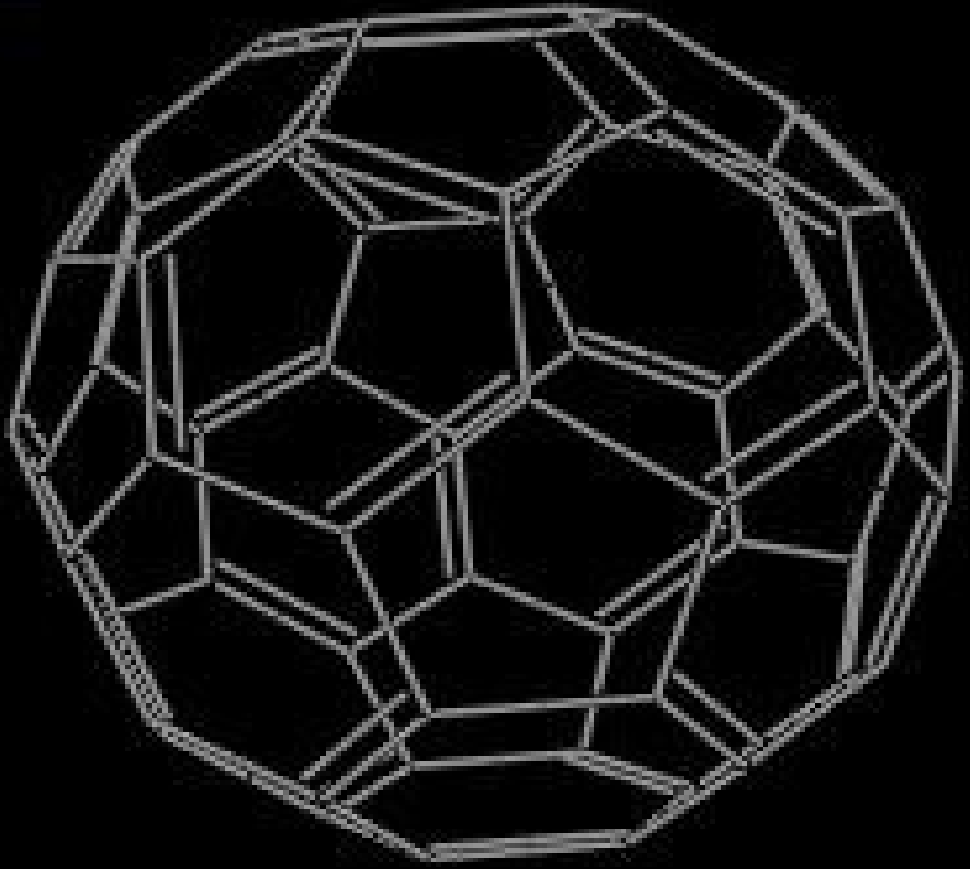
Chapter 15
Carbon Group



C Carbon

Si Silicon

Ge Germanium

Sn Stannum

Pb Plumbum

Catalogue

§15 - 1 General characteristic of carbon

§15 - 2 Simple substance and compound

§ 15 - 3 Hydrolyse of inorganic compounds

§ 15 - 1 General characteristic of carbon

$ns^2\ np^2$

C Si Ge Sn Pb

covalent radius ↗

ioniztion energy ↘

electronegativity ↘

+2 oxidation state stablity ↗

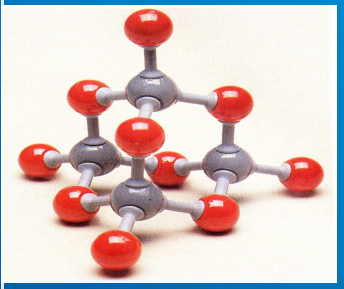
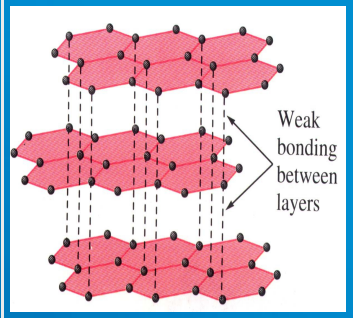
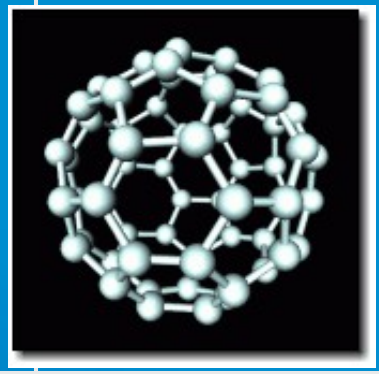
+4 oxidation state stablity ↘

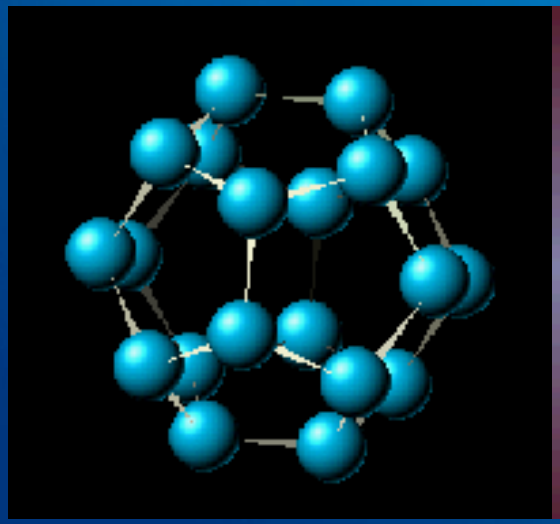
§15 - 2 Simple substance and compound

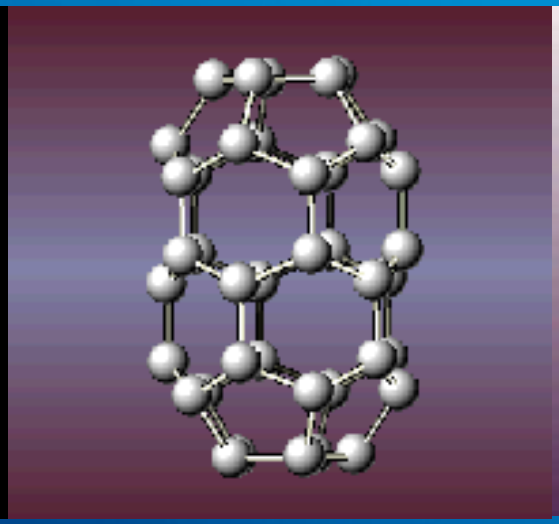
2 - 1 Simple substance

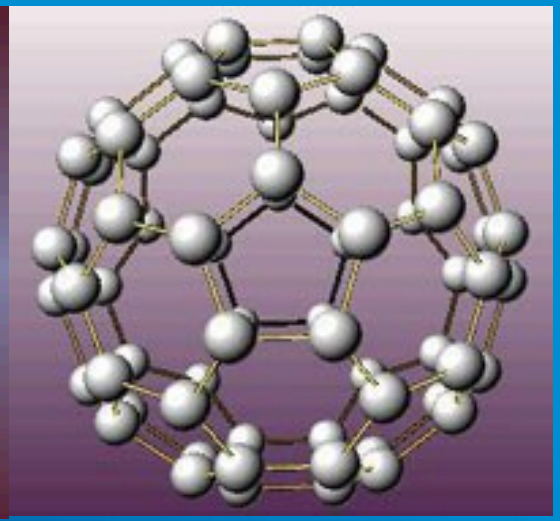
一、 Carbon

Allotrope of carbon
- diamond
- graphite
- Fullerene C_{20} 、 C_{60} (1985)

