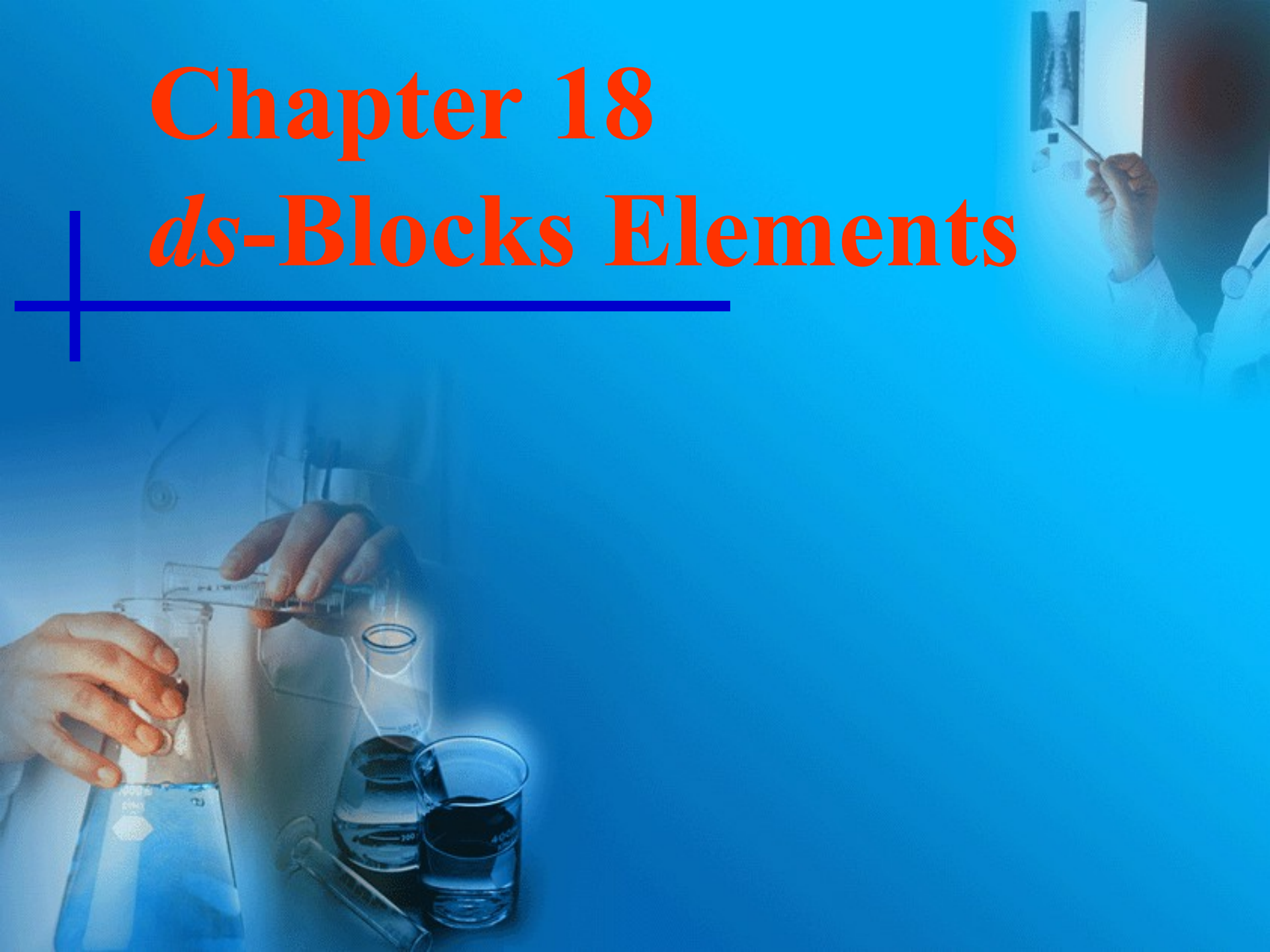
Chapter 18
ds-Blocks Elements



ds-block ： I B 、 II B subgrou

Period	I B	II B	
four	Cu	copper	zinc
five	Ag	Silver	cadmium
six	Au	gold	mercury

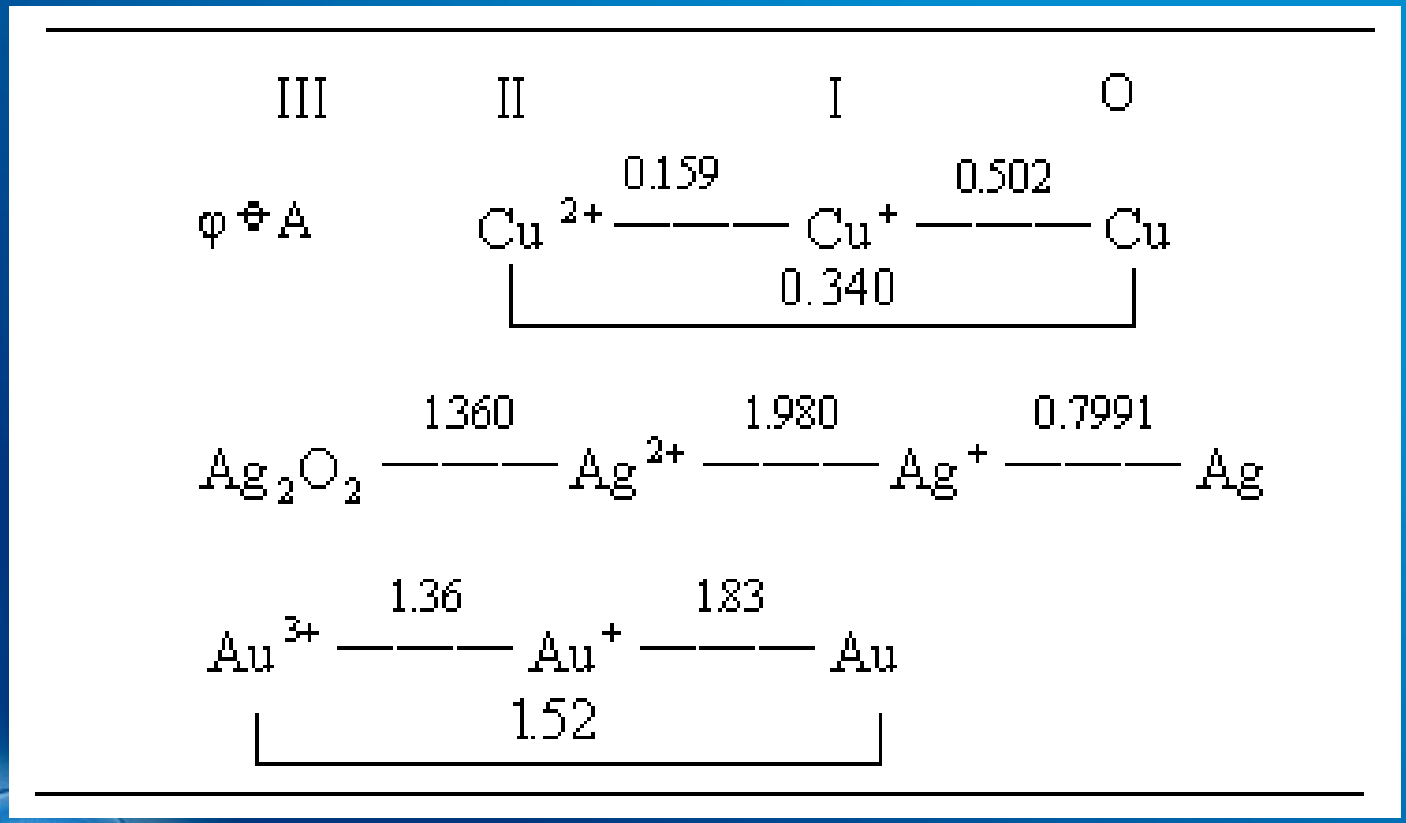
§18 — 1 Copper-grounp element

1–1 General characteristic

- Valence electron configuratio : $(n - 1)d^{10}$

- I_1 higher than I_1 of alkali : reason Z^* of IB ,higher
- Heat of sublimation and Melting point: higer than that of alkali reason : reason d electrons included in Metal-Metal bond
- Covalence and lattice energy: stronger than that of alkali
- Polarization effect: stronger than that of alkali
- Stability : higher than that of alkali

Common oxidation number ： Cu +2 、 Ag +1 、 A



Chemical activity: Cu>Ag>Au

1-2、 Chemical Properties

1. Reaction with oxygen

for copper $2\,Cu + O_2 + H_2O + CO_2 = Cu(OH)_2 \cdot CuCO_3$.

for Ag and Au : no reaction with O_2 of air heated

2. Reaction with H_2S

Cu and Ag can react with O_2 mixed by H_2S or S ,but Au can not.

$$4Ag + 2H_2S + O_2 = 2Ag_2S + 2H_2O$$

3. Reaction with acid

Cu, Ag, and Au can not be dissolved by dilute HCl acid or H_2SO_4, *but Cu can react with them* including air or coordination substance.

