

# Chemistry

## Physical part

### 19: lattice energy

One bond energy equal to two atomization energy of gas atom

Do not forget to \*2 for certain enthalpy if there is chemical like  $\text{CaCl}_2$

**lattice energy**: ionic radius > larger radius > smaller charge density > smaller attraction > less exothermic

**solubility**:  $\Delta H_{\text{sol}} = \Delta H_{\text{hyg}} (\text{gaseous ion to aq}) - \Delta H_{\text{latt}} (\text{gaseous ions to solid})$   
sulfates and nitrates / hydroxides: less/more soluble (down the group) both hyg and latt become less negative down the group;  $\Delta H_{\text{hyg}}/\Delta H_{\text{latt}}$  decreases more;  $\Delta H_{\text{sol}}$  gets less/more exo  
(别忘了 common ion effect) ;

**Thermal stability**: increases down the group; radius of cation increases; less charge density so less polarization/ distortion of anion

Ease of decomposition : 同上 也看阳离子 radius

Affinity: greater nuclear charge > greater attraction

**Enthalpy change of atomization**: enthalpy change when 1 mole of gaseous atoms is formed from its elements under standard conditions

**Lattice Energy**: enthalpy change when one mole of an ionic compound is formed from its gaseous ions under standard conditions.

**First electron Affinity**: enthalpy change when 1 mole of electrons is added to 1 mole of gaseous atoms to form 1 mole of gaseous anions under standard conditions

### 20: electrochemistry

电解 at cathode Cu Ag 比  $\text{H}^+$  先出 at anode 浓溶液先出卤素 稀溶液先出氧气

**看表**判断反应  $E_{\text{v}} > 0$  reversible  $v > 0.3$  complete

Electrode half cell 有金属单质用单质 无单质用 platinum

Equilibrium 往右  $E_{\text{v}}$  increase 往左  $E_{\text{v}}$  decrease

$E = E_{\text{standard}} - 0.059/z \cdot \log [\text{half cell}]$

Standard cell 画图要素 : 1 atm 298k  $1\text{mol/dm}^3$  platinum saltbridge voltmeter

**Standard electrode (redox) potential:** the electrode potential of a half cell measured under standard conditions of 1 atm, 298K, solutions being 1 mol dm<sup>-3</sup> using a standard hydrogen electrode as the other half cell

**Standard cell potential:** the difference in standard electrode potential between two half cells

## 21: equilibria

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

$$K_{sp} \quad \text{e.g. } Mn(OH)_2 \quad K_{sp} = [Mn^{2+}][OH^-]^2 \quad [OH^-] = 2[Mn]$$

K<sub>pc</sub> 溶解的程度 看 solute 和 solvent 是 polar 还是 non polar

$$pH = pK_a + \lg \frac{[salt]}{[acid]}$$

**Buffer solution:** a solution in which pH doesn't change significantly when small amounts of acids or alkali added

**Solubility product (K<sub>sp</sub>):** product of conc. of each ion in a saturated solution of sparingly soluble salt at 298K raised to the power of moles in dissociation equation

**Common ion effect:** lowering of solubility of an ionic compound by addition of a common ion to the solution

## 22: reaction kinetics

Why large excess of one reactant: keep **[reactant]** constant; does not affect the rate

**Rate** =  $k[A]^a[B]^b$  according to the chemical equation at rate determined step

Overall order = a + b

If a chemical is first order, its half life is constant

Unit of rate : mol dm<sup>-3</sup> s<sup>-1</sup>

unit of k, do not forget s<sup>-1</sup>

use concentration and initial rate to calculate magnitude of k

increase temperature: 同 AS 用分子层面来解释

order of reaction : the power to which a concentration of a reactant is raised in the **rate equation**

**Rate of reaction** is the change in concentration of products/reactants per unit time

**Rate-determining step:** the slowest step in a reaction mechanism

## 23: entropy and gibbs free energy

$\Delta S$  products – reactants

$$\Delta G = \Delta H - \Delta ST$$

$\Delta G$  越负 reaction 越 feasible

$\Delta G = -nFE_{\text{cell}}$  n number of mol of electrons F = 96500C/mol

Mol 越多 或者气体越多 entropy 越大

## 24: transition elements

Property of transition element: variable oxidation states ; behave as catalyst; form complex ions; coloured compounds

Why colourless: no d electrons (1) cannot absorb photons (1)

Why colour: 1.dsubshell splits 2.photon has been absorbed 3.electron are excited 4.colour seen is complementary to color absorbed

Why colour different: the gap between the d orbits is different so wavelength absorbed is different

Ligand: species that donates (看题填数字) lone pair to form a dative to a central metal atom

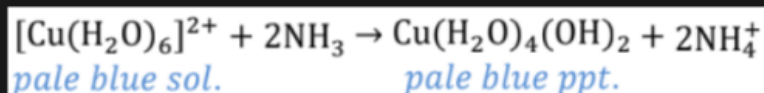
Transition metal complex: a molecule or ion formed by a central metal atom surrounded by ligands