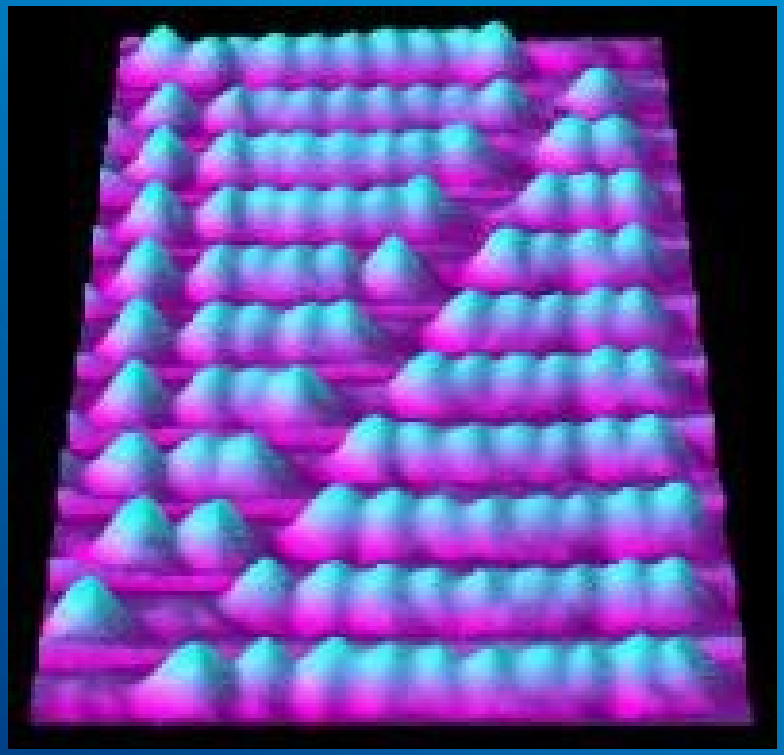
charater	diamond	graphite	C_{60}
Configuration	 tetrahedron	 Π_m^m	
Hybrid mode	sp^3	sp^2	$sp^{2.28}$
C-C-C bond angle	109.5°	120°	116°
Density g/cm^3	3.514	2.266	1.678
Crystals form	Atomic crystals	Between Atomic crystals and Molecular cry-stals	Molecular crystals





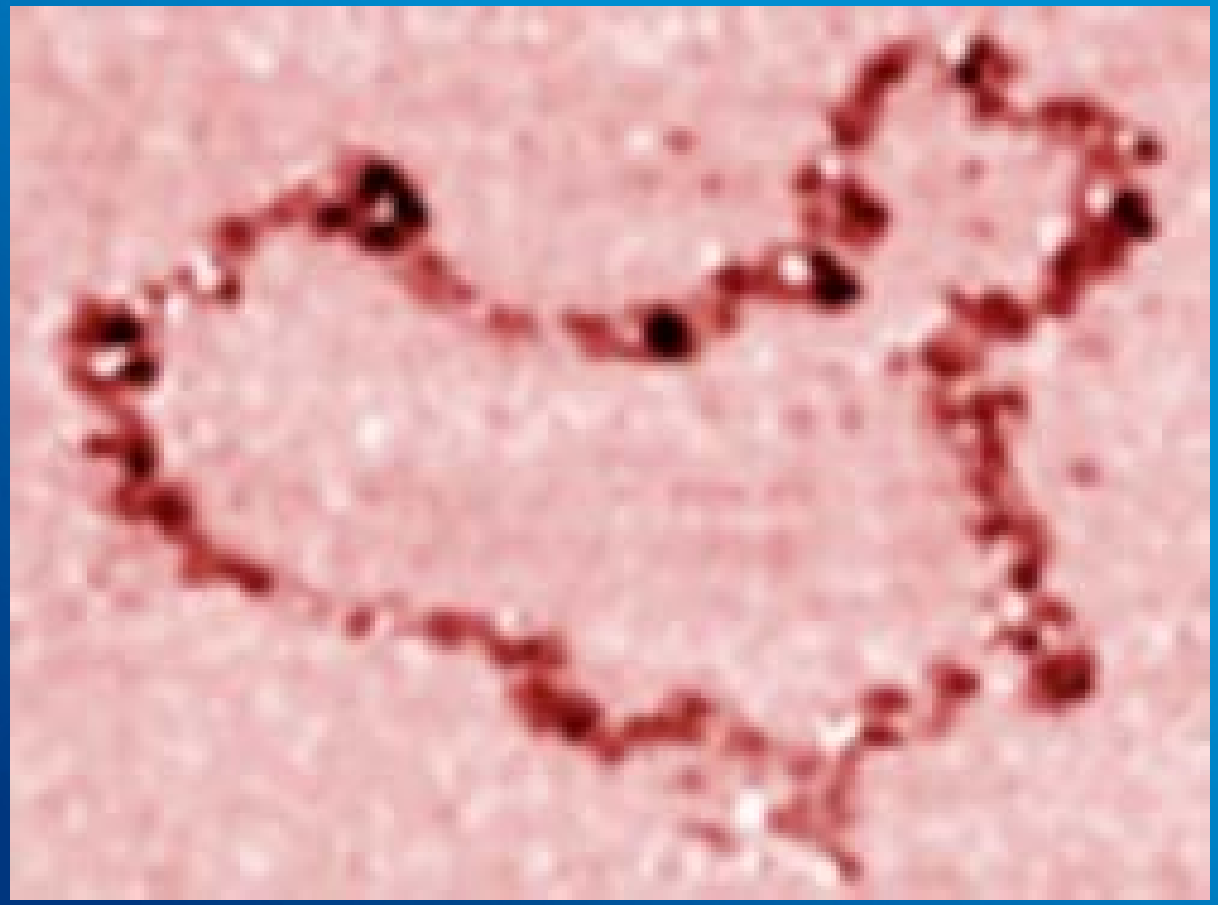


C_{20} C_{40} C_{70}



Shensuanzi of nanotechnology
- molecular abacus

IBM company(1996 .11)

