

# Quiz 1

## I. Quantum Mechanics

### 1. Electromagnetic Radiation:

$$c = \lambda \cdot \nu$$

The electromagnetic spectrum

Some ranges:

- ① Infrared light:  $\lambda > 700\text{nm}$
- ② Visible light:  $400\text{nm} < \lambda < 700\text{nm}$
- ③ Ultraviolet light:  $\lambda < 400\text{nm}$

### 2. Black body radiation

Incandescence: When an object's temperature is high, it will glow.

As the temperature rises:

- ① Intensity of all wavelength  $\uparrow$
- ② Peaks move toward shorter wavelength (Wien's Law)

$$T \cdot \lambda_{max} = b$$

$$(b = 2.897 \times 10^{-3} \text{m} \cdot \text{K})$$

Stefan-Boltzmann Law:

$$\text{Total intensity} = \text{const} \times T^4$$

$$(\text{Const} = 5.67 \times 10^{-8} \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-4})$$

### 3. Light emission spectrum of hydrogen

$$\nu = R \cdot \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$(\text{Rydberg constant: } R = 3.29 \times 10^{15} \text{s}^{-1})$$

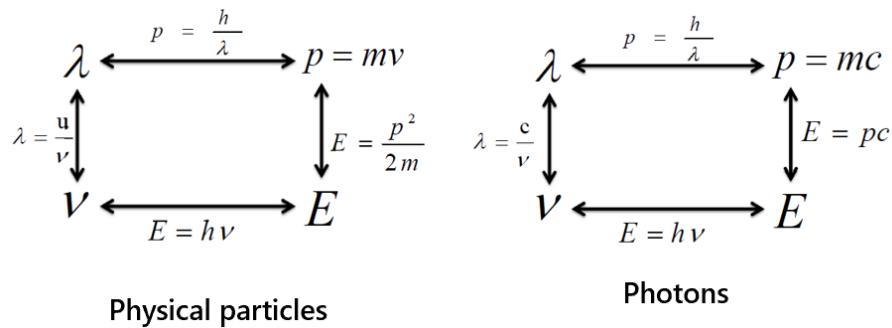
### 4. Quanta

Quanta is the smallest unit/packet of energy transfer

$$E = h \cdot \nu$$

$$(\text{Plank's constant: } h = 6.626 \times 10^{-34} \text{J} \cdot \text{s})$$

## 5. de Broglie wave



## 6. Photoelectric effect

A “strong” photon could eject one electron from an atom.

$$h\nu = \phi + \frac{1}{2}mv^2 = h\nu_0 + \frac{1}{2}mv^2$$

$\phi$ : Minimal work needed for the effect to happen

$\nu_0$ : Threshold frequency – the minimal frequency required for the light

$m$ : Mass of ejected electrons

$v$ : The speed of the ejected electrons

## 7. Particles in a box

One dimensional box

- ① Wave function:  $\psi_n(x) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n\pi x}{L}\right)$
- ② Probability density function:  $p_n(x) = \psi_n^2(x)$
- ③ Energy function:  $E_n = \frac{n^2 h^2}{8mL^2}$
- ④ Nodes (where the probability is 0):  $N = n - 1$

Three dimensional box

$$\text{Total energy: } E = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

Degeneracy: same energy but different functions

## 8. Heisenberg's uncertainty principle

$$\Delta x \cdot \Delta p = \Delta x \cdot (m \cdot \Delta v) \geq \frac{h}{4\pi}$$

## II. Atom

### 1. Quantum number

Symbol	Name	Values	Specifies ...	Indicates...
$n$	Principal QN	1, 2, 3,...	Shell	Size & Energy
$l$	Orbital angular momentum QN	0 (s), 1 (p), 2 (d),...(n-1)	Subshell	Shape & Energy
$m_l$	Magnetic QN	$-l \sim l$	Orbital	Orientation
$m_s$	Spin magnitude QN	$\pm \frac{1}{2}$	Spin state	Spin direction

### 2. Atomic Orbitals

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

Nodes:

- a) Total nodes =  $n - 1$
- b) Radial/Spherical nodes =  $n - l - 1$
- c) Angular/Planar nodes =  $l$

### 3. Energy levels of multi-electron atoms

Build-up rules  $\times 4$

- ① Aufbau principle: electrons like to occupy lower-energy orbitals first
- ② Pauli exclusion principle: 2 electrons in the same orbital have different spin directions
- ③ Hund's first rule: In the same sub-shell, electrons tend to occupy different orbitals first. And have same directions.
- ④ Hund's second rule: In a specific sub-shell, electrons tend to form a structure of full, half-full or empty.

\* Generally, the energy rank is:  $s < p < d < f$ . Due to the penetration effect, in some atoms:  $4s < 3d$ . But when  $Z > 20$ ,  $4s > 3d$ .  $\rightarrow$  Transition metals always lose electrons from their 4s-orbital first.

### 4. Atoms' radius

- ① Number of valence shells  
Valence shells  $\uparrow \rightarrow$  Radius  $\uparrow$
- ② Effective nuclear charge  
Effective nuclear charge  $\uparrow \rightarrow$  Radius  $\downarrow$

## 5. Ionization energy

Minimal energy needed to remove an electron from a neutral gas phase atom

- ① Atom's radius
- ② Effective nuclear charge
- ③ Hund's second rule

First IE < Second IE < Third IE < ...