Melting point: stronger **attraction** to cation as more **delocalized** electrons

Cu 加稀硫酸生成铜六水络合物 只有铜氨深蓝 铜氨黄色 其他都浅蓝

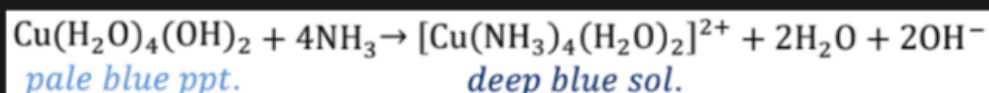
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Small amount of ammonia



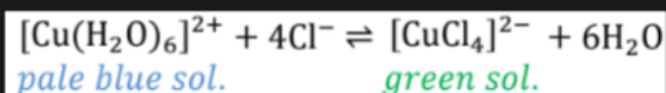
- Initially, ammonia acts as a base and hydrogen ions are pulled off the hexaaqua ion as above.

Excess ammonia



- Ammonia replaces water as a ligand
- Only 4 of the 6 water molecules replaced

Reaction with Chloride Ions



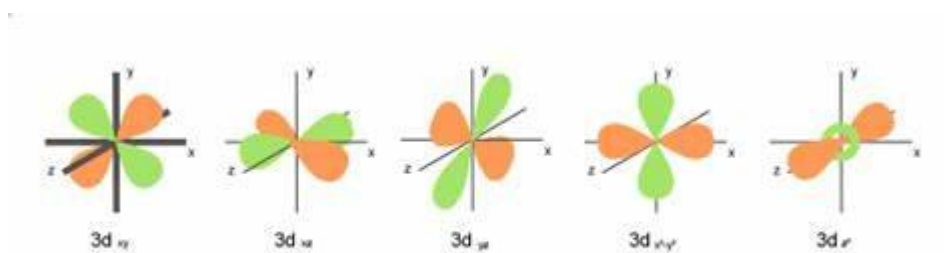
- 6 water molecules replaced by 4 chloride ions

$$K_{\text{stab}} = \frac{[\text{CuCl}_4]^{2-}}{[\text{Cu}^{2+}][\text{Cl}^-]^4} \quad \text{【product】 / 【reactant】}$$

(Kstab is) the **n** for the formation of a complex (ion) (in a solvent from its constituent ions/molecules)