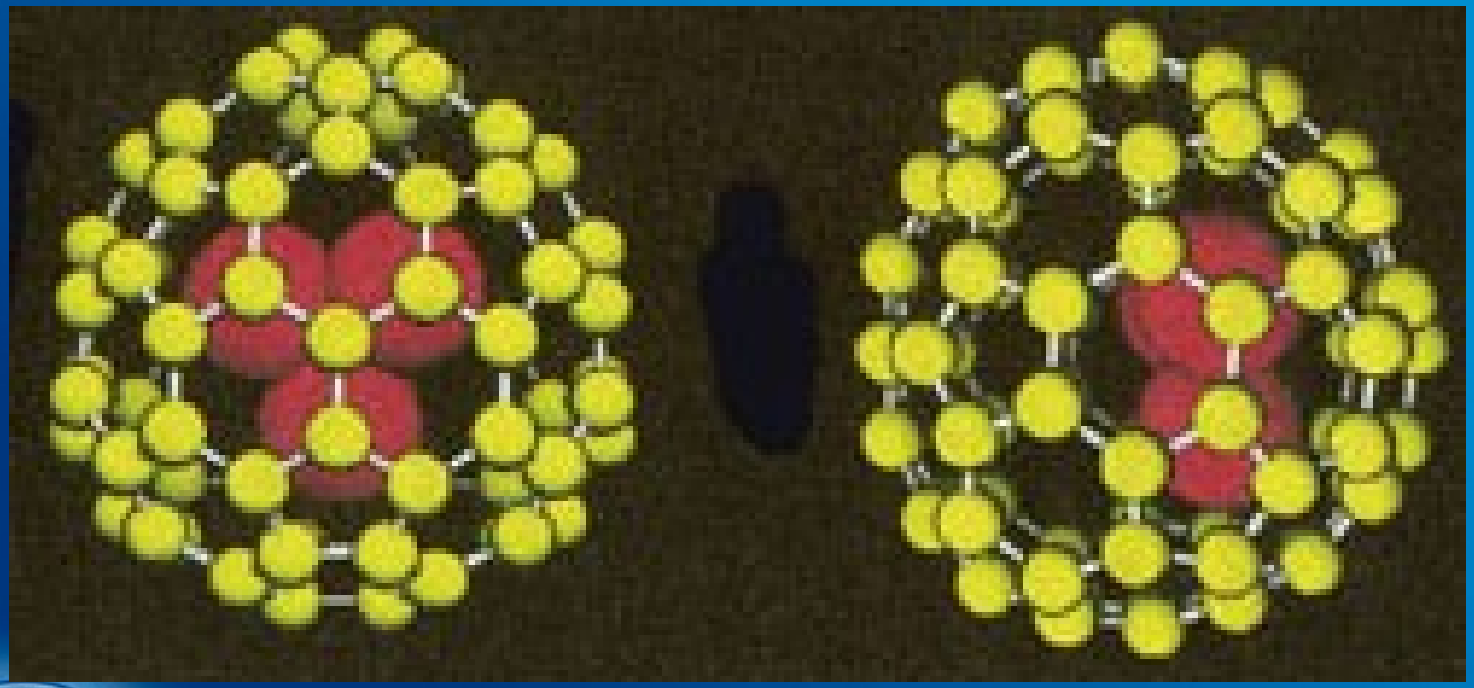


The world's smallest Chinese map through the relocation of C atoms in the graphite surface .

-- Chemical by the Chinese Academy of Sciences

(1999)

metallofullerite (laser evaporation)



二、 Silicon

$$SiO_2 + C + 2Cl_2 = SiCl_4 + CO_2$$

$$SiCl_4 + 2H_2 = Si + 4HCl$$

Chemical property of Si

1. Reaction with nonmetal

Room temperature, Silicon only can react with F_2 :

$$Si + 2F_2 \xrightarrow{R.T.} SiF_4 \uparrow$$

$$Si + 2Cl_2 \xrightarrow{400℃} SiCl_4$$

$$Si + C \xrightarrow{1500℃} SiC$$

2. Reaction with acid

$$Si + 4HF \xrightarrow{200\sim400℃} SiF_4 + 2H_2\uparrow$$

Si: passivation in oxacid. When having oxidatant (HNO_3、 CrO_3、 $KMnO_4$、 H_2O_2 et c.) react with it

$$3Si + 4HNO_3 + 18HF = 3H_2SiF_6 + 4NO\uparrow + 8H_2O$$

strong acid

3. Reaction with strong base

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2\uparrow$$

三、Ge、Sn、Pb

		Ge	Sn	Pb
颜色状态		银白色硬金属	灰锡 $\xleftarrow{\langle 286K}$ 白锡 $\xrightarrow{\rangle 434K}$ 脆锡 (α型) (β型) (γ型)	暗灰色，重而软的金属
氧化态		+IV 和 +II		
稳定性	+IV	Ge>Sn>Pb		
	+II	Ge<Sn<<Pb		

Chemical Property

1. Reaction with O_2

$$Pb \xrightarrow{air} PbO \text{ or } Pb_2(OH)_2CO_3$$

$$Ge、Sn \xrightarrow{air} ?$$

$$Ge、Sn \xrightarrow{\text{high temperature}} MO$$

2. Reaction with other nonmetals

$Pb+X_2=PbX_2$

$Sn+X_2=SnX_4(q.s.SnX_2)$

$Ge+X_2=GeX_4$

$Pb+S=PbS$

$Sn+S=SnS_2(q.s.SnS)$

$Ge+S=GeS_2$

3. Reaction with acid

☆ Ge :not reacting with unoxacid

☆ Sn 、 Pb: M(+2) compound

$$Sn + 2HCl(thick) = SnCl_2 + H_2\uparrow$$

$$Pb + 2HCl = PbCl_2\downarrow + H_2\uparrow$$ (not easy)

$$Pb + 4HCl(thick) = H_2[PbCl_4] + H_2\uparrow$$

☆ Ge 、 Sn $\xrightarrow{\text{oxacid}}$ M(IV)