## 6. Electron affinity

The amount of energy released or spent when an electron is added to a neutral atom or molecule in the gaseous state to form a negative ion.

- ① Atom's radius
- ② Effective nuclear charge
- ③ Hund's second rule

$$\Delta E = E_{final} - E_{initial}$$
$$E_A = -\Delta E$$

$E_A > 0$ : Release energy

$E_A < 0$ : Spend/absorb energy

# III. Chemical Bonds

## 1. Ionic Bond

Electrons transfer from one atom to another, and both become ions. The entire compound is held together by the electrostatic attraction between all the ions.

- ① Electric charge  $\uparrow \rightarrow$  Bond strength  $\uparrow$
- ② Radius of ions  $\downarrow \rightarrow$  Bond strength  $\uparrow$

## 2. Lattice energy

The energy released when separated cations and anions bounded together

\*How to calculate LE according to the cycle?

## 3. Lewis symbol

- ① A single dot: an electron alone in an orbital
- ② A pair of dots: paired electrons in one orbital
- ③ Single line: one sharing pair, 2 electrons
- ④ Double lines: two sharing pairs, 4 electrons

...

#### 4. Resonance structure

Usually more than one Lewis structures are capable of representing a molecule. The blending of these structures are called resonance. The real structure of the molecule is a resonance hybrid.

- ① Electrons are delocalized but atoms are localized.
- ② Structures with lower energy contribute more to the real structure.

#### 5. Formal charge

Formal charge is the criterion of the stability of Lewis structures.

$$FC = n_v - (n_l + n_b)$$

$n_v$ : number of valence electrons

$n_l$ : number of electrons in lone pairs/lone electrons

$n_b$ : number of bonds

A resonance structure has a lower energy if

- ① Formal charges are closest to 0
- ② Charges of the same sign are not adjacent
- ③ The more electronegative atoms have negative formal charges
- ④ The structure is symmetric

#### 6. Covalent bond

- ① Single bond:  $\sigma \times 1$
- ② Double bond:  $\sigma \times 1, \pi \times 1$
- ③ Triple bond:  $\sigma \times 1, \pi \times 2$

### IV. Molecular Theory

#### 1. VSEPR

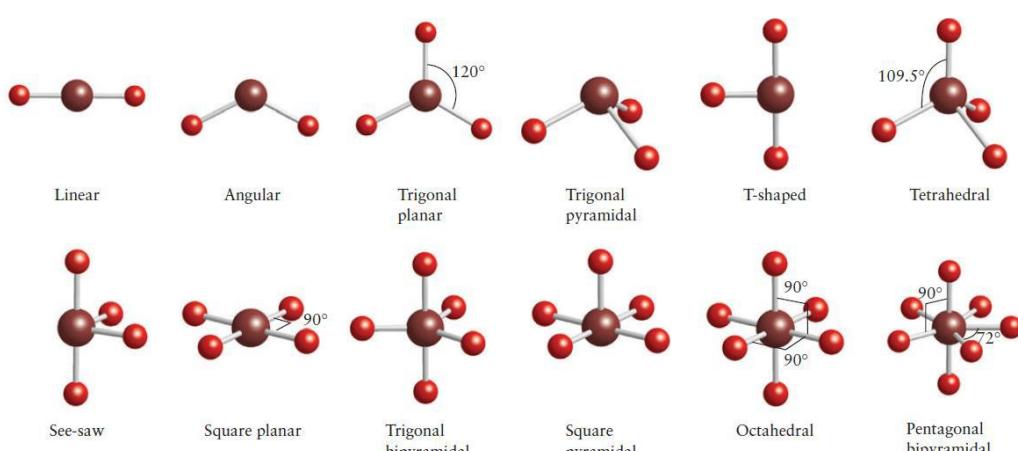


A: central atom

X: a bonded atom

E: a lone pair

Repulsion force: Lone pair > Triple bond > Double bond > Single bond



## 2. Hybridization

The hybridization scheme can be determined by VSEPR.

$\text{AX}_n\text{E}_m$

$n + m =$

- 2: sp hybridized
- 3:  $\text{sp}^2$  hybridized
- 4:  $\text{sp}^3$  hybridized
- 5:  $\text{sp}^3\text{d}$  hybridized
- ...

## 3. Molecular orbital diagram

When constructing a MO diagram, the atomic orbitals for bonding atoms are on the sides, and molecular orbitals are in the center. Molecular orbitals are sorted, according to their energy, as

- ① Bonding, whose energy is lower than composing atomic orbitals.
- ② Nonbonding, whose energy is the same as composing atomic orbitals.
- ③ Antibonding, whose energy is higher than composing atomic orbitals.

The numbers of bonding and antibonding orbitals are the same.