Larger Kstab more stable higher concentration

Higher concentration means larger Kstab



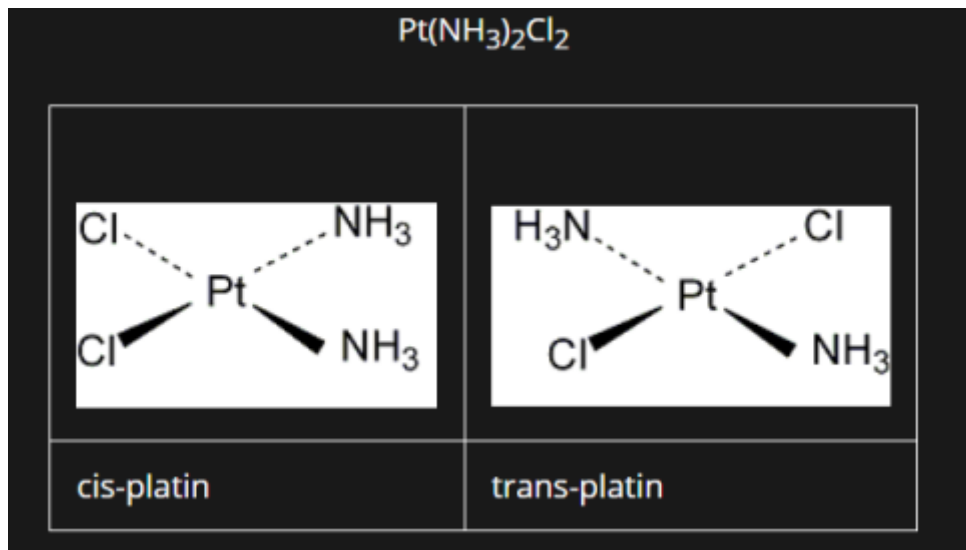
Shape    octahedral    一般都是

Tetrahedral    Cl 作为 ligand 因为它比较大 排斥力也大

Square planar    一般 Ni Pt    cis trans    用两种不同的线来画 (虚线 三角形) 每种线要有两种不同的 group

Linear            Ag

画 stereoisomer 考虑 optical 和 cis-trans



## Organic part

### 25: Benzene

三溴苯胺是白色沉淀

还原苯环  $\text{H}_2$  Pt/Ni heat

Functional group: phenyl / aryl 立 group

## Acyl Chlorides

前缀+oyl chloride e.g. propanoyl

Carboxylic acid 和  $\text{SOCl}_2$  反应 会有  $\text{SO}_2$  和  $\text{HCl}$  heat

$\text{PCl}_3$

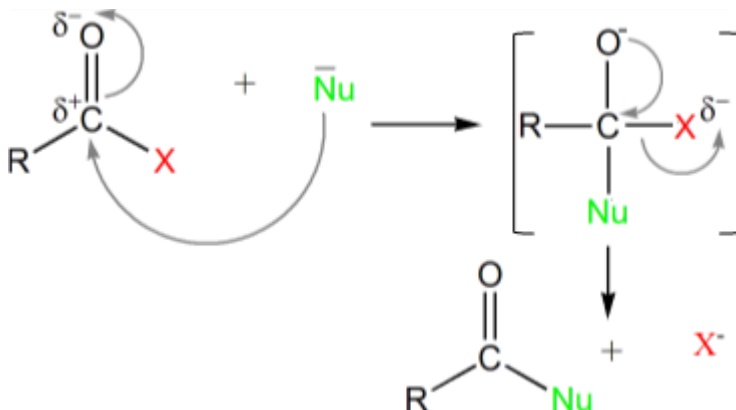
$\text{H}_3\text{PO}_3$

heat

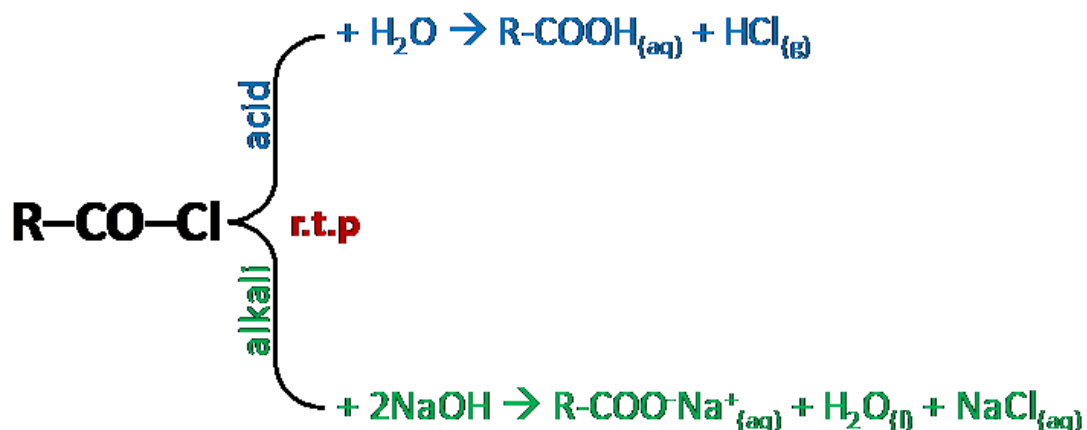
$\text{PCl}_5$

$\text{POCl}_3$

$\text{HCl}$  room



Hydrolysis



### Ease of hydrolysis

Aryl chlorides do not undergo hydrolysis at r.t.p because the p-orbitals from chlorine overlap with delocalized p-electrons giving the C-Cl bond a double bond character

Alkyl chlorides require a strong alkali (NaOH) under reflux to be hydrolysed as carbon doesn't have a high  $\delta^+$

Acyl chlorides undergo hydrolysis with neutral water at r.t.p because the carbon atom is bonded to two highly electronegative atoms hence has a high  $\delta^+$  therefore attack by a nucleophile is much more rapid

26:carboxylic

Electron withdrawing group

Fehling's reagent (can react) : methanoic acid

H+ MnO4-: methanoic and ethanedioic

判断酸碱性 Acidity : electron withdrawing/donating group ; weaken/strengthening OH bond H+ is easier/more difficult to release

halogen electronegative weakening OH bond

Amide is neutral CH3 electron donating group strengthening OH bond

带苯环的 (benzoic acid) : lp electron on O is delocalized into ring ; charge density of ring increase phenoxide ion is not stabilised

## 27:organic nitrogen

NO2 =nitro

CN nitrile 被 H2 pt 还原成 CH2NH2

Basicities: lp overlap with delocalized ring less basic

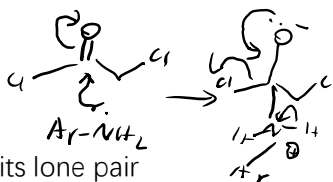
Alkyl group is Donating

酸性条件 多个氢 + 标 N e.g. --N+H3

碱性条件 O-

Addition elimination mechanism

Why can nucleophile: N can donate its lone pair



Diazonium ion 水解 >10°C + H2O

## 28:polymerization

Condensation

Addition

Non-solvent-based adhesive : epoxy resin allow super glues (不在考纲)

## 29:analytical

H NMR 看表 more electronegative larger shift in D2O OHNH will disappear due to proton will exchange with D

TMS as a reference

苯环上的 H 会有很多 peak 不在考纲之内

Why triplet or other splitting pattern: (填数字 splitting -1 e.g. triplet 就是 3-1 = 2)

H on neighbouring C atom

C NMR 对称不用数

TLC stationary phase: silica or alumina mobile phase : organic solvent

Separation mechanism adsorption(唯一一个)