$$2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O$$

$$2Cu + 8HCl = 2H_3[CuCl_4] + H_2\uparrow$$

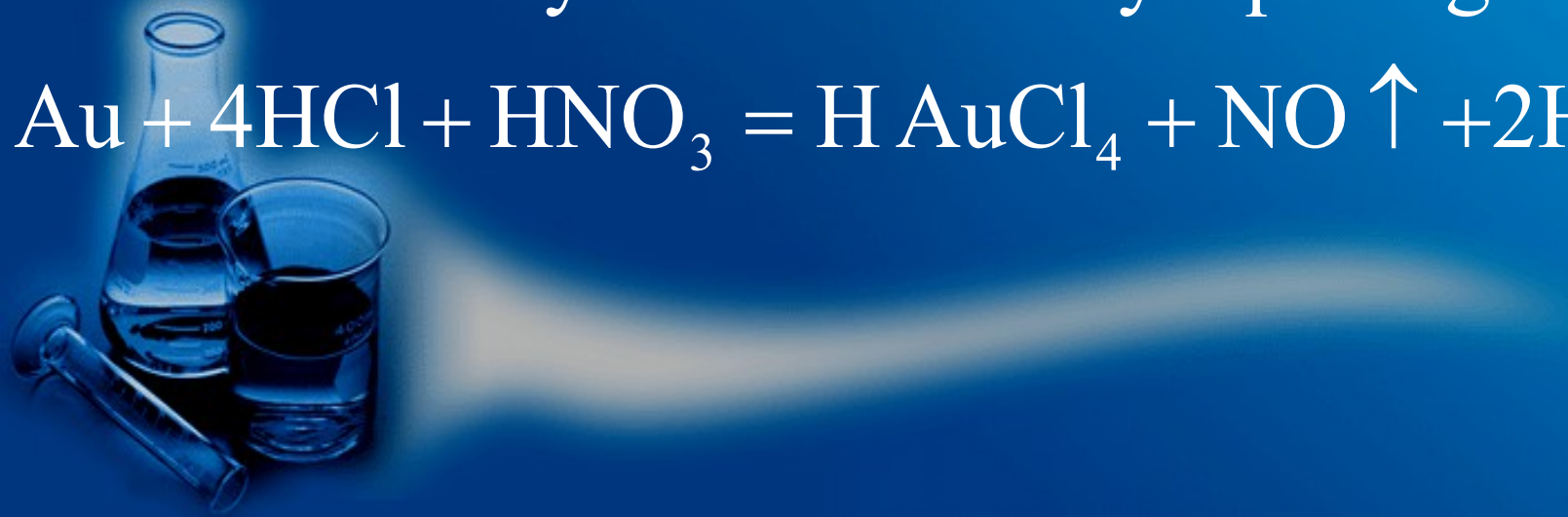
Cu and Ag can be dissolved easily by HNO_3 or hot H_2SO_4 *solution*,

$$Cu + 2H_2SO_4(hot, thick) = CuSO_4 + SO_2\uparrow + 2H_2O$$

$$3Ag + 4HNO_3 = 3AgNO_3 + NO\uparrow + 2H_2O$$

but Au can only be dissolved by aqua regia

$$Au + 4HCl + HNO_3 = H\,AuCl_4 + NO\uparrow + 2H_2O$$



4. Coordinated reaction of Ag 、 Au with KCN

$Ag(CN)_2^-$ $Au(CN)_4^-$

5. Coordinated reaction of Cu with NH_3H_2O

$$4Cu + O_2 + 8NH_3 + 2H_2O = 4Cu(NH_3)_2^+ + 4OH^-$$

colorless

↓ O_2

$Cu(NH_3)_4^{2+}$ blue

1–3 Important compounds of copper-group element

1.Oxidation number +1

Cu(I) : d^{10} , no d – d transition diamagnetic

1.1 oxide compound

Cu_2O Ag_2O

red dark brown

Covalent 、 hardly soluble

1).*Thermal stability : Cu_2O higher, Ag_2O lower*

$$2\,Ag_2O \xrightarrow{\Delta} 4\,Ag + O_2\uparrow$$

2). Cu_2O 、 Ag_2O can be dissolved by ammonia

$$Cu_2O + 4\,NH_3 + H_2O = 2\,Cu(NH_3)_2^+ + 2\,OH^-$$

$$\downarrow O_2$$

$$Cu(NH_3)_4^{2+}$$

$$Ag_2O + 4\,NH_3 + H_2O = 2[Ag(NH_3)_2]OH$$

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O$$

1.2 Hydroxides

$AgOH\ (white): stable\ at\ below - 45\,°C,$

decomposed at higer temperature than - 45°C

$CuOH\ (yellow): not\ stable, usually\ Cu_2O\ (red)$

1.3 nitrate

No nitrate of Cu(I)

$AgNO_3$

$$Ag + 2HNO_3(浓) = AgNO_3 + NO_2\uparrow + H_2O$$
$$3Ag + 4HNO_3(稀) = 3AgNO_3 + NO\uparrow + 2H_2O$$

$$2AgNO_3 \xrightarrow[\text{or } h\nu]{713K} 2Ag + 2NO_2\uparrow + O_2\uparrow$$

1.4 Halide

1.CuX

歧 化

CuF (red , soluble , dismutation)
CuCl , CuBr , CuI (white , insoluble)

Solubility : CuF>CuCl>CuBr > CuI
Covalence : weak strong

1). Preparation

$$2Cu^{2+} + 2X^- + SO_2 + 2H_2O \xrightarrow{\triangle} 2CuX\downarrow + 4H^+ + SO_4^{2-}$$

$$Cu^{2+} + 2HCl(浓) + Cu \xrightarrow{\triangle} 2H[CuCl_2]$$

H_2O → 泥黄色 $CuCl\downarrow$

$$2Cu^{2+} + 4I^- = 2CuI\downarrow + I_2$$

♦ 2).Chemical properties

i). Reaction with excessive X^-

$$CuCl+HCl=H[CuCl_2]$$

ii). CuCl solution dissolved in HCl absorbs CO

$$CO+CuCl+H_2O=Cu(CO)Cl$$

2.AgX

Solubility : All the halide compound AgX but **AgF** can not be dissolved by H_2O and dilute HNO_3.

Color : reason is Charge Transfer : L-M

Covalence : *weaker* F Cl Br I *stronger*

Chemical properties :

$$AgCl + 2\,NH_3 = [Ag(NH_3)_2]^+ + Cl^-$$

$$AgBr + 2\,S_2O_3^{2-} = [Ag(S_2O_3)_2]^{3-} + Br^-$$

$$AgI + 2\,CN^- = [Ag(CN)_2]^- + I^-$$

AgCN and AgSCN: insoluble ,

AgCN : reacted with excessive KCN:$[Ag(CN)_2]^-$

1.5 Sulfide

Cu_2S andAg_2S

black,

insoluble in water and non-oxidizing acid ，

soluble in hot and concentrated HNO_3 andKCN.

$$3Cu_2S + 16HNO_3(浓) \xrightarrow{\Delta}$$

$$6Cu(NO_3)_2 + 3S\downarrow + 4NO\uparrow + 8H_2O$$

$$3Ag_2S + 8HNO_3(浓) \xrightarrow{\Delta}$$

$$6AgNO_3 + 3S\downarrow + 2NO\uparrow + 4H_2O$$

$$M_2S + 4CN^- = 2[M(CN)_2]^- + S^{2-}$$

1.6 Coordination Compound

centerbody ： Cu^{+} 、 Ag^{+} : d^{10}

configuration ， *s* ， *p empty orbital*

Ligand ： X^{-} 、 NH_3 、 $S_2O_3^{2-}$ 、 CN^{-} etc

Coordination Number ： 2 、 4

Structure ： line or tetrahedron

Coordination Compound of Cu^+ 、 Ag^+ 、 Au^+

Soft acid：　Cu+ 、 Ag+ 、 Au+

1). Cu^+

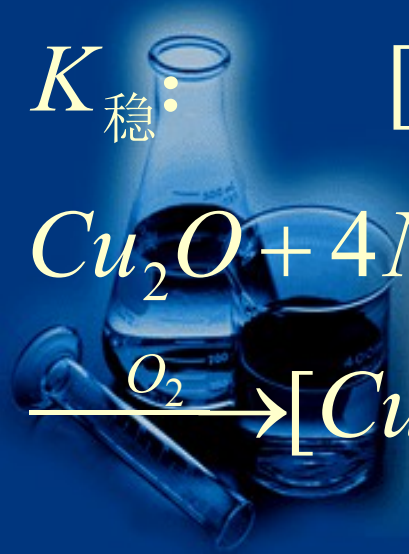
$$Cu^+ + X^- \rightarrow CuX\downarrow \xrightarrow{X^-} [CuX_2]^-$$

precipitation　　was dissolved

$K_{稳}$:　　$[CuCl_2]^- < [CuBr_2]^- < [CuI_2]^-$

$$Cu_2O + 4NH_3 \cdot H_2O \rightarrow 2[Cu(NH_3)_2]^+ (colorless)$$

$$\xrightarrow{O_2} [Cu(NH_3)_2]^{2+} (deep\text{-}blue)$$



2) Ag^+

i)halide

$$Ag^+ + X^- \rightarrow AgX\downarrow \xrightarrow{X^-} [AgX_2]^-$$

$K_{稳}$: $[AgCl_2]^- < [AgBr_2]^- < [AgI_2]^-$

ii)other ligand

$$\left.\begin{matrix} AgCl \\ AgBr \\ AgI \end{matrix}\right\} \xrightarrow{NH_3\cdot H_2O} \left\{\begin{matrix} [Ag(NH_3)_2]^+ \\ \left.\begin{matrix} AgBr \\ AgI \end{matrix}\right\} \xrightarrow{S_2O_3^{2-}} \left\{\begin{matrix} [Ag(S_2O_3)_2]^{3-} \\ AgI \xrightarrow{CN^-} [Ag(CN)_2]^- \end{matrix}\right. \end{matrix}\right.$$