Magnetic properties:

- ① Paramagnetic: has unpaired electrons
- ② Diamagnetic: has no unpaired electrons

Bond order:

$$\text{B. O.} = \frac{n_{\text{bonded electrons}} - n_{\text{antibonded electrons}}}{2}$$

## V. Gas

### 1. STP & SATP

STP:  $T = 0^\circ\text{C}/273.15\text{K}$ ;  $P = 1 \text{ atm}$ ;  $1 \text{ mol gas} = 22.41\text{L}$

SATP:  $T = 25^\circ\text{C}/298.15\text{K}$ ;  $P = 1 \text{ bar}$ ;  $1 \text{ mol gas} = 24.79\text{L}$

### 2. Ideal gas law

Clapeyron equation

$$PV = nRT$$

$P$ : Pressure of the system

$V$ : Volume of the gas

$n$ : Amount of the gas

$R$ : Gas constant

$T$ : Temperature in Kelvin ( $K$ )

### 3. Dalton's law

$$\begin{aligned} P &= P_A + P_B + P_C + \dots && \text{atm} \\ &= \frac{n_A}{n_A + n_B + \dots} P + \frac{n_B}{n_A + n_B + \dots} P + \dots \\ &= X_A P + X_B P + \dots \end{aligned}$$

where  $X_A + X_B + \dots = 1$

### 4. Kinetic molecular theory

It's a theory on large number of moving molecules

$$\begin{aligned} E_k &= \frac{1}{2} M v_{rms}^2 = \frac{3}{2} RT, \quad (v_{rms} = \sqrt{v_x^2 + v_y^2 + v_z^2}) \\ v_{rms} &= \sqrt{\frac{3RT}{M}} \end{aligned}$$

### 5. Maxwell distribution of speed

Most possible speed:

$$v_{mps} = \sqrt{\frac{2RT}{M}}$$

### 6. Molecular Effusion and Diffusion

Effusion:

$$\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}$$

Diffusion: slowed by gas molecules colliding with each other

### 7. Real gas

Van der Waals equation:

$$P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

( $a$ : attraction,  $b$ : repulsion)

# Quiz 2

## I. Liquid and Solid

### 1. Intermolecular interaction

- ① Ion-dipole (e.g. hydration)
- ② Dipole-dipole

When rotating: distribute more in lower energy orientation

- ③ Dipole-induced dipole
- ④ London force (induced dipole-induced dipole)
  - a) Mass of the molecules
  - b) Shape of the molecules
- ⑤ Hydrogen bonding (dipole-dipole)

Specific molecules with hydrogen attached to a strong electronegative atom, form bridging hydrogen bonds to electron lone pairs on N, O, F...

Every lone pairs could form 1 hydrogen bond

### 2. Liquid

- ① Viscosity
- ② Surface tension
- ③ Adhesion & Cohesion
- ④ Hydrophobicity of surface
- ⑤ Capillary action

### 3. Solid

Crystalline solids:

- ① Molecular solid: intermolecular forces
- ② Atomic solid: strong covalent bonds
- ③ Metallic solid: metallic bonds
- ④ Ionic solid: ionic bonds

Closed-packed:

- ① HCP: hexagonal closed packed (...-A-B-A-B-...)
- ② CCP: cubic closed packed (...-A-B-C-A-B-C-...)

**Unit cell:**

The smallest region of the crystal lattice that repeats itself

- ① Simple cubic
- ② Body-centered cubic (BCC)
- ③ Face-centered cubic (FCC/CPP)

Density calculation based a unit cell

$$\rho = \frac{ZM}{VN_A}$$

Z: Number of atoms in a cell

V: Volume of the cell

## II. Thermodynamics

### 1. Thermodynamics systems

System + Surrounding

- ① Open system: energy and matters transferred
- ② Closed system: no matter transfer
- ③ Isolated system: no energy and matter transfer

### 2. Reversible process

A process that can be reversed by an infinitely small change in a variable  
(e.g. isothermal expansion process; phase change at boiling/freezing point)

### 3. Expansion work

- ① Constant pressure (irreversible)

$$W = -P_{ex} \cdot \Delta V = -P_{ex} \cdot (V_f - V_i)$$

- ② Isothermal (reversible)

$$W = -nRT \cdot \ln \frac{V_f}{V_i}$$

### 4. Internal energy

Symbol: U

The capacity of a system to do work, includes potential energy and kinetic energy of atoms, nuclei...

- a) Translation: three directions in  $x, y, z \rightarrow \frac{3}{2}RT$

- b) Rotation: linear molecule  $\rightarrow RT$ ; non-linear  $\rightarrow \frac{3}{2}RT$

- c) Vibration: only at high temperature:

$$\text{n-molecule linear: } (3n - 5) \times \left(\frac{1}{2}RT + \frac{1}{2}RT\right)$$

$$\text{n-molecule non-linear: } (3n - 6) \times \left(\frac{1}{2}RT + \frac{1}{2}RT\right)$$

## 5. First Thermodynamic law

The change of internal energy is related to heat and work:

$$\Delta U = q + w$$

The internal energy of an isolated system is a constant:

$$\Delta U = 0$$

At constant volume, no expansion work is done ( $w=0$ )

$$\Delta U = q$$

Constant volume heat capacity ( $V=Const, w=0$ )

$$C_V = \frac{\Delta U}{\Delta T}$$

## 6. Enthalpy

$$H = U + PV$$

When with constant pressure and no non-expansion work:

$$\begin{aligned}\Delta H &= q + w + P \cdot \Delta V \\ &= q - P \cdot \Delta V + P \cdot \Delta V \\ &= q\end{aligned}$$

## 7. Heat capacity

How much heat is transferred to increase one degree of temperature.