☆ Pb $\xrightarrow{\text{oxacid}}$ M (+ II)

$$Ge + 4H_2SO_4(thick) = Ge(SO_4)_2 + 2SO_2\uparrow + 4H_2O$$

Easy hydrolysis

$GeO_2 \cdot H_2O$

$$Ge + 4HNO_3(thick) = GeO_2 \cdot H_2O\downarrow + 4NO_2\uparrow + 2H_2O$$

$$Sn + 4H_2SO_4(\text{thick}) = Sn(SO_4)_2 + 2SO_2\uparrow + 4H_2O$$

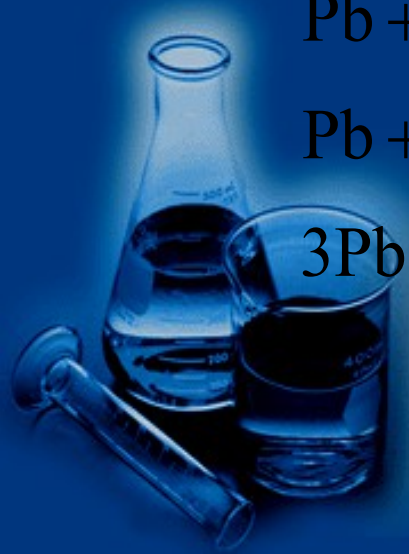
$$Sn + 4HNO_3(\text{thick}) = H_2SnO_3\downarrow + 4NO_2\uparrow + H_2O$$

$$4Sn(\text{excessive}) + 10HNO_3(\text{cold diluted}) = 4Sn(NO_3)_2\downarrow + NH_4NO_3 + 3H_2O$$

$$Pb + H_2SO_4(\text{diluted}) = PbSO_4\downarrow + H_2\uparrow$$ **(not easy)**

$$Pb + 3H_2SO_4(\text{thick}) = Pb(HSO_4)_2 + SO_2\uparrow + 2H_2O$$

$$3Pb + 8HNO_3(\text{diluted}) = 3Pb(NO_3)_2 + 2NO\uparrow + 4H_2O$$



Pb: not reacting with concentrated nitric acid

3. Reaction with base

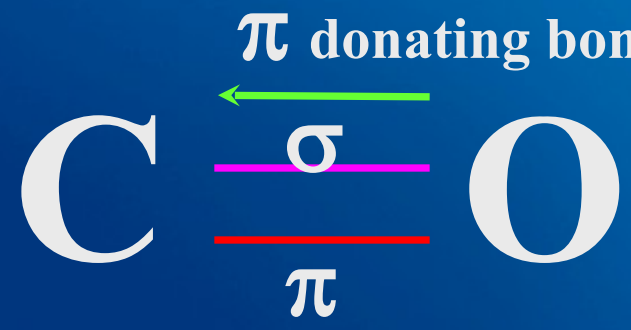
Ge $\xrightarrow{\text{NaOH}}$ **insoluble** (except for having H_2O_2) **Sn**、**Pb** $\xrightarrow{\text{NaOH}}$ **H_2** (slowly)

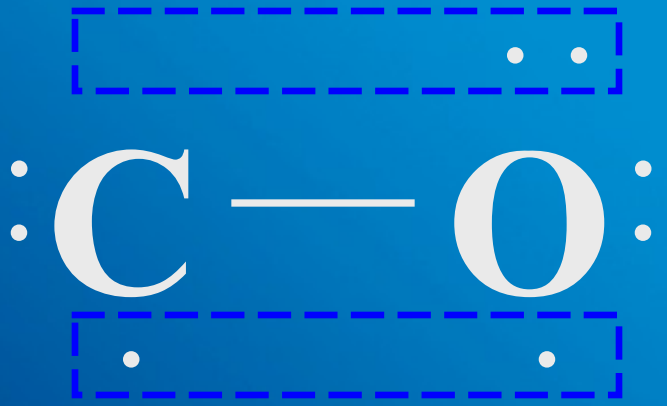
$$Sn + 2OH^- + 2H_2O = Sn(OH)_4^{2-} + H_2\uparrow$$

2 - 2 Oxidate

一、 CO 和 CO_2

π donating bond





$KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py})^2(\pi_{2pz})^2(\sigma_{2px})^2$

CO

a. moleculat structure

CO 与 N_2、CN^-、NO^+（亚硝酸离子）互为 isoelectronic species。

：C≦O：　　1σ + 1π + 1π donating bond

∴CO dipole moment little：

μ 值：　CO　　0.11 D

H_2O　　1.85 D

NH_3　　1.47 D

HF　　1.98 D

Some think　　others think

δ^-　δ^+　　δ^+　δ^-

：C≦O：　　：C≦ O ：

$$CO + 2Ag(NH_3)_2OH = 2Ag\downarrow + (NH_4)_2CO_3 + 2NH_3$$

CO VS N_2

共同点：

1. 电偶极矩很小；
2. C 作为配位原子（Lewis base）

M ←：CO

$$N_2\left[KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_2py,\pi_2pz)^4(\sigma_2px)^2(\pi^*_2py,\pi^*_2pz)^0\right]$$

$$CO\ [(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2(2\pi)^0]$$

键级 =（6-0）/2 = 3

分子	键级	键能 /kJ • mol^{-1}	键长/pm
N_2	3	941.69	110
CO	3	1070.3	113

（a）强还原性

R.T.，CO 对 O_2、O_3、H_2O_2 皆很稳定，日光下也无作用，但高温下，CO 在空气中燃烧生成 CO_2。

例 1. $Fe_2O_{3(s)} + 3CO \overset{\Delta}{=} 2Fe + 3CO_2\uparrow$

例 2. $PdCl_2(aq) + 2CO(g) + H_2O \overset{NaAc(aq)}{=\!=} Pd\downarrow + CO_2\uparrow + 2HCl$

检定 CO

（b）强配位性

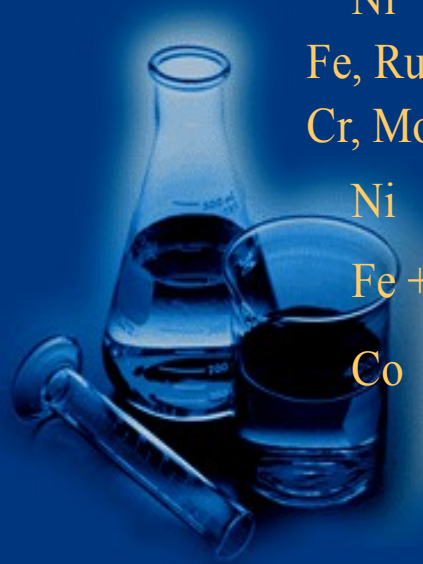
1. 羰基配合物 $M_{(s)} + x\,CO_{(g)} = M(CO)_x$

M	x 值	颜色、状态	$M(CO)_x$ 几何构型
Ni	4	无色液体	正四面体
Fe, Ru, Os	5	(Fe)黄色液体	三角双锚体
Cr, Mo, W, V	6	(Cr)晶体，真空中升华	正八面体