3) Au^+

$$Au + 4CN^- + \frac{1}{2}O_2 + H_2O = 2Au(CN)_2^- + 2OH^-$$

1.7 oxidization of Ag^+

H_3PO_3
N_2H_4
NH_2OH

reaction with Ag^+ produce $Ag\downarrow$

2. Oxidation Number +2

2.1 $Cu(OH)_2$ and CuO

$Cu(OH)_2$: light blue flocculent precipitate

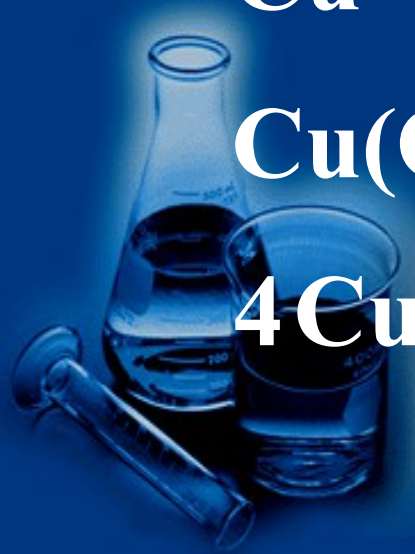
淡 蓝 色 絮 状沉 淀

CuO : black precipitate

$$Cu^{2+} + 2OH^- = Cu(OH)_2 \downarrow$$

$$Cu(OH)_2 \xrightarrow{353\,K} CuO + H_2O$$

$$4CuO \xrightarrow{\rangle 1273\,K} 2Cu_2O + O_2 \uparrow$$



Chemical Properties

1). $Cu(OH)_2$ weakly amphoteric compound

微弱两性化合物

$$Cu(OH)_2 + 2OH^-(concentrated) = [Cu(OH)_4]^{2-}$$

能溶纤维，遇酸后又析出，用来制人造丝

2). oxidizability

$$Cu(OH)_4^{2-} + C_6H_{12}O_6 = CuOH + 2H_2O + C_6H_{12}O_7$$

$$\downarrow$$

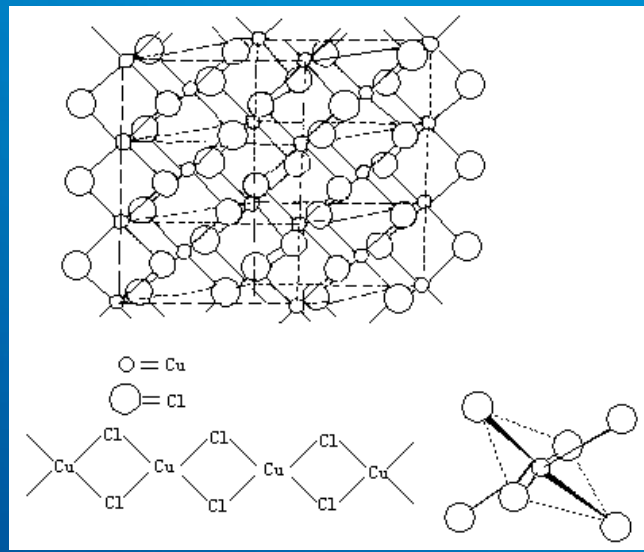
$Cu_2O\downarrow$ （ red ）

2.2 CuX_2

$$CuCl_2 \cdot 2H_2O \xrightarrow[\text{HCl flow}]{412\sim423\ K} CuCl_2 + 2H_2O$$

Yellow-brown

anhydrous CuX_2 : covalent compound



Chemical properties

1) anhydrous $CuCl_2$ decompose

:

$$2CuCl_2 \xrightarrow{773K} 2CuCl + Cl_2\uparrow$$

2)Easy to be dissolved by

H_2O, CH_3CH_2OH, acetone :

