Chemical Equilibrium

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Physical Chemistry
Paper-IA
Lecture-01

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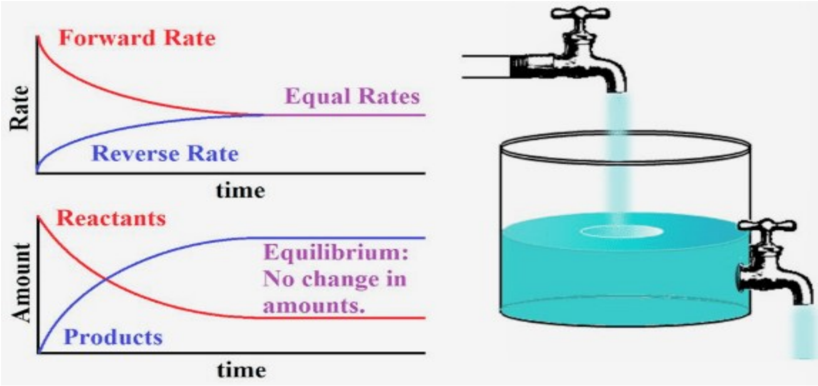
Chemical Equilibrium

- Chemical Equilibrium
- Reversible and irreversible reaction
- Statement of law of Mass action and its kinetic derivation
- Equilibrium constant for homogeneous and heterogeneous reaction
- Relationship between Kc, Kp and Kx

Chemical Equilibrium

- Chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time, so that there is no observable change in the properties of the system.
- Reversible chemical reaction
- No net change in the amounts of reactants and products occurs.
- Rate of forward reaction is equal to rate of backward reaction at equilibrium



Note: A reversible chemical reaction is one in which the products, as soon as they are formed, react to produce the original reactants.

Equilibrium Position