$$C = \frac{q}{\Delta T}$$

Specific heat capacity:  $C_s = \frac{c}{m}$

Molar heat capacity:  $C_s = \frac{c}{n}$

Exothermic:  $q < 0$

Endothermic:  $q > 0$

Heat capacity at constant pressure

$$C_P = \frac{q}{\Delta T} = \frac{\Delta H}{\Delta T}$$

For ideal gases:

$$\begin{aligned}C_P &= \frac{\Delta U + nR\Delta T}{\Delta T} = \frac{\Delta U}{\Delta T} + nR = C_V + nR \\ C_{P,m} &= C_{V,m} + R\end{aligned}$$

	Monoatomic	Linear	Nonlinear
$C_{v,m}$	$\frac{3}{2}R$	$\frac{5}{2}R$	$3R$
$C_{p,m}$	$\frac{5}{2}R$	$\frac{7}{2}R$	$4R$

## 8. Hess's law

The overall reaction enthalpy is the sum of the reaction enthalpies of the steps into which the reaction can be divided.

## 9. Born-Haber cycle

The Born-Haber cycle is a closed path of steps.

- ① Break apart the bulk elements into atoms
- ② Ionize the atoms
- ③ Combine the gaseous ions to form the ionic solid
- ④ Form the elements again from the ionic solid

## 10. Entropy

Symbol: S

It's a measure of disorder.

At constant temperature, and in a reversible process:

$$\Delta S = \frac{q_{rev}}{T}$$

Entropy change calculation:

- ① Temperature change

$$\Delta S = \int_{T_1}^{T_2} \frac{C dT}{T} = C \cdot \ln \frac{T_2}{T_1}$$

\* If  $P$  is constant, use  $C = nC_{P,m}$

\* If  $V$  is constant, use  $C = nC_{V,m}$

- ② Constant temperature

$$\Delta S = nR \cdot \ln \frac{V_2}{V_1} = nR \cdot \ln \frac{P_1}{P_2}$$

## 11. Second Thermodynamic law

The entropy of an isolated system increases in the course of any spontaneous change (from order to disorder)

$$\Delta S_{tot} = \Delta S + \Delta S_{surr}:$$

- ①  $\Delta S_{tot} > 0$ : Spontaneous
- ②  $\Delta S_{tot} < 0$ : Non-spontaneous
- ③  $\Delta S_{tot} = 0$ : Equilibrium

## 12. Third Thermodynamic law

The entropy of a system approaches a constant value as the temperature approaches absolute zero, is equal to the natural logarithm of the number of microscopic states

The Boltzmann formula:

$$S = k \cdot \ln W$$

$$k = Const = 1.381 \times 10^{-23} \text{ J/K}$$

$W$ : the number of microstates (the number of different arrangements corresponding to the same energy)

### 13. Gibbs free energy

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

At constant temperature:

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

At constant temperature and pressure:

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = \Delta S - \Delta H/T$$

$\Delta G = -T \cdot \Delta S_{tot}$ :

- ①  $\Delta G < 0$ : Spontaneous
- ②  $\Delta G > 0$ : Non-spontaneous
- ③  $\Delta G = 0$ : Equilibrium

## III. Physical Equilibrium

### 1. Vapor pressure

It's a representation of the volatility of matters, depends on intermolecular forces and temperature

Low intermolecular forces → High vapor pressure → Low boiling point / More volatile  
Clausius – Clapeyron Equation:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H^\circ_{vap}}{R} \cdot \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{P}{P^\circ} = -\frac{\Delta H^\circ_{vap}}{RT} + \frac{\Delta S^\circ_{vap}}{R}$$

### 2. Phase diagram

\* How to read the phase diagram?

### 3. Vapor pressure of multiple-component system

Raoult's law (for the vapor pressure of solution):

$$\begin{aligned} P_{solvent} &= X_{solvent} \cdot P_{pure} \\ P_{solution} &= P_{solvent,A} + P_{solvent,B} + \dots \end{aligned}$$

### 4. Solubility

Like dissolves like: polar solvent dissolves polar solute; non-polar solvent dissolves non-polar solute

For gases – Henry's law:

$$solubility = k_H \cdot P$$

High temperature accelerates dissolution, but doesn't necessarily increase solubility

## 5. Molality

$$\text{molality} = \frac{n_{\text{solute}}}{m_{\text{solvent}}} \left[ \frac{\text{mol}}{\text{kg}} \right]$$
$$\text{Molarity} = \frac{n_{\text{solute}}}{V_{\text{solution}}} \left[ \frac{\text{mol}}{\text{L}} \right]$$

## 6. Boiling point & freezing point

Freezing-point depression =  $i \cdot k_f \times \text{molality}$

Boiling-point elevation =  $i \cdot k_b \times \text{molality}$

$i$ : van't Hoff factor (e.g.  $i_{\text{HCl}} = 2$ ,  $i_{\text{CaCl}_2} = 3$ )