Highly concentrated $CuCl_2$: yellow-green

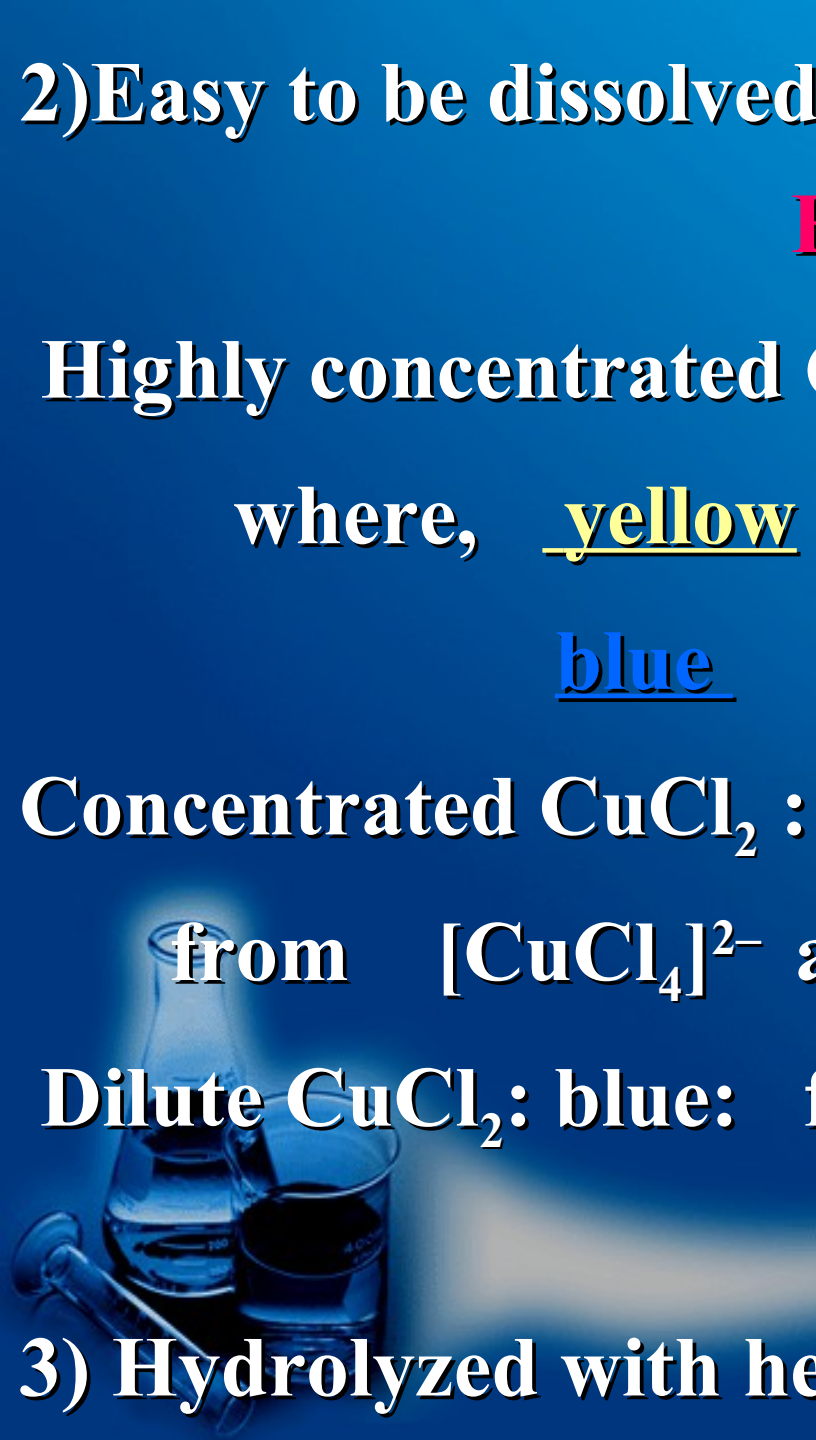
where, yellow from $[CuCl_4]^{2-}$ ions

blue from $Cu(H_2O)_4]^{2+}$ ions

Concentrated $CuCl_2$: green

from $[CuCl_4]^{2-}$ and $[Cu(H_2O)_4]^{2+}$

Dilute $CuCl_2$: blue: from $[Cu(H_2O)_4]^{2+}$



3) Hydrolyzed with heat

2.3 copper sulfate

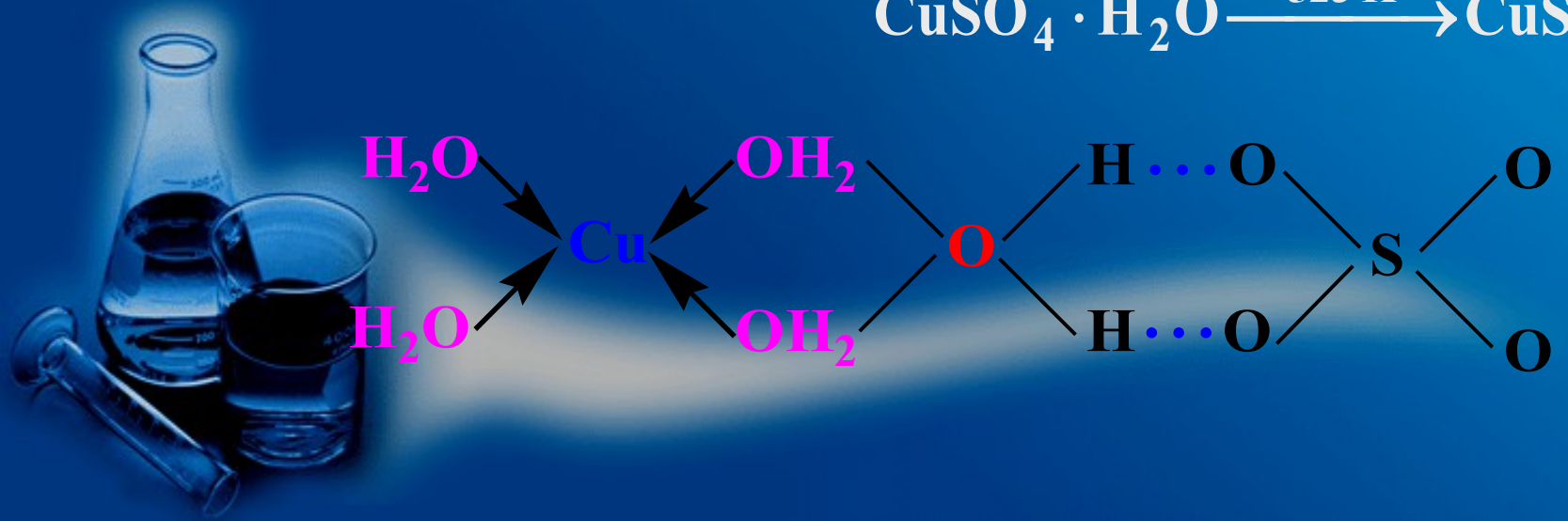
$$Cu + 2H_2SO_4(浓) \xrightarrow{\triangle} CuSO_4 + SO_2\uparrow + 2H_2O$$

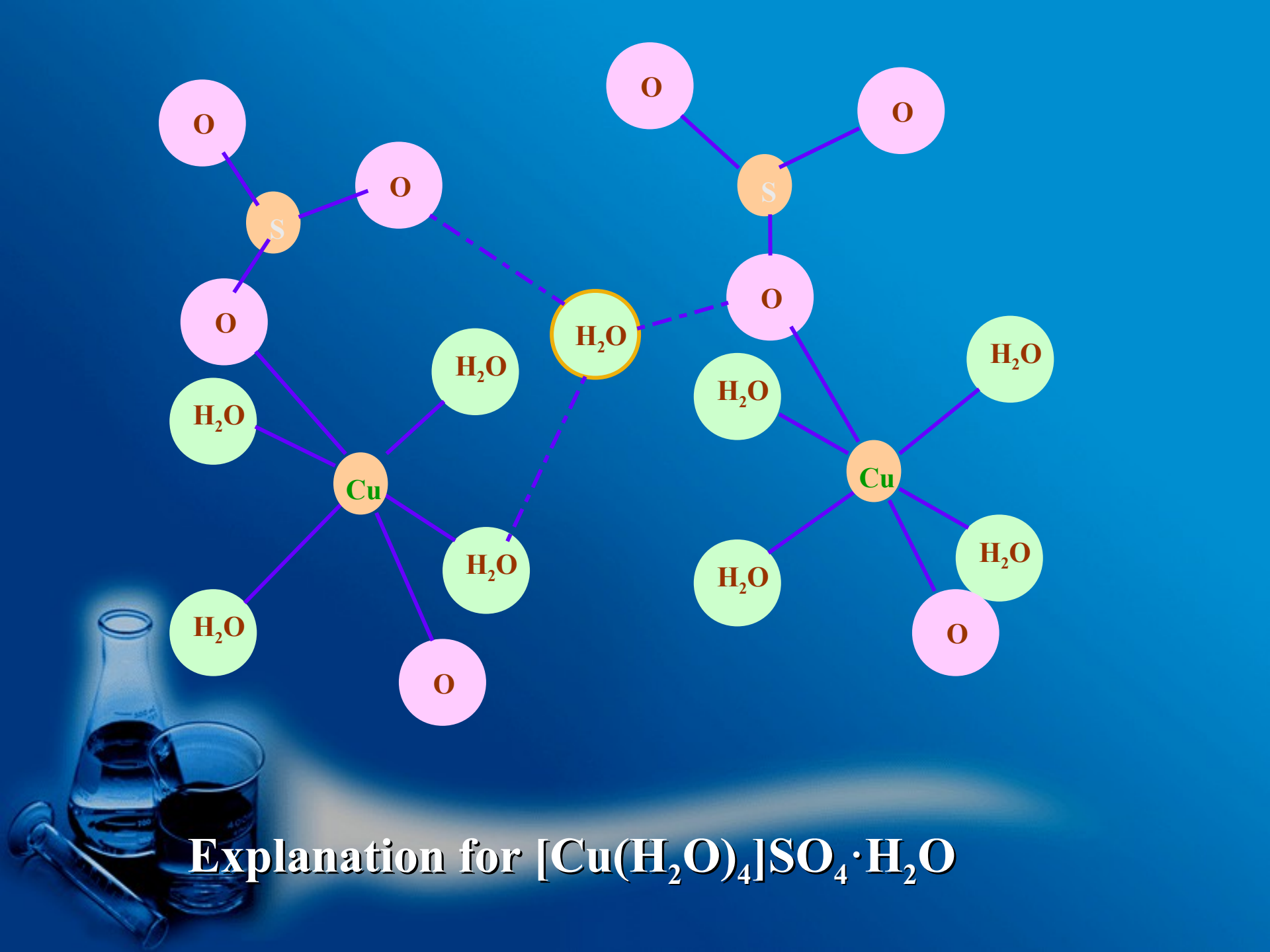
$$2Cu + 2H_2SO_4(稀) + O_2 \xrightarrow{\triangle} 2CuSO_4 + 2H_2O$$

$CuSO_4 \cdot 5H_2O$

$$CuSO_4 \cdot 5H_2O \xrightarrow{375\,K} CuSO_4 \cdot 3H_2O \xrightarrow{423\,K}$$

$$CuSO_4 \cdot H_2O \xrightarrow{523\,K} CuSO_4$$





Explanation for $[Cu(H_2O)_4]SO_4 \cdot H_2O$

Chemical properties

$$CuSO_4 \xrightarrow{NH_3 \cdot H_2O} Cu(OH)_2SO_4\downarrow \text{(light blue)}$$

$$Cu(OH)_2SO_4 \xrightarrow{NH_3 \cdot H_2O} [Cu(NH_3)_4]^{2+}$$

Deep blue

$$2Cu^{2+} + [Fe(CN)_6]^{4-} = Cu_2[Fe(CN)_6]\downarrow$$

brick red

Detection of Cu^{2+}

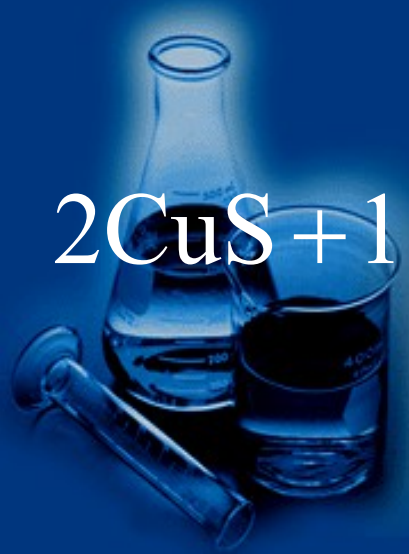
2.4、Cu

S CuS(Black) $K_{sp}^{\theta} = 8.5 \times 10^{-45}$

CuS can be dissolved by only hot nitrate acid or concentrated NaCN

$$3CuS + 2NO_3^- + 8H^+ \xrightarrow{\triangle} 3Cu^{2+} + 2NO\uparrow + 3S\downarrow + 4H_2O$$

$$2CuS + 10CN^- = 2Cu(CN)_4^{3-} + 2S^{2-} + (CN)_2\uparrow$$



2.5 Coordination Compound

Cu^{2+} + CN^-

$$2Cu^{2+} + 4CN^- = 2CuCN\downarrow + (CN)_2\uparrow$$

(white)