Ni $\quad \overset{0}{Ni}(CO)_{4(l)} \xrightarrow{\Delta} Ni_{(s)} + CO\uparrow$

Fe $\quad Fe + x\,CO(g) \xrightarrow{R.T} \overset{0}{Fe}(CO)_5$ 提纯金属

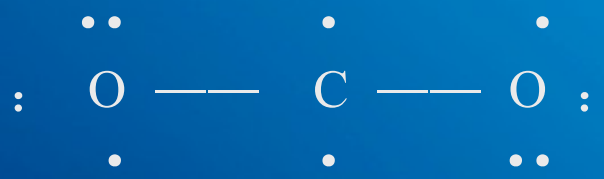
Co $\quad \overset{+1\ -1}{H\,Co}l(CO)_4$



CO_2

a．分子结构

CO_2 与 N^{3-}、N_2O（笑气）、NO_2^+、OCN^-、SCN^- 互为等电子体---16 电子体。



$$2\sigma + 2\Pi_3^4$$

C—O 键级 $= 1 + 2 \times 0.5 = 2$

b．性质

（1）酸性氧化物

（2）CO_2 灭火器不可用于活泼金属 Mg、Na、K 等引起的火灾：

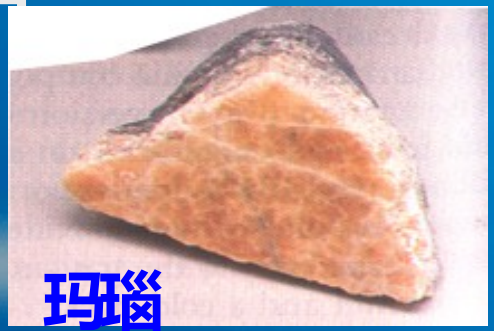
$$CO_{2(g)} + 2Mg_{(s)} = 2MgO_{(s)} + C_{(s)}$$

二、 SiO_2 (silicon dioxide)

SiO_2
- 无定型体：石英玻璃，硅藻土
- 晶体：天然为石英（原子晶体）
  - 纯石英：水晶
  - 含有杂质的石英：玛瑙


紫晶


水晶


玛瑙

SiO_2 :colorless 、 infusible solid ； inso-luble in water and acid (except for HF) ； soluble in heated strong base and fused $NaCO_3$.

$$SiO_2 + 4HF(g) = SiF_4\uparrow + 2H_2O$$

$$SiO_2 + 6HF(aq) = H_2SiF_6 + 2H_2O$$

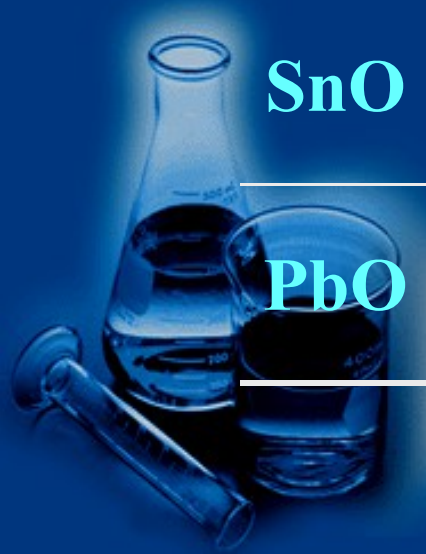
$$SiO_2 + 2OH^- = SiO_3^{2-} + H_2O$$

$$SiO_2 + NaCO_3(fusion) = Na_2SiO_3 + CO_2\uparrow$$

三、 oxide of Sn 、 Pb

MO	colors tate	acidity basicity	MO_2	color state	acidity basicity
GeO	black(s)	两性	GeO_2	white(s)	弱酸性
SnO	black(s)	两性略偏碱性	SnO_2	white(s)	两性偏酸性
PbO	yellow(s)	两性偏碱性	PbO_2	棕黑(s)	两性略偏酸性

酸性增强



☆ SnO_2 通常难溶于酸或碱

- $$SnO_2 + 2NaOH \xrightarrow{\text{fusion}} Na_2SnO_3 + H_2O$$

$$SnO_2 + 2Na_2CO_3 + 4S$$

$$= Na_2SnS_3 + Na_2SO_4 + 2CO_2\uparrow$$

☆ PbO 易溶于醋酸或硝酸得到 Pb(II) 盐，难溶于碱。

PbO_2 两性略偏酸性

$$PbO_2 + NaOH = Na_2PbO_3 + H_2O$$

$$PbO_2 + 4HCl = PbCl_2 + Cl_2\uparrow + H_2O$$

$$2PbO_2 + 2H_2SO_4(\text{hot thick}) = 2PbSO_4 + O_2\uparrow + 2H_2O$$

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O$$

$$PbO_2 \xrightarrow{\sim 600K} \underset{(PbO\cdot PbO_2)}{Pb_2O_3} \xrightarrow{\sim 700K} \underset{(2PbO\cdot PbO_2)}{Pb_3O_4} \xrightarrow{\sim 800K} PbO$$

$$\mathbf{Pb_3O_4 + HNO_3 = PbO_2 + Pb(NO_3)_2 + H_2O}$$

惰性电子对效应

均呈两性 $\begin{cases} +2\text{氧化态}: \text{BA} & \text{均很弱} \\ +4: \quad\quad \text{AB} & \text{均很弱} \end{cases}$

PbO_2 强氧化性：

$$5PbO_2(s) + 2Mn^{2+} + 4H^{+} = 5Pb^{2+} + 2MnO_4^{-} + 2H_2O$$

棕黑

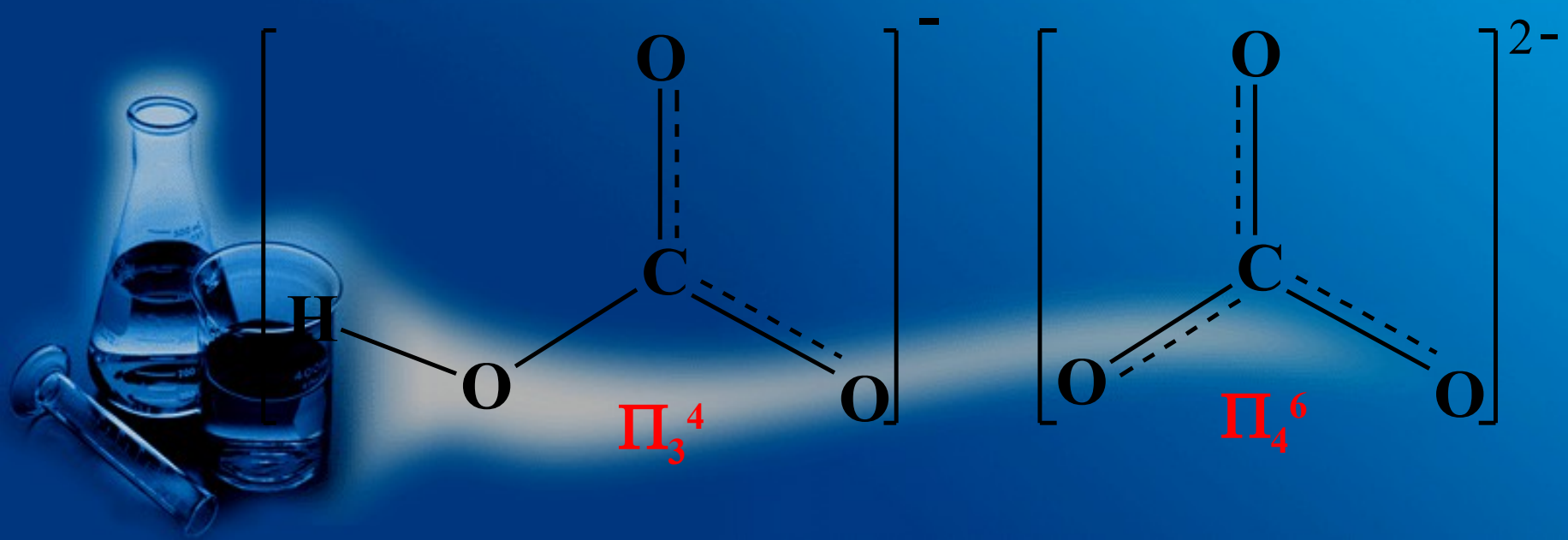
$6s^0$ $\qquad\qquad\qquad\qquad$ $6s^2$