## 7. Osmosis

The flow of solvent through a membrane into a more concentrated solution

Osmotic pressure: the pressure needed to stop the flow of solvent

$$\Pi = iRTM$$

$\Pi$ : Osmotic pressure

$i$ : van't Hoff factor

$M$ : Molarity

# VC210 BIg Recitation Class for Final

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# Contents

## 1 Chemical Equilibrium

- Equilibrium Constant
- Le Chatelier's Principle

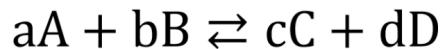
## 2 Acid & Base

- Acid & Base Theories
- pH

## 1 Chemical Equilibrium

## 2 Acid & Base

# Equilibrium Constant



$$K = \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b}$$

$$K = \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b} \Rightarrow$$

$$K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

$$K_P = \frac{(P_C)^c \cdot (P_D)^d}{(P_A)^a \cdot (P_B)^b}$$

◆ The relation between  $K_c$  &  $K_P$

$$K_P = (RT)^{\Delta n} \cdot K_c, \quad (\text{where } \Delta n = \Sigma n_{prod} - \Sigma n_{reac})$$

## Kinetic View of K

Forward:  $Rate_f = k_f \cdot [A]^a[B]^b$

Backward:  $Rate_b = k_b \cdot [C]^c[D]^d$

At equilibrium:

$$Rate_f = Rate_b$$

$$K = \frac{k_f}{k_b} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

# Thermodynamic view

$$\Delta G_r = \Delta G_r^\circ + RT \cdot \ln \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b}$$

Denote  $Q = \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$

So  $\Delta G_r = \Delta G_r^\circ + RT \cdot \ln Q$

At eq.  $\Delta G_r = 0; K = Q$

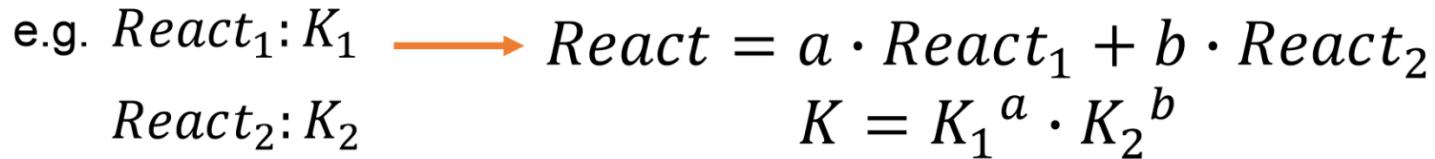
Therefore  $-\Delta G_r^\circ = RT \cdot \ln K$

$$\Delta G_r = -RT \cdot \ln K + RT \cdot \ln Q$$

$$\begin{cases} Q < K: \Delta G_r < 0, \text{ Forward} \\ Q = K: \Delta G_r = 0, \text{ Equilibrium} \\ Q > K: \Delta G_r > 0, \text{ Backward} \end{cases}$$

# Calculation of K

## ① Combination reaction



## ② ICE Table

	Matter 1	Matter 2	Matter 3	...
Initial				
Change				
Equilibrium				

↓

Substitute into the formula of  $K$ ,  
and solve for the answer

# Reactions include heat change

For reactions include heat change:

$$\ln \frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (1)$$

# Le Chatelier's Principle

- Disturbed equilibrium re-approaches equilibrium

## ① Add/remove reactants/products:

- a) Add reactants/remove products: forward reaction
- b) Add products/remove reactants: backward reaction
- Adding/remove solids/liquid doesn't change equilibrium

## ② For reactions include gases:

- a) Increase pressure:
  - i) If it changes the concentration of components to the direction that decreases pressure
  - ii) If it doesn't change the concentration of components equilibrium won't change
- b) Decrease pressure: similar

## 1 Chemical Equilibrium

## 2 Acid & Base

# Acid & Base Theories

## 1. Arrhenius

- ① Acid produces  $\text{H}^+$  in water
- ② Base produces  $\text{OH}^-$  in water

Only considers one solvent; not all base reactions produce  $\text{OH}^-$ ; the key process in an acid and base reaction is a proton ( $\text{H}^+$ ) transfer

## 2. Lowry & Bronsted

- ① Acid is a proton( $\text{H}^+$ ) donor
- ② Base is a proton( $\text{H}^+$ ) acceptor

Strong acid/base: completely deprotonated/protonated in solution

Weak acid/base: partially deprotonated/protonated

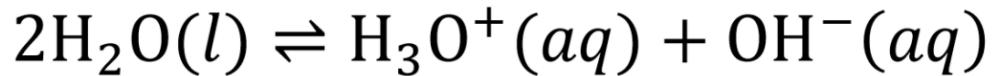
# Acid & Base Theories

## 3. Lewis

- ① Acid accepts electron pair
- ② Base donates electron pair

- **Amphoteric:** a molecule or ion that can react both as an acid as well as a base.  
E.g.  $\text{Al}(\text{OH})_3$ ,  $\text{Al}_2\text{O}_3$
- **Amphiprotic:** a molecule can act both as a proton donor and as a proton acceptor.

# Water and pH



- Recall the equilibrium constant:

$$K_W = [\text{H}_3\text{O}^+][\text{OH}^-]$$

- At 25°C, in pure water

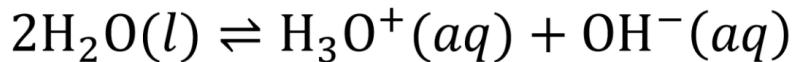
$$[\text{H}_3\text{O}^+] = 1 \times 10^{-7}; [\text{OH}^-] = 1 \times 10^{-7}$$

$$K_W = 1 \times 10^{-14}$$

- Remember that  $K_W$  is only related to  $T$

- So at certain temperature, the product of  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  in a solution is constant.