CN^-

$Cu(CN)_2^-$

CN^- can be used to separate Cu^{2+} and Cd^{2+}

Cu^{2+} *reacts with* reductive ligand and produces compound of Cu^{+}

CN^-, SCN^-, I^- $\xrightarrow{Cu^{2+}}$

$$2Cu^{2+} + 4CN^- = (CN)_2 + 2CuCN\downarrow$$

$$CuCN + 3CN^- = [Cu(CN)_4]^{3-}\text{(四面体)}$$

$$2Cu^{2+} + 4SCN^- = (SCN)_2 + 2CuSCN\downarrow$$

$$CuSCN + 3SCN^- = [Cu(SCN)_2]^-$$

$$2Cu^{2+} + 4I^- = I_2 + 2CuI\downarrow$$

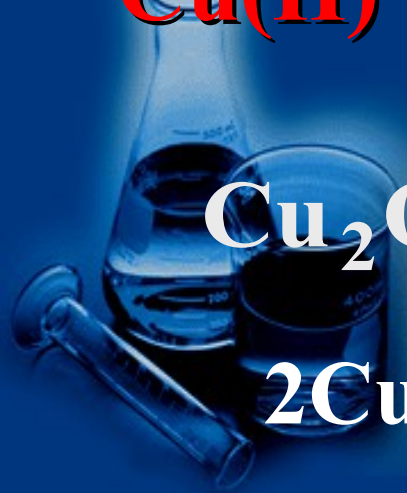
$$I^- + CuI = [CuI_2]^-$$

3. Cu(II) and Cu(I)

$Cu^{2+} \xrightarrow{0.153V} Cu^{+} \xrightarrow{0.52V} Cu$ $\qquad$ $I_2 \xrightarrow{0.535V} I^-$

$$2Cu^{2+} + 4I^- = 2CuI\downarrow + I_2 \quad K_{sp}^{\theta} = 5.06 \times 10^{-12}$$

▼ 1). in solution ： **stability Cu(I) < Cu(II)**



$$Cu_2O + H_2SO_4 \xrightarrow{\textit{caused by hydration heat}} CuSO_4 + Cu + H_2O$$

$$2Cu^{+} \longrightarrow Cu^{2+} + Cu \quad K^{\theta} = 1.2 \times 10^{6}$$

▼2). Coordination and precipitate can stabilize the Cu(I) compound.

Caused by reduction of electrode potential

$$Cu_2O + 2HCl = 2CuCl\downarrow + H_2O$$

$$H^+$$

$$H[CuCl_2]$$

3).high temperature or solid state ：

stability Cu(I) > Cu(II)

Caused by higher I_2 of Cu(I) with $3d^{10}$ configuration

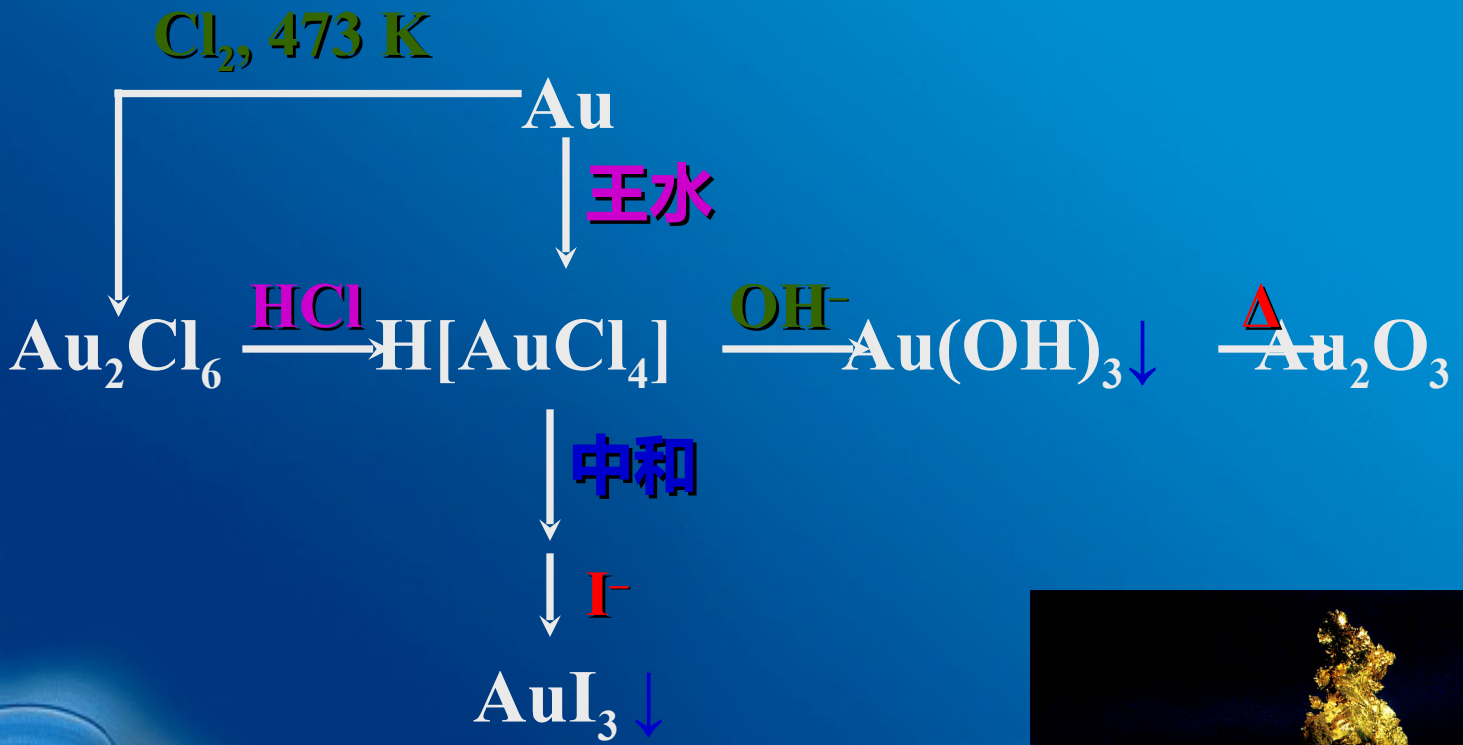
$$Cu_2(OH)_2CO_3 \xrightarrow{200°C} 2CuO(s,棕黑) + CO_2 + H_2O$$

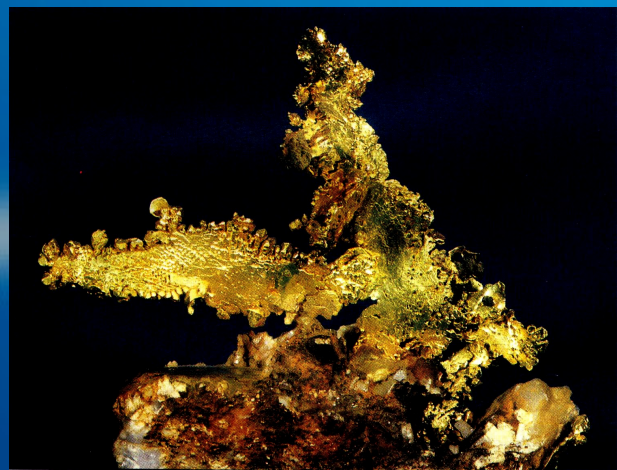
$$4CuO(s) \xrightarrow{>1000°C} 2Cu_2O(s,暗红) + O_2\uparrow$$

$$\xrightarrow{1800℃} 4Cu(s) + O_2\uparrow$$

$$2CuCl_2(s) \xrightarrow{990°C} 2CuCl(s) + Cl_2\uparrow$$

4. Compounds with oxidation number + 3





§18 — 2 Zinc-Grounp Element

1–1 General Properties

1、Electron Configuration

Zn Cd Hg

- valence electron: $(n-1)d^{10}ns^2$
- higher Z^* (effective charge) :
  - I_1 higher than I_1 of IIA element
  - and radius less than that of IIA element

2、 *Reducibility of Metal*

$Zn^{2+} + 2e^- = Zn$ $\varphi^\ominus = -0.786V$

$Cd^{2+} + 2e^- = Cd$ $\varphi^\ominus = -0.4026V$

$Hg_2^{2+} + 2e^- = 2Hg$ $\varphi^\ominus = 0.7986V$

$2Hg^{2+} + 2e^- = 2Hg_2^{2+}$ $\varphi^\ominus = 0.905V$

$Ca^{2+} + 2e^- = Ca$ $\varphi^\ominus = -2.76V$

Reducibility :

- **far weaker than reducibility of alkali earth metal**
- **Zn→Cd→Hg reducibility :weaker**

3、significant polarization effect

- 1) IIB: oxidation number:+II(Hg +I)

- 2) IIB: stronger polarization
- stronger deformability
- stronger covalence effect