$$PbO_{2\,(s)} + 4\,HCl\,(浓) = PbCl_2 + Cl_2\uparrow + 2H_2O$$

2 - 3 Oxacid and Salt

一、 Carbonic acid and Carbonate

1. Carbonic acid



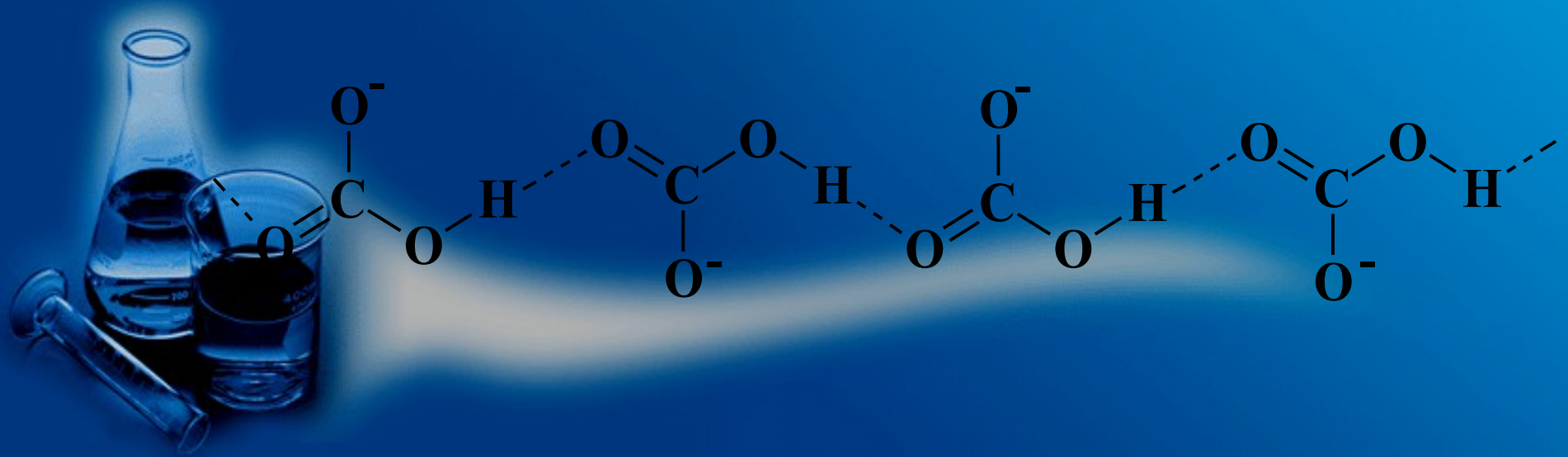
2. Porperty of Carbonate

(1) Dissolvability

All the bicarbonate can dissolve into water.

Normal salt:ammonium、 thalium salt、 alk ali metal salt can dissolve into water.other metal salt are not dissolution(solubility: bicarbonate > normal salt).

Alk ali metal (except for Li) and NH_4^+ have solid bicarbonate (solubility: > normal salt).



(2) hydrolysis

when adding insoluble carbonate to metallic salt except for alk ali metal 、 NH_4^+ and Tl:

① M^{n+} non-hydrolysis → carbonate

② M^{n+} **easily hydrolze ， and $K_{sp,M(OH)}$ little ，** for example Al^{3+} 、 Cr^{3+} and Fe^{3+} etc. → $M(OH)_n\downarrow$

$$2Al^{3+} + 3CO_3^{2-} + 3H_2O = 2Al(OH)_3\downarrow + 3CO_2\uparrow$$

③ some metal ion such as Cu^{2+}、 Zn^{2+}、 Pb^{2+} and Mg^{2+}etc. ， the solubility of hydroxide and carbonate is almost the sameless.

(Basic Carbonate)

$$2Cu^{2+} + 2CO_3^{2-} + H_2O = Cu_2(OH)_2CO_3 \downarrow + CO_2 \uparrow$$

(3) Heat Endurance

general ：

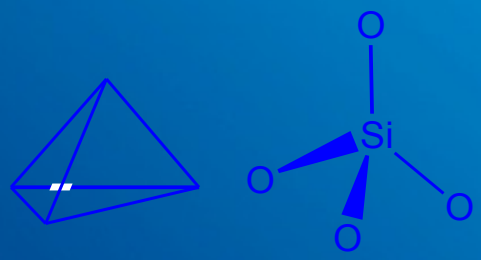
$$M_2CO_3 > MHCO_3 > H_2CO_3$$

二、 Silicic acid and Silicate

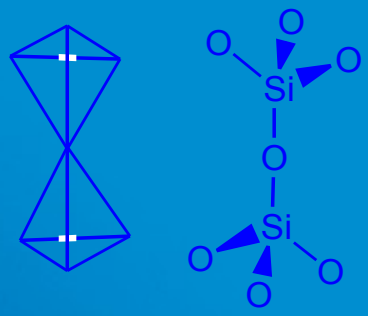
Siliicic acid

$x\ SiO_2 \cdot yH_2O$

- H_4SiO_4(x=1,y=2)
- H_2SiO_3(x=1,y=1)
- $H_6Si_2O_7$(x=2,y=3)
- $H_4Si_3O_8$(x=3,y=2)
- $H_2Si_2O_5$(x=2,y=1)