# pH



- Recall the equilibrium constant:

$$K_W = [\text{H}_3\text{O}^+][\text{OH}^-]$$

- At 25°C, in pure water

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-7}; [\text{OH}^-] = 1 \times 10^{-7}$$

$$K_W = 1 \times 10^{-14}$$

- Remember that  $K_W$  is only related to  $T$ 
  - So at certain temperature, the product of  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  in a solution is constant.

End

Good luck in final!

*VC210 FA2020*

# FINAL

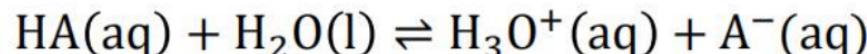
Solution & Kinetic

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Dec.4 2020

# Buffer

- A buffer is an aqueous solution which resists a change in pH when small amounts of strong acids or bases are added.
- A buffer is made by a weak acid with its conjugate base or a weak base with its conjugate acid.
- Essence: the shift of equilibrium



# Buffer

- Henderson-Hasselbalch (approximation)

$$pH = pK_a + \log \frac{[Base]_{(initial)}}{[Acid]_{(initial)}}$$

$$pOH = pK_b + \log \frac{[Acid]_{(initial)}}{[Base]_{(initial)}}$$

# Buffer

## Halfway Stoichiometric Point

For weak-acid solution, at halfway stoichiometric point, the concentrations of acid and its conjugate base are equal.

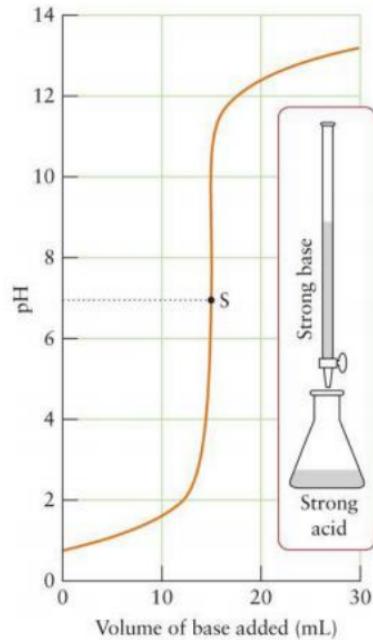
$$\text{pH} = \text{pK}_a$$

For bases, , at halfway stoichiometric point, the concentrations of bases and its conjugate acid are equal.

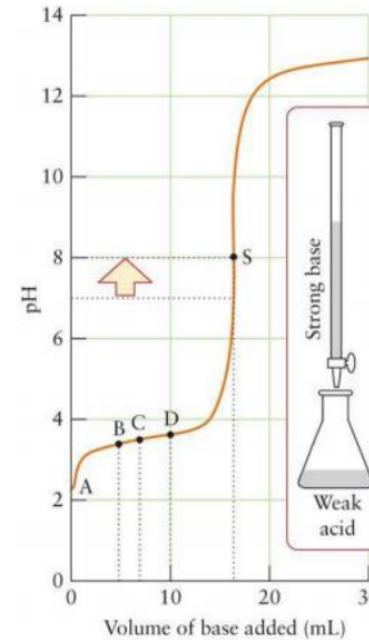
$$\text{pOH} = \text{pK}_b$$

# Titration

## 1. Strong → Strong

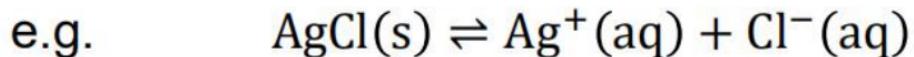


## 2. Strong → Weak



# Solubility Equilibria

- Solubility Product ( $K_{SP}$ )



$$K_{SP} = [\text{Ag}^+][\text{Cl}^-]$$

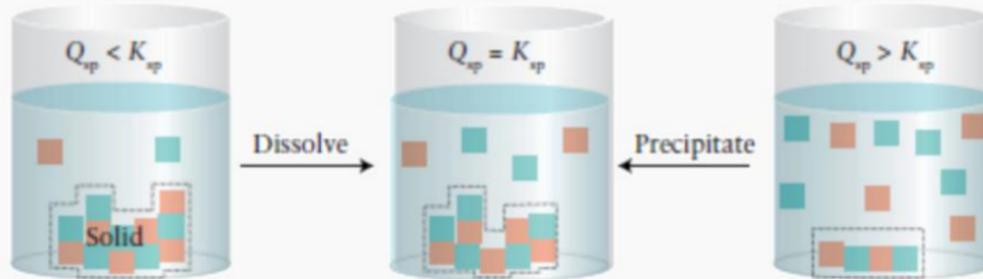
- Common-ion effect

- Based on Le Chatelier's principle
- Precipitate unwanted ions by adding common ions
- E.g. By adding  $\text{Cl}^-$

→ equilibrium will shift to the left

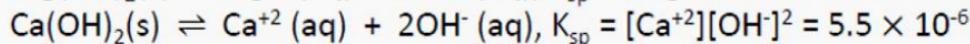
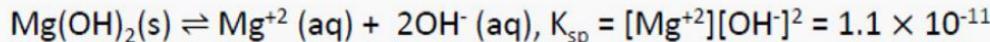
→  $\text{Ag}^+$  will precipitate

# Solubility Equilibria



# Solubility Equilibria

- Order of precipitation
  - Compare the solubility of the precipitant
  - The one with smaller  $K_{SP}$  will precipitate first



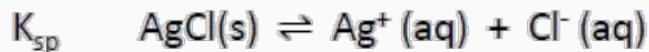
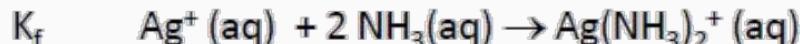
The  $K_{sp}$   $\text{Mg(OH)}_2 \ll K_{sp}$   $\text{Ca(OH)}_2$  which gives us a general idea of what to expect -  $\text{Mg}^{2+}$  would be precipitate first.