3) Acid-base properties

- $Be(OH)_2$ and $Zn(OH)_2$: amphoteric hydroxide 两性氢氧化物
-

4) Coordination effect

	硝酸盐	碳酸盐	硫酸盐	水解性
IIA	易溶	难溶	微溶或难溶	钙锶钡的盐不水解
IIB	易溶	难溶	易溶	有一定程度的水解

1–2 Simple Substance

1、 physical property

1) MP and BP : Zn 、 Cd 、 Hg lower 。

caused by M—M bond

Mercury

✓ *Superconductor Metal firstly found at 4.2K*

✓ *First M—M bond in Hg_2^{2+} ion*

Amalgam 汞齐

Hg can dissolve many kinds of metal :

Na 、
K 、 Ag 、 Au 、 Zn 、 Cd 、 Sn 、 Pb 、 Tl

2. Chemical Properties

- **1) reaction with O_2**

Wet air ：

$$4Zn + 2O_2 + CO_2 + 3H_2O$$

$$= ZnCO_3 \cdot 3Zn(OH)_2 \text{ 致密}$$

$$2Zn + O_2 \xrightarrow{\triangle} 2ZnO(s, white)$$

$$2Cd + O_2 \xrightarrow{\triangle} 2CdO(s, red - brown)$$

$$2Hg + O_2 \underset{> 773\ K}{\overset{\triangle \text{ 至沸}}{\rightleftharpoons}} 2HgO(s\ ,\ red\ 、\ yellow\ )$$

Stability: ZnO>CdO>HgO

caused by polarization of metal

- 2) reaction with S

$M + S \longrightarrow MS$

ZnS (white)
CdS (yellow)
HgS (red ，朱砂)
(black ，辰砂)

辰砂

- 3) reaction with OH^-,NH_3

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

$$Zn + 4NH_3 + 2H_2O = Zn(NH_3)_4^{2+} + H_2\uparrow + 2OH^-$$

- 3) reaction with acid

- Zn 、 Cd can be dissolved by dilute HCl or H_2SO_4

- Hg can only be dissolved by hot and concentrated H_2SO_4 or HNO_3

$$M + 2H^+(\text{稀}) = M^{2+} + H_2\uparrow \quad (M = Zn, Cd)$$

$$Hg + 2H_2SO_4(\text{热浓}) = HgSO_4 + SO_2\uparrow + 2H_2O$$

$$Hg + 4HNO_3(\text{浓}) = Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

$$3Hg + 8HNO_3(\text{稀,过量}) = 3Hg(NO_3)_2 + 2NO\uparrow + 4H_2O$$

$$6Hg(\text{过量}) + 8HNO_3(\text{冷,稀}) = 3Hg_2(NO_3)_2 + 2NO\uparrow + 4H_2O$$

1–3 Important compound of Zinc-group

Stronger polarization and deformability ⇒

$$\text{compound}\begin{cases}\text{colour}:\text{deeper}\\ \text{solubility}:\text{lower}\end{cases}$$

ZnS	CdS	HgS
白，难溶	黄，难溶	红或黑，极难溶
ZnI_2	CdI_2	HgI_2
无色，易溶	黄，可溶	红或黄，微溶
ZnO	CdO	HgO
白，难溶	棕灰，难溶	红或黄，极难溶

1、 compound with oxidation number +2

1)hydroxide and oxide

i) For Zn and Cd

$$Zn^{2+} \underset{H^+}{\overset{\text{适量 } OH^-}{\rightleftharpoons}} Zn(OH)_2\downarrow \text{(白)} \xrightarrow{\text{过量 } OH^-} Zn(OH)_4^{2-}$$

amphoteric compound

两性化合物

$Zn(OH)_2 \xrightarrow{\triangle} ZnO(s)$ 白色颜料，晶体缺陷

$$Cd^{2+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Cd(OH)_2\downarrow \xrightarrow{\Delta} CdO$$

weakly alkaline

$$M^{2+} + 2\,NH_3\cdot H_2O = M(OH)_2\downarrow + 2\,NH_4^+$$

$$(M = Zn, Cd)$$

$$M(OH)_2 + 2\,NH_4^+ + 2\,NH_3 = M(NH_3)_4^{2+} + 2\,H_2O$$

可用OH^-分离Zn^{2+}与Cd^{2+}，而不能用$NH_3\cdot H_2O$

ii) For Hg

$$Hg^{2+} \xrightarrow{OH^-} HgO(s,黄) \xrightarrow{400℃} Hg(s) + \frac{1}{2}O_2$$

$$Hg(NO_3)_2 + NaCO_3 \xrightarrow{\triangle} HgO\downarrow + CO_2\uparrow + 2NaNO_3$$

红

$$2Hg(NO_3)_2 \xrightarrow{缓慢加热} 2HgO\downarrow + 4NO_2\uparrow + O_2\uparrow$$

红

regularity

a. Thermal stability： ZnO>CdO>HgO

b. Thermal stability ： $Zn(OH)_2$>$Cd(OH)_2$>Hg(OH

总极化作用：Zn<Cd<Hg

2)、 halide

i) $ZnCl_2$

Solubility: $ZnCl_2$ the solid salt with the highest solubility (283K, 333g/100gH_2O)

$ZnCl_2$ easy to hydrolyze, acidic

$$ZnCl_2 \cdot H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl$$

$$ZnCl_2 \cdot H_2O \xrightarrow{\Delta, HCl} ZnCl_2$$

$ZnCl_2$ 浓溶液称为“熟镪水”，焊接除锈

$$ZnCl_2 + H_2O = H[ZnCl_2(OH)]$$

$$FeO + 2H[ZnCl_2(OH)] = Fe[ZnCl_2(OH)] + H_2O$$

ii). $HgCl_2$ (升汞)

$HgCl_2$ white needle crystal,
slightly soluble,
highly toxic

$$HgCl_2 + 2\,Cl^-\,(excessive) = HgCl_4^{2-}$$

precipitation dissolved

a). hydrolyzation

$HgCl_2 + H_2O = Cl{-}Hg{-}OH + HCl$

b). ammonolysis

$$HgCl_2 + 2NH_3 = Cl{-}Hg{-}NH_2\downarrow + NH_4Cl$$

white

NH_4Cl → $[Hg(NH_3)_4]^{2+}$

$$HgCl_2 + 4NH_3 \xrightarrow{NH_4Cl} [Hg(NH_3)_4]^{2+} + 2Cl^-$$

precipitation — dissolved

c). oxidizability

Used to detect Hg^{2+}

$$2HgCl_2 + SnCl_2 + 2HCl = Hg_2Cl_2\downarrow + H_2[SnCl_6]$$

white

$$Hg_2Cl_2 + SnCl_2 + 2HCl = 2Hg\downarrow + H_2[SnCl_6]$$

black

iii) $Hg(NO_3)_2$

unstable

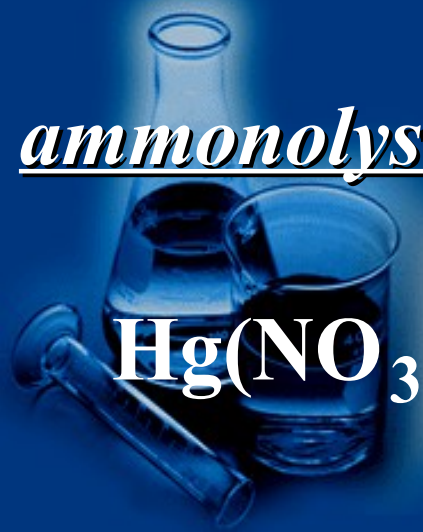
$$2\,Hg(NO_3)_2 \xrightarrow{\Delta} 2\,HgO + 4\,NO_2\uparrow + O_2\uparrow$$

hydrolysis

$$Hg(NO_3)_2 + H_2O = Hg(OH)NO_3 + HNO_3$$

ammonolysis

$$Hg(NO_3)_2 + 2\,NH_3 = HgNH_2NO_3\downarrow + NH_4NO_3$$



iv) mercuric iodide

$$Hg^{2+} + 2\ I^- = HgI_2\downarrow(\ \text{orange-red}\ )$$

$$\downarrow\ I^-$$

$$[HgI_4]^{2-}\ (\ \text{colorless}\ )$$

solution of $K_2[HgI_4]$ in KOH called "Nessler reagent"

used to detect micro NH_4^+ :

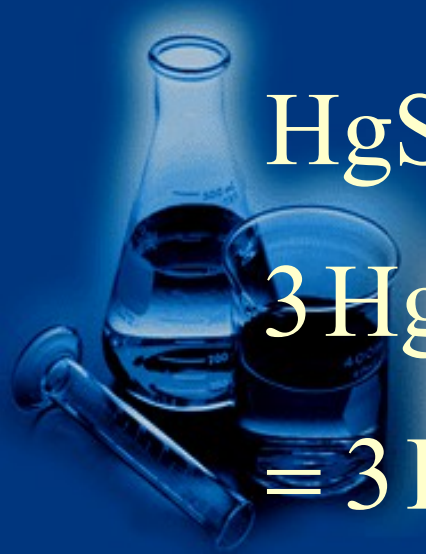
$$NH_4^- + 2\,[HgI_4]^{2-} + 4\,OH^- = \left[\begin{array}{c} Hg \\ O \quad NH_2\ I \\ Hg \end{array}\right]\downarrow + 7I^- + 3H_2O$$