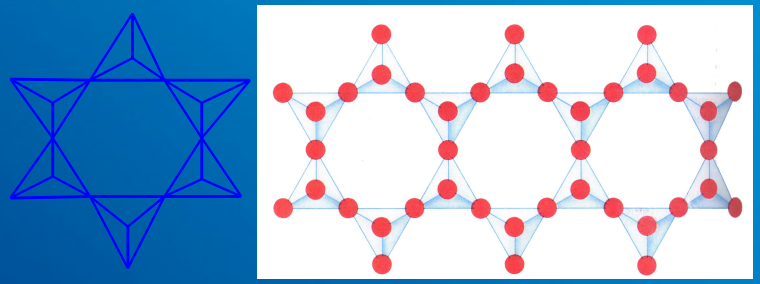


$[SiO_4]^{4-}$



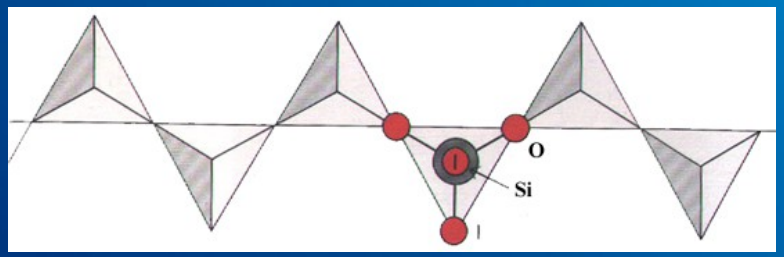
$[Si_2O_7]^{6-}$

$NaAl(SiO_3)_2$

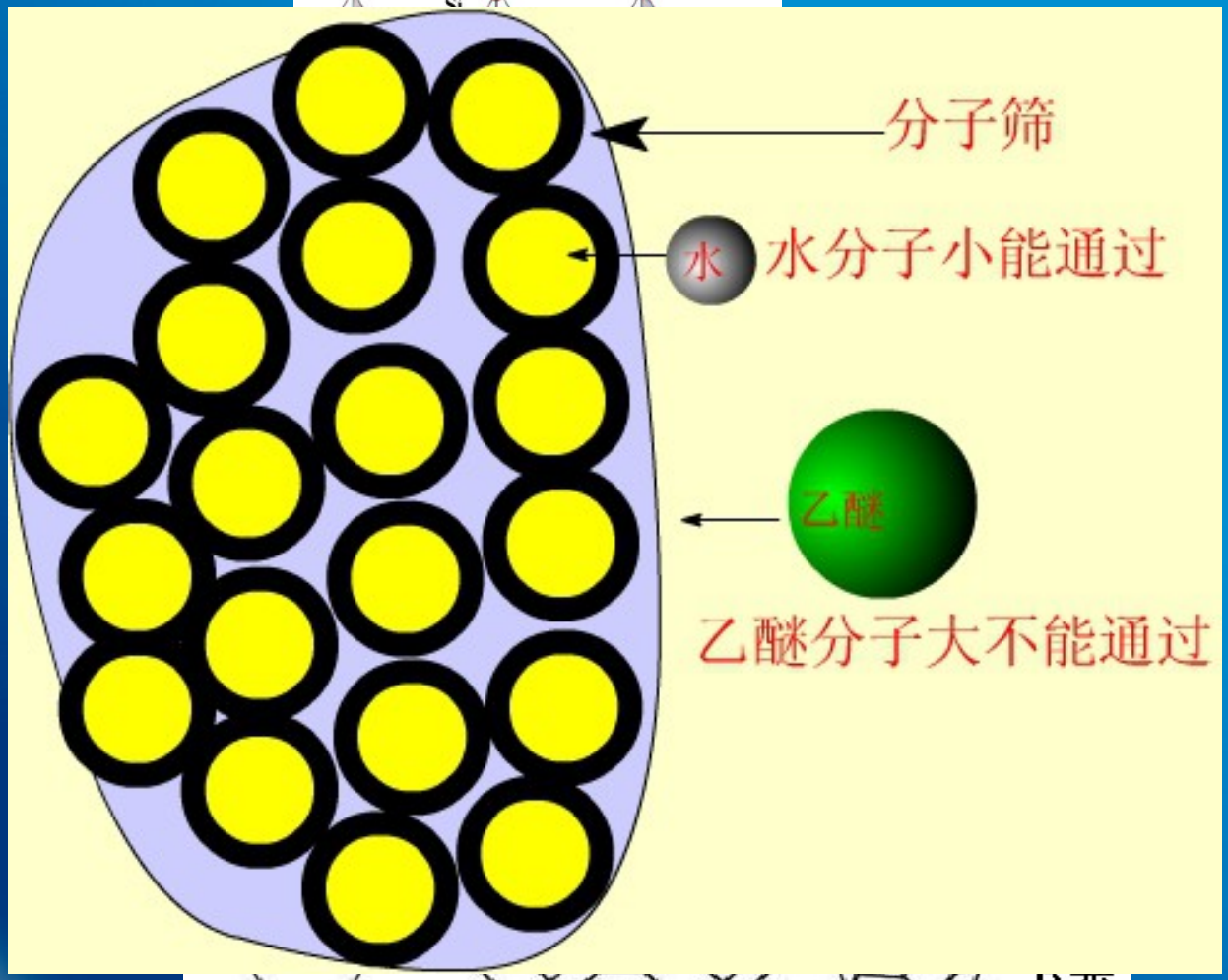


$[Si_6O_{18}]^{12-}$

Silicate { Solubleness : Na_2SiO_3 、 K_2SiO_3
Insolubleness : the majority are difficult in dissloving and colored.



Water Glass
$Na_2O \cdot nSiO_2$



六元环窗口

A型分子筛结构

三、Hydroxide and salt of Ge、Sn、Pb

acidity ↗

acidity ↗

$Ge(OH)_2$ white	$Sn(OH)_2$ white	$Pb(OH)_2$ white
$Ge(OH)_4$ brown	$Sn(OH)_4$ white	$Pb(OH)_4$ brown

basicity ↗

basicity ↗

Hydroxide are all amphoteric compounds.

$$Sn(OH)_2 + H^+ = Sn^{2+} + H_2O$$

$$Sn(OH)_2 + OH^- = [Sn(OH)_3]^-$$

$$Sn(OH)_2 + 2OH^-(excessive) = [Sn(OH)_4]^{2-}$$

$$\mathbf{2\,Bi^{3+} + 3\,[Sn(OH)_4]^{2-} + 6\,OH^-}$$

$$\mathbf{= 2\,Bi\downarrow + 3\,[Sn(OH)_6]^{2-}}$$

2 - 4 Hydride

SiH_4

:reductive、hydrolysis、autoigition.