## Exercise

Calculate the solubility of  $\text{CaSO}_4(\text{s})$  in 0.300 M  $\text{Na}_2\text{SO}_4(\text{aq})$  at 25°C. The  $K_{SP}$  of  $\text{CaSO}_4$  is  $4.93 \times 10^{-5}$ .

# Solubility Equilibria

We have 2 reactions



- The formation constant is much greater than the solubility product,  $[\text{Ag}^+]$  is consumed immediately after it is formed,
- we can combine the above reaction to remove  $\text{Ag}^+$ :

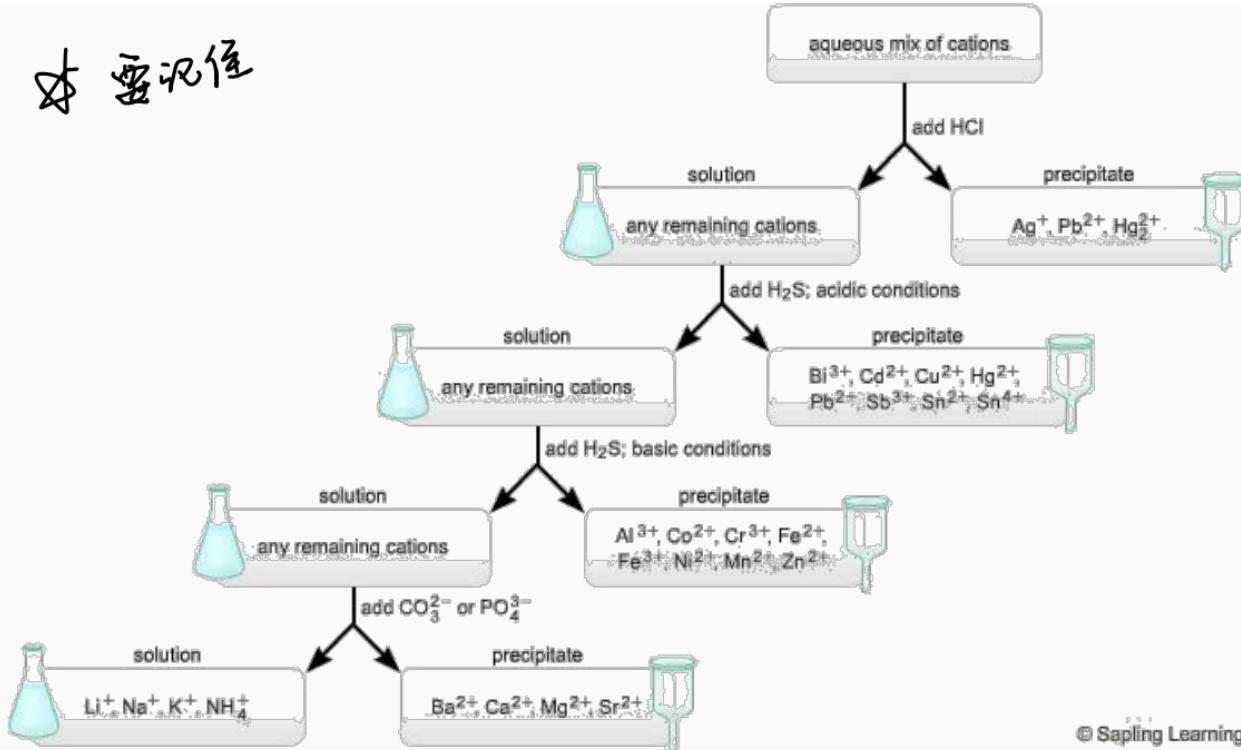


The overall solubility is measured by the concentration of  $\text{Cl}^-$  or  $\text{Ag}(\text{NH}_3)_2^+$  and the equilibration constant are product of the combination.

$$K_{net} = K_f \cdot K_{sp} = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} [\text{Ag}^+][\text{Cl}^-] = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2}$$

# Solubility Equilibria

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# Rate law

The rate law is the equations relating the reaction rate with instantaneous concentrations.

The general form of rate law is  $\text{rate} = k \times [\text{concentration}]^\alpha$ . The power of concentration is the order of the reaction. In the textbook, three cases are mainly discussed: zero, first, and second.

Note that for different orders of reaction, the rate constant should have different units to ensure that the rate is in mol/L/s.

# Rate law

Applying integration, the concentration change of a first-order reaction is

$$[A]_t = [A]_0 e^{-k_r t}$$

This is called exponential decay. We can transform this into  $\ln [A]_t = \ln [A]_0 - k_r t$ . Therefore, a plot of  $\ln [A]_t$  against  $t$  should be a straight line with slope  $-k_r$ , and intercept  $\ln [A]_0$ .

