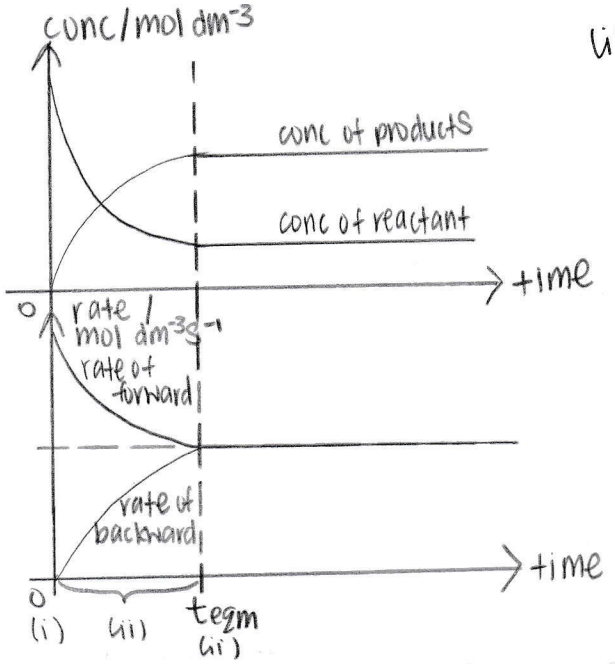
Chapter 8 : Chemical Equilibrium

Dynamic Equilibrium

A state of dynamic equilibrium is reached when the rate of the forward reaction is equal to the rate of the backward reaction in a reversible reaction and the concentrations of the reactants and the products are constant.



(i) At $t = 0$,
reactants are allowed to mix in a closed container
↳ forward reaction occurs

(ii) As reactants are turned into products
[reactants] decreases
↳ rate of forward reaction decreases
Since products are formed,
↳ backward reaction commences
[products] increases
↳ rate of backward reaction increases

(iii) rate of products reacting to form reactants
= rate of reactants reacting to form products
↳ dynamic equilibrium
[reactants] & [products] = constant
↳ no net change in amount of reactants and products
↳ reaction is incomplete

conditions for dynamic equilibrium

① closed system
↳ if products escape, the concentration will decrease
↳ backward reaction cannot occur

② Reaction is reversible

Types of Equilibria

① Homogeneous equilibrium : products and reactants all same phase

② Heterogeneous equilibrium : products and reactants different phase

Equilibrium constant : K_c

Q_c : reaction quotient at any given time

↳ ratio of the concentrations of the reactants and products raised to their stoichiometric ratios.

$$mA(aq) + nB(aq) \rightleftharpoons pC(aq) + qD(aq)$$

$$Q_c = \frac{[C]^p [D]^q}{[A]^m [B]^n} \rightsquigarrow \frac{\text{products}}{\text{reactants}}$$

↓ changes with time

At equilibrium $Q_c = K_c$

↳ unique to the reaction

↳ units : $(\text{mol dm}^{-3})^{(p+q)-(m+n)}$

↳ constant at a given temperature

↳ measures the extent to which reactants are converted to products at equilibrium

- higher K_c value, higher proportion of products

Equilibrium constant : K_p

- only useful for gaseous systems

$$mA(g) + nB(g) \rightleftharpoons qC(g)$$

$$K_p = \frac{(P_C)^q}{(P_A)^m (P_B)^n} \rightsquigarrow \frac{\text{product}}{\text{reactant}}$$

- unique to the reaction
- units : $(\text{Pa or atm})^{q-(m+n)}$
- constant at a given temperature

Things to exclude for both K_c and K_p expressions

① concentration of pure solids

conc of solids are densities

↳ constant

↳ independent on the mass of solid present

② concentration of pure liquids

conc of liquids are calculated from densities

↳ constant

③ concentration of solvent

present in excess

↳ constant at 55.5 mol dm^{-3}

↳ much larger than the concentration of the solute

↳ does not change significantly throughout

Significance of K_c and K_p

- indicates the extent of the forward reaction at equilibrium at a given temperature
  - ↳ large value → forward reaction is almost complete
    → mainly products present
  - ↳ small value → forward reaction does not occur to any appreciable extent
    → mainly reactants present
- unaffected by changes in concentration of either products or reactants
  - ↳ position of equilibrium will change such that the final concentration will give the same K_c and K_p value
- magnitude of K_c and K_p do not give any information about the rate of forward and backward reaction

Le Chatelier's Principle (LCP)

LCP states that when a system at equilibrium is disturbed, the system will react to counteract the change imposed by shifting the position of the equilibrium in a direction that tends to reduce that change so as to re-establish the equilibrium.