(P_4、 P_2H_4、AsH_3、 B_2H_6、 SiH_4)

$$SiH_4 + 2O_2 \xrightarrow{autoignition} SiO_2 + 2H_2O$$

$$SiH_4 + 2MnO_4^- = 2MnO_2\downarrow + SiO_3^{2-} + H_2\uparrow + H_2O$$

$$SiH_4 + 8Ag^+ + 2H_2O = 8Ag\downarrow + SiO_2\downarrow + 8H^+$$

$$SiH_4 + (n+2)H_2O = SiO_2\cdot nH_2O + 4H_2\uparrow$$

2 - 5 Halide and Sulfide

一、 Halide

C 、 Si : MX_4

Ge 、 Sn 、 Pb : MX_4 and MX_2

1. MX_4

SiF_4 :colorless gas with irritant smell

, $SiCl_4$ 、 $GeCl_4$ and $SnCl_4$: liquid

(room temperature) 、 hydrolysis (smoke).

$$3SiF_4(g) + 4H_2O = H_4SiO_4\downarrow + 2H_2[SiF_6]$$

$$SiCl_4(l) + 3H_2O = H_4SiO_4\downarrow + 4HCl$$

$$SnCl_4 + (2+x)H_2O = SiO_2\cdot xH_2O\downarrow + 4HCl$$

(α *s*tannic acid)

2. MX_2

$SnCl_2$ easy hydrolysis , easy being oxidized.

$$SnCl_2 + H_2O = Sn(OH)Cl\downarrow (white) + HCl$$

$$2Sn^{2+} + O_2 + 4H^+ = 2Sn^{4+} + 2H_2O$$

Making up $SnCl_2$ liquor: dissolving into concentrated hydrochloric acid, diluting, adding tin powder.

$$Sn + Sn^{4+} = 2Sn^{2+}$$

$PbCl_2$ difficult to dissolve in cold water, soluble in water, can also dissolve in the hydrochloric acid.

$$PbCl_2 + 2HCl = H_2[PbCl_4]$$

PbI_2: a bright yellow silk of precipitation, soluble in boiling water, or generating complex and being dissolved in the solution of KI.

$$PbI_2 + 2KI = K_2[PbI_4]$$

二、Sn、Pb sulfide of

SnS_2	SnS	PbS
yellow	brown	black

Not dissolving into water and diluted acid, but can react with concentrated hydrochloric acid (coordiantion).

$$MS + 4HCl = H_2[MCl_4] + H_2S\uparrow$$

$$SnS_2 + 6HCl = H_2[SnCl_6] + 2H_2S\uparrow$$

SnS soluble in the liquor of

Na_2S_x or $(NH_4)_2S_x$ sulfostannate

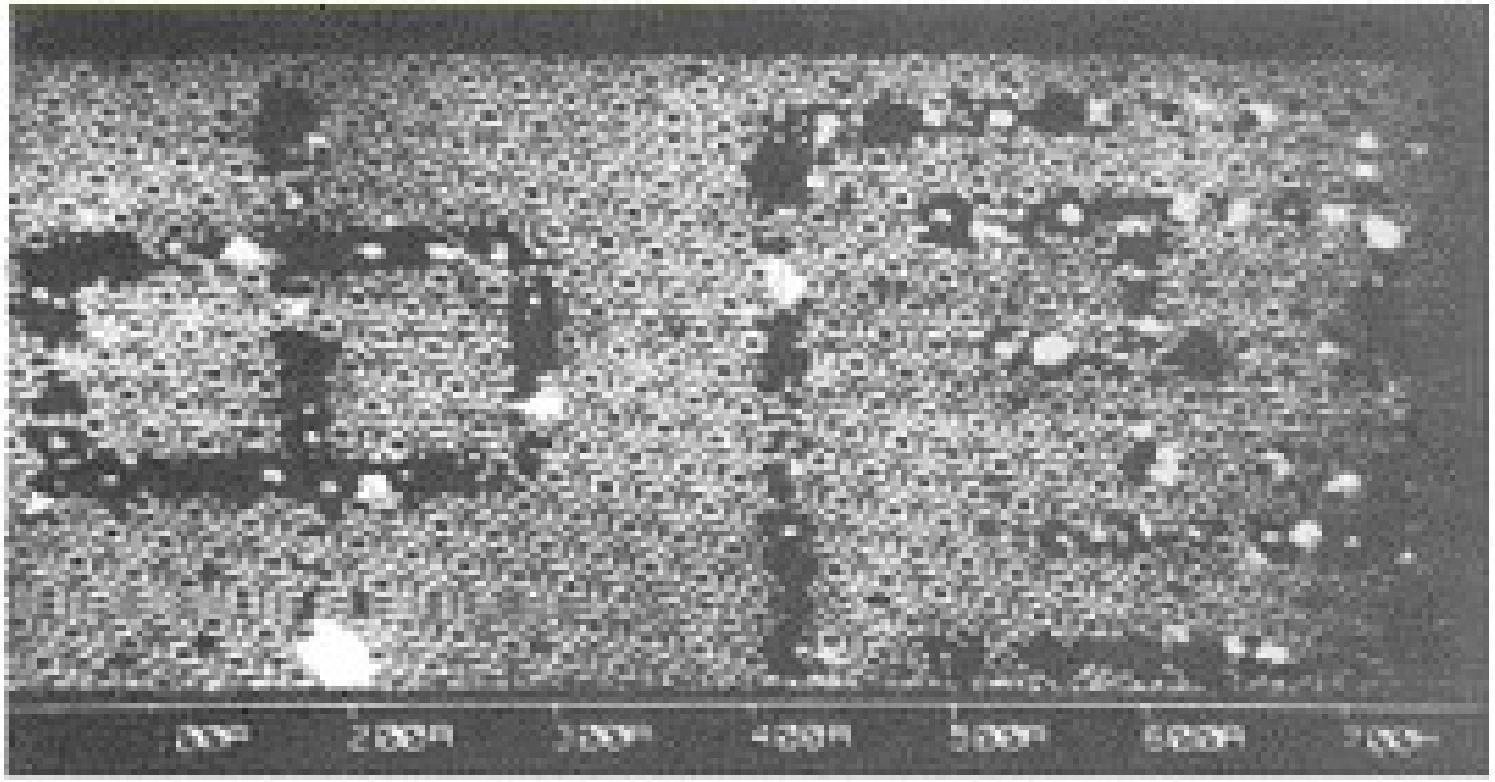
$$SnS + S_2^{2-} = SnS_3^{2-}$$

SnS_2 soluble in the liquor of

Na_2S or $(NH_4)_2S$ sulfostannate

$$SnS_2 + S^{2-} = SnS_3^{2-}$$

$$3PbS + 8H^+ + 2NO_3^- = 3Pb^{2+} + 3S\downarrow + 2NO\uparrow + 4H_2O$$



硅表面硅原子的排列