A unique character for first-order reaction is that it has a fixed half-life, the time for which the concentration is reduced by half.

$$t_{1/2} = \frac{\ln 2}{k_r}.$$

# Rate law

Similar integration gives the change of concentration for a second-order reaction is

$$[A]_t = \frac{[A]_0}{1 + k_r t [A]_0}$$

Transform the equation to a linear relation shows

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + k_r t.$$

The concentration change for zero-order reaction is extremely simple

$$[A]_t = [A]_0 - kt.$$

# Reaction Mechanism

Reaction mechanism is a sequence of elementary reactions by which the total reaction can be divided. Obviously, the sum of elementary steps should be the overall reaction.

The rate laws of the elementary reactions follows directly from the formula. The rate for each step is proportional to the product of concentrations of each reactant. If one reactant has a stoichiometric coefficient greater than 1, we need to raise it to the same power. Finally, we multiply it by a constant  $k$ .

For example, for the step  $2A + B \rightleftharpoons C + D + E$ , the forward rate is  $k[A]^2[B]$ , the reverse rate is  $k'[C][D][E]$ . Note that the coefficient for opposing directions are not equal.

# Combining Elementary Rate Laws

To get the rate of a reaction, we need to express the rate of consumption of reactants or rate of formation of products. The key is to use steady-state approximation, that is to assume the concentration of intermediates are constant, so that the rate of formation and consumption for them are the same.

Note that, in a proposed mechanism, some steps are reversible, so that we need to consider both directions, and some are not. Some steps are fast (with a large  $k$ ), and some are slow (with a small  $k$ ), so that approximations can be made when a very small number is added or subtracted.

# Combining Elementary Rate Laws

For example, a proposed two-step mechanism for a reaction is:  
 $H_2A + B \longrightarrow HB^+ + HA^-$  and its reverse, both of which are fast,  
followed by  $HA^- + B \longrightarrow HB^+ + A^{2-}$ , which is slow. Find the  
rate law with  $HA^-$  treated as the intermediate and write the  
equation for the overall reaction.

We can easily see the overall reaction is

The steady-state approximation is

$$k_1[H_2A][B] - k'_1[HB^+][HA^-] - k_2[HA^-][B] = 0$$

Rearrange,  $[HA^-] = \frac{k_1[H_2A][B]}{k'_1[HB^-] + k_2[B]} = \frac{k_1[H_2A][B]}{k'_1[HB^-]}$ .

So, the rate of formation of  $A^{2-}$  is

$$k_2[B][HA^-] = \frac{k_1 k_2 [H_2A][B]^2}{k'_1[HB^-]}$$

# Effect of temperature

Generally speaking, chemical reactions are faster at high temperatures than at low temperatures. To describe the relation we use the empirical equation

$$\ln k_r = \ln A - \frac{E_a}{RT}$$

Or, after rearrangement

$$k_r = Ae^{-E_a/RT}$$

$E_a$  in the equation is the activation energy, we can see that reactions with high activation energies tend to have small  $k_r$ .

This Arrhenius relation applies to reactions of any order.



# Effect of temperature

To increase the rate of reactions, catalysts can be used, which lowers the activation energy and gives larger  $k_r$ .

In a proposed mechanism, the catalyst is often consumed first, and then produced. While an intermediate is first produced then consumed.

Despite the catalyst changes the activation energy, it doesn't effect the Gibbs energy change and the equilibrium constant.

# Calculating the Occupation Ratio for FCC and BCC

Weili Shi  
 October 26, 2020

## 1. Occupation ratio for FCC (face centered cubic)

We suppose that the radius of each atom is  $r$ , and the length of the side of the cell is  $a$ . We first find the relation between  $r$  and  $a$ . We observe the triangle, we have:

$$(4r)^2 = a^2 + a^2$$

and therefore we have:

$$a = 2\sqrt{2}r.$$

The volume of the entire cell is:

$$V_{fcc} = a^3 = (2\sqrt{2}r)^3 = 16\sqrt{2}r^3.$$

Since there are effectively 4 atoms inside the cell, the volume that the atoms occupy is:

$$V_{atoms} = 4 \cdot \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3.$$

Therefore, the occupation ratio is

$$Ratio = \frac{V_{atoms}}{V_{fcc}} = \frac{\pi}{3\sqrt{2}} \approx 74\%.$$

## 2. Occupation ratio for BCC (body centered cubic)

Similarly, we suppose that the radius of each atom is  $r$ , and the length of the side of the cell is  $a$ . We first find the relation between  $r$  and  $a$ . We observe the triangle, we have:

$$(4r)^2 = a^2 + 2a^2$$

and therefore we have:

$$a = \frac{4}{\sqrt{3}}r.$$

The volume of the entire cell is:

$$V_{bcc} = a^3 = \left(\frac{4}{\sqrt{3}}r\right)^3 = \frac{64\sqrt{3}}{9}r^3.$$

Since there are effectively 2 atoms inside the cell, the volume that the atoms occupy is:

$$V_{atoms} = 2 \cdot \frac{4}{3}\pi r^3 = \frac{8}{3}\pi r^3.$$

Therefore, the occupation ratio is

$$Ratio = \frac{V_{atoms}}{V_{bcc}} = \frac{\sqrt{3}\pi}{8} \approx 68\%.$$