- if a substance is added → concentration increases → system will re-adjust to remove the substance added
- if a substance is removed → concentration decreases → system will re-adjust to replace the substance removed
- increase in concentration of reactants → position of equilibrium will be shifted to the right → favour forward reaction

disturbance
1. change in concentration
2. change in partial pressure
3. Adding an inert gas
4. change in temperature
5. Adding a catalyst

① Change in concentration

↑ in conc of a reactant
↳ rate of forward reaction increases
- conc of other reactant ↓ } ∴ LCP
- conc of product ↑
↳ forward rate will start to ↓, backward rate will start to ↑
↳ backward rate catch up
- equal to forward rate
↳ re-establish equilibrium
↳ Q_c rises until it reaches K_c
↳ new equilibrium position
↳ conc of product and added reactant will be higher than original
conc of other reactant will be lower

↓ in conc of a reactant
↳ rate of backward reaction increases
- conc of other reactant ↑
- conc of product ↓
↳ forward rate will start to ↑, backward rate will start to ↓
↳ forward rate catch up
- equal to forward rate
↳ re-establish equilibrium
↳ Q_c drops until it reaches K_c
↳ new equilibrium position
↳ conc of product and added reactant will be higher than original
conc of other reactant will be lower

② Change in partial pressure : only affect gases

(a) constant temperature, change the gaseous particles

removal of products
↳ partial pressure of product ↓
↳ by LCP, the system will adjust to increase the partial pressure
↳ position of equilibrium will shift to the right

removal of reactants
↳ partial pressure of reactants ↓
↳ by LCP, the system will adjust to increase the partial pressure
↳ position of equilibrium will shift to the left

(b) constant temperature, change volume of vessel

(i) no. of gaseous particles on both sides are equal
When volume of the vessel ↓ / ↑
↳ neither the forward nor the backward reaction will be favoured
∴ number of gaseous particles on both sides is equal

(ii) When the number of reactants is more than products

When volume of vessel ↓
↳ partial pressure of the gases ↑
↳ by LCP, the system will counteract
↳ position of equilibrium shifts to the right
↳ the side with less gas particles present so as to re-establish equilibrium
↳ forward reaction will be favoured

When volume of vessel ↑
↳ partial pressure of the gases ↓
↳ by LCP, the system will counteract
↳ position of equilibrium shifts to the left
↳ the side with more gas particles present so as to re-establish equilibrium
↳ backward reaction favoured

(iii) When the number of products is more than reactants

When volume of vessel ↓
↳ partial pressure of the gases ↑
↳ by LCP, the system will counteract
↳ position of equilibrium shifts to the left
↳ the side with less gas particles present so as to re-establish equilibrium
↳ backward reaction favoured

When volume of vessel ↑
↳ partial pressure of the gases ↓
↳ by LCP, the system will counteract
↳ position of equilibrium shifts to the right
↳ the side with more gas particles present so as to re-establish equilibrium
↳ forward reaction favoured

③ Adding an inert gas

(a) constant volume

- total pressure increases
- partial pressure of the reactants and products remain constant
- system is not disturbed
  ↳ equilibrium position remains unchanged

(b) constant pressure

- volume must increase to keep pressure constant
- partial pressure of the reactants and products decrease
- by LCP, equilibrium position will shift to the left / right
  ↳ the side with more gas particles
- forward / backward reaction favoured

④ Changing temperature

(a) Exothermic forward reaction

When temperature ↑
↳ by LCP, the system will adjust to remove excess heat
↳ endothermic backward reaction is favoured
↳ position of equilibrium shifts to the left
↳ When temperature increases
- kinetic energy of both products and reactants will increase
- both forward and backward reaction will become faster
- rate of backward reaction increases more than forward reaction
∴ backward is endothermic
- position of equilibrium is shifted to the left

↳ K_c ↓
↳ equilibrium is reached faster

When temperature ↓,
↳ by LCP, the system will adjust to release more heat
↳ exothermic forward reaction is favoured
↳ position of equilibrium shifts to the right
↳ When temperature decreases
- kinetic energy of both products and reactants decrease
- both forward and backward reaction will become slower
- rate of backward reaction decreases more than forward reaction
∴ forward is exothermic
- position of equilibrium is shifted to the right

↳ K_c ↑
↳ equilibrium is reached slower

(b) Endothermic forward reaction

When temperature ↑
↳ by LCP, the system will adjust to remove excess heat
↳ endothermic forward reaction will be favoured
↳ position of equilibrium shifts to the right
↳ When temperature increases
- kinetic energy of both products and reactants will increase
- both forward and backward reaction will become faster
- rate of forward reaction increases more than backward reaction
∴ forward is endothermic
- position of equilibrium shifted right

↳ K_c ↑

When temperature ↓
↳ by LCP, the system will adjust to release more heat
↳ exothermic backward reaction is favoured
↳ position of equilibrium shifts to the left
↳ When temperature decreases
- kinetic energy of both products and reactants will decrease
- both forward and backward reaction will become slower
- rate of forward reaction decreases more than backward reaction
∴ backward is exothermic
- position of equilibrium is shifted to the right

↳ K_c ↓

⑤ Adding a catalyst

- no effect on composition
- no effect on K_c or K_p
- catalyst increases the rates of reaction
  - ↳ lowers activation energy of both reactions by the same amount
  - ↳ equilibrium is reached more quickly

Degree of dissociation

- the fraction or percentage of reactant that has dissociated at a particular temperature

$$\text{Degree of dissociation, } \alpha = \frac{\text{amount dissociated}}{\text{total initial amount}}$$

ICE boxes

equation			→		
initial amount / mol					
change in amount / mol					
equilibrium amount / mol					

OR

equation			→		
initial pressure / Pa					
change in pressure / Pa					
equilibrium pressure / Pa					

Industrial Application: Haber process

principles of industrial processes:

① take place quickly
② minimise cost
↳ use catalyst
↳ avoid very high temperature
↳ avoid very high pressures

⇒ maximum amount of product
shortest time
minimum cost

Haber process

- temperature : 450°C
- pressure : 200 atm
- catalyst : finely divided Fe with Al_2O_3
- continuous removal of NH_3
↳ shifts the equilibrium position right
- molar ratio of $N_2 : H_2 = 1 : 3$
↳ minimise excess

Gibbs free energy, G

- temperature and pressure dependent
- At a given temperature and pressure, a chemical reaction will occur in whatever direction that leads to a decrease in the value of G
↳ G minimum = equilibrium

$$\Delta G = \Delta H - T\Delta S = G_2 - G_1$$

- $\Delta G > 0$
↳ BACKWARD reaction is spontaneous
↳ backward reaction occurs at a faster rate than the forward reaction
↳ decrease the total G

- $\Delta G < 0$
↳ FORWARD reaction is spontaneous
↳ forward reaction occurs at a faster rate than the backward reaction
↳ increase the total G

- $\Delta G = 0$
↳ forward and backward reaction occurs at the same rate
↳ minimum G
↳ dynamic equilibrium

$$\Delta G^{\circ} = -RT \ln K$$

- R: molar gas constant
- T: temperature
- K: equilibrium constant

- gives the information on the composition of reaction at equilibrium and spontaneity of the reaction

- $\Delta G^{\circ} < 0$, K would be very big, > 1
  - ↳ high proportion of products
  - ↳ reaction is almost complete
  - ↳ equilibrium lies very much to the right
  - ↳ forward reaction is spontaneous
- $\Delta G^{\circ} > 0$, K would be small, $0 < K < 1$
  - ↳ low proportion of products
  - ↳ most reactants are left unreacted
  - ↳ equilibrium lies very much to the left
  - ↳ backward reaction is spontaneous
- ΔG° close to zero
  - ↳ approximately equal reactants and products
  - ↳ backward and forward reactions are both spontaneous