红色 ， 碘化氨基 · 氧合二汞 (II)

3) . Sulfide

Sulfide with lowest solubility

	ZnS	CdS	HgS
	white	yellow	black
K_{sp}^{θ} :	1.2×10^{-23}	3.6×10^{-39}	3.5×10^{-52}
	溶于稀 HCl 不溶于 HAc	溶于浓HCl 、 浓H_2SO_4 、 热稀 HNO_3	溶于王水、 浓Na_2S 溶液



$$HgS + Na_2S = Na_2[HgS_2]$$

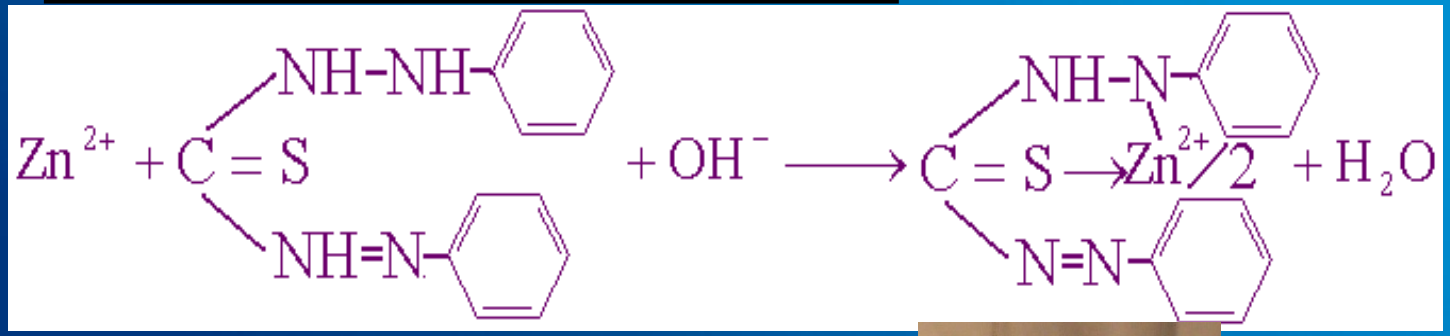
$$3HgS + 8H^+ + 2NO_3^- + 12Cl^- = 3HgCl_4^{2-} + 2NO\uparrow + 3S\downarrow + 4H_2O$$

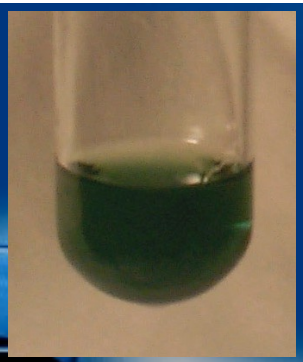
$ZnS \cdot BaSO_4$ 锌钡白（立德粉）

$ZnSO_4 + BaS = ZnS \cdot BaSO_4$

CdS 镉黄，可做颜料。颜色变化来自晶格缺陷

- Zn^{2+} 的鉴定（碱性条件）





二苯硫腙

(CCl_4 溶液)

绿色

粉红色 （水层）

棕色 (CCl_4 层）

HgS ，红与黑的颜色变化来自晶格转变

4、 Coordination compound

M^{2+} soft acid ， form ML_4

$$Zn^{2+} + 4CN^- \longrightarrow Zn(CN)_4^{2-} \qquad K_{稳}^{\theta} = 5.0 \times 10^{16}$$

$$Cd^{2+} + 4CN^- \longrightarrow Cd(CN)_4^{2-} \qquad K_{稳}^{\theta} = 1.3 \times 10^{18}$$

$$Hg^{2+} + 4CN^- \longrightarrow Hg(CN)_4^{2-} \qquad K_{稳}^{\theta} = 2.5 \times 10^{41}$$

Hg^{2+} stronger polarization and deformability

- stability of halide of Hg2+ ： $Cl^- < Br^- < I^-$

$$Hg^{2+} + 4Cl^- \longrightarrow HgCl_4^{2-} \qquad K_{稳}^{\theta} = 1.2 \times 10^{15}$$

$$Hg^{2+} + 4I^- \longrightarrow HgI_4^{2-} \qquad K_{稳}^{\theta} = 6.8 \times 10^{29}$$

2、 Compound with oxidation number +1

Hg_2Cl_2 (甘汞) : white powder , nontoxic
slightly soluble ,
decompose with light

$^{+}Hg \cdot - \cdot Hg^{+}$: *linear*,

no sin *gle electron*,

anti – magnetic

$$Hg_2Cl_2 \xrightarrow{h\nu} HgCl_2 + Hg$$

ammonolysis ： to detect Hg_2^{2+} ion

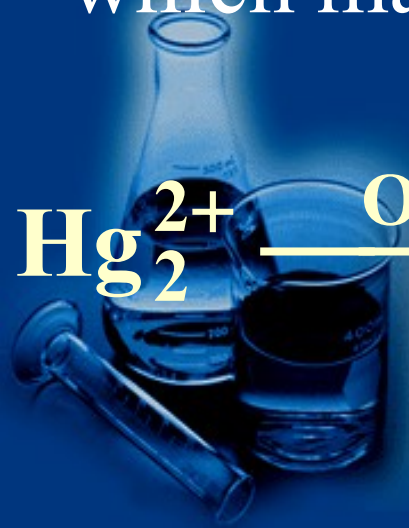
$$Hg_2Cl_2 + 2\,NH_3$$

$$= Cl\text{–}Hg\text{–}NH_2\downarrow(white) + NH_4Cl + Hg\downarrow(black)$$

Condition： *with* Cl^- *ion*，

can produce pricipitate of lower Ksp ,

which make equilibrium move forward



$$Hg_2^{2+} \xrightarrow{OH^-} Hg_2O(s,褐) \longrightarrow HgO(s) + Hg$$

$Hg_2(NO_3)_2$ ：无色，易溶于水 ，可提供 Hg_2^{2+}。

Unstability ：

$$Hg_2(NO_3)_2 \xrightarrow{\Delta} 2HgO + 2NO_2\uparrow$$

hydrolyzation

$$Hg_2(NO_3)_2 + H_2O = Hg_2(OH)NO_3 + HNO_3$$

ammonolysis

$$Hg_2(NO_3)_2 + 2NH_3 = HgNH_2NO_3\downarrow + Hg\downarrow + NH_4NO_3$$

reducibility :

easy to be oxidized to Hg^{2+} *by air*

$$Hg_2(NO_3)_2 + O_2 + 4HNO_3 = 4Hg(NO_3)_2 + 2H_2O$$

检验 $Hg_2^{2+} \xrightarrow{I^-} Hg_2I_2\downarrow \longrightarrow HgI_2 + Hg$

草绿色

过量 I^- → $HgI_4^{2-} + Hg\downarrow$

3. Hg(Ⅰ) and Hg(Ⅱ)

add coordination or precipitation reagent of Hg^{2+}

1)、$Hg_2^{2+} \rightarrow Hg^{2+}$:

$$Hg_2^{2+} + 2OH^- = HgO\downarrow + Hg\downarrow + H_2O$$

$$Hg_2^{2+} + H_2S = HgS\downarrow + Hg\downarrow + 2H^+$$

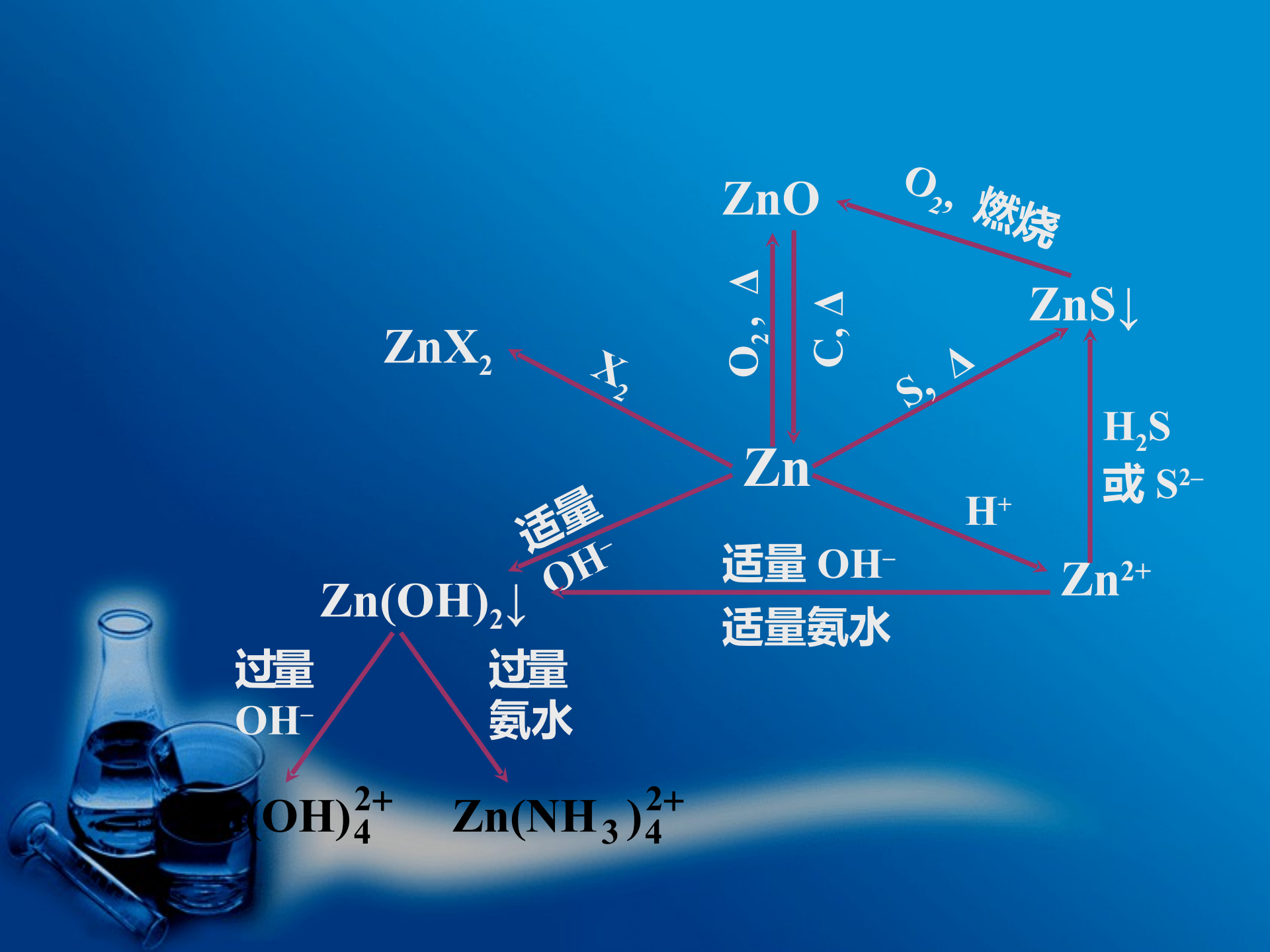
$$Hg_2^{2+} + 4I^-(excessive) = HgI_4^{2-} + Hg\downarrow$$

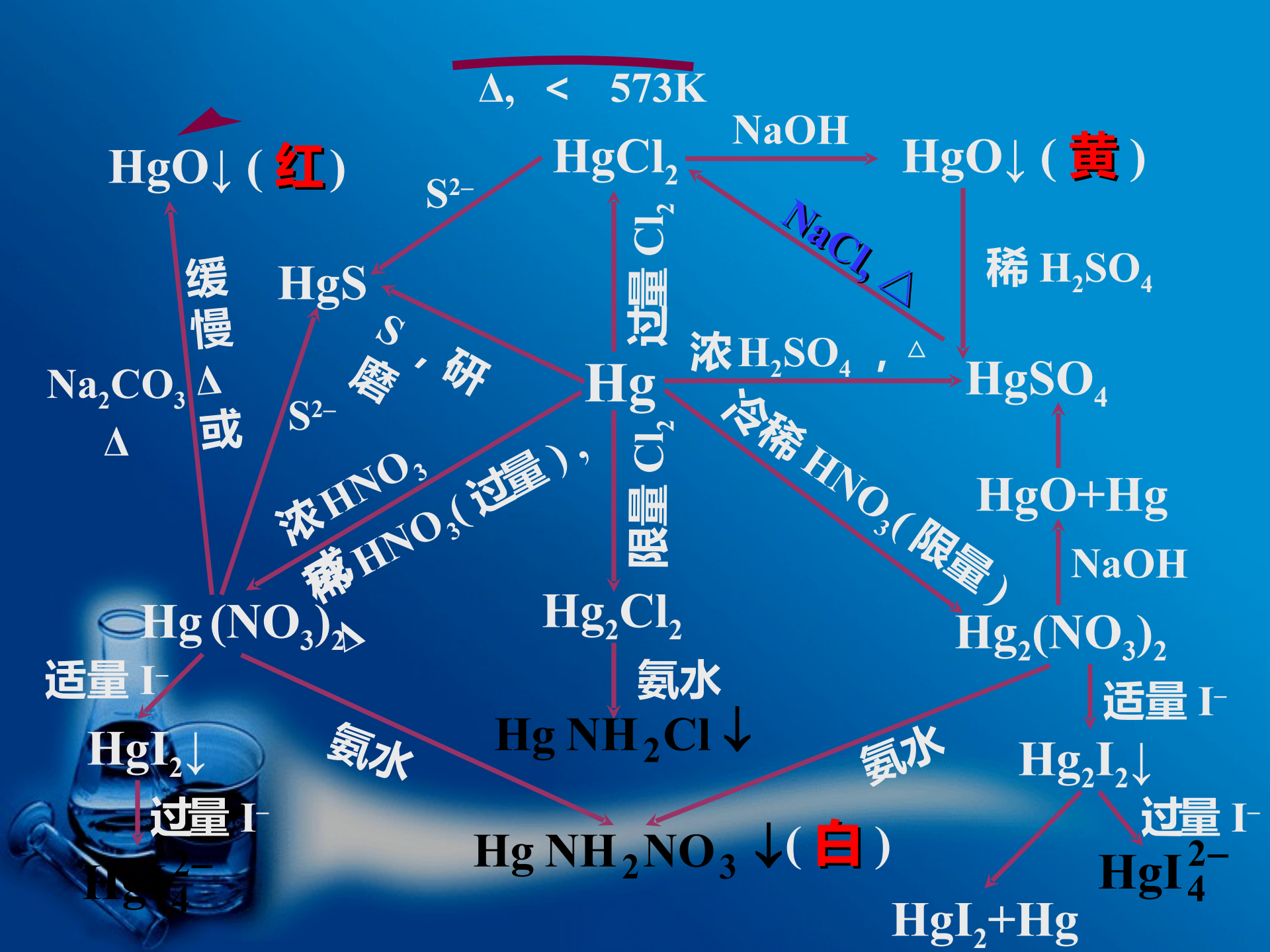
$$Hg_2^{2+} + 4CN^- = Hg(CN)_4^{2-} + Hg\downarrow$$

Hg^{2+} { 配合剂: I^-、CN^-、SCN^-
沉淀剂: OH^-、NH_3、S^{2-}、CO_3^{2-}

2)、$Hg^{2+} \rightarrow Hg_2^{2+}$: *add* reductant

$$HgCl_2 + \begin{cases} Hg \\ SO_2 \\ SnCl_2 \end{cases} \rightarrow Hg_2Cl_2$$


ZnO
O_2，燃烧
O_2，△
C，△
ZnS↓
ZnX_2
X_2
S，△
H_2S
或 S^{2-}
Zn
H^+
适量
OH^-
适量 OH^-
Zn^{2+}
适量氨水
$Zn(OH)_2$↓
过量
OH^-
过量
氨水
$(OH)_4^{2+}$
$Zn(NH_3)_4^{2+}$


Δ, < 573K
HgO↓(红)
HgCl2
NaOH
HgO↓(黄)
S2−
NaCl, Δ
稀 H2SO4
缓慢 Δ 或
Na2CO3 Δ
HgS
S 磨·研
过量 Cl2
浓 H2SO4, Δ
HgSO4
Hg
浓 HNO3
稀 HNO3(过量),
冷稀 HNO3(限量)
限量 Cl2
HgO+Hg
NaOH
Hg(NO3)2
Hg2Cl2
Hg2(NO3)2
适量 I−
氨水
HgI2↓
过量 I−
HgI4 2−
Hg NH2Cl↓
氨水
氨水
Hg2I2↓
过量 I−
HgI4 2−
Hg NH2NO3↓(白)
HgI2+Hg

IIB 与 IIA 元素的对比

1. 溶点、沸点：

锌族金属的熔点、沸点比碱土金属低，汞在常温下是液体。

2. 化学活泼性：锌族元素较碱土金属差。

- 表现在常温下和在干燥空气中锌族元素不发生变化；
- 都不能从水中置换出氢气；
- 在稀盐酸中，锌易溶解，镉溶解较慢，汞完全不溶。
- 同族元素金属活泼性恰好与 IIB 族相反。

3. 键型和配位能力：

锌族元素形成共价化合物和配合物的倾向都比碱土金属要强的多。

4. 氢氧化物的酸碱性及其变化规律：

锌族元素的氢氧化物是弱碱性，易脱水分解，氢氧化锌和氢氧化钡都是两性氢氧化物。

锌族元素从上到下，氢氧化物的碱性增强，而金属活泼性却是减弱的；

碱土金属的活泼性以及它们氢氧化物的碱性从上到下都是增强的。

5. 盐类的溶解性与盐的水解：

IIA 和 IIB 两族元素的硝酸盐都易溶于水；它们的碳酸盐又难溶于水；锌族元素的硫酸盐易溶于水，而钙、锶、钡的硫酸盐则微溶于水。锌族元素的盐在水溶液中都有一定程度的水解，而钙、锶、钡的盐一般不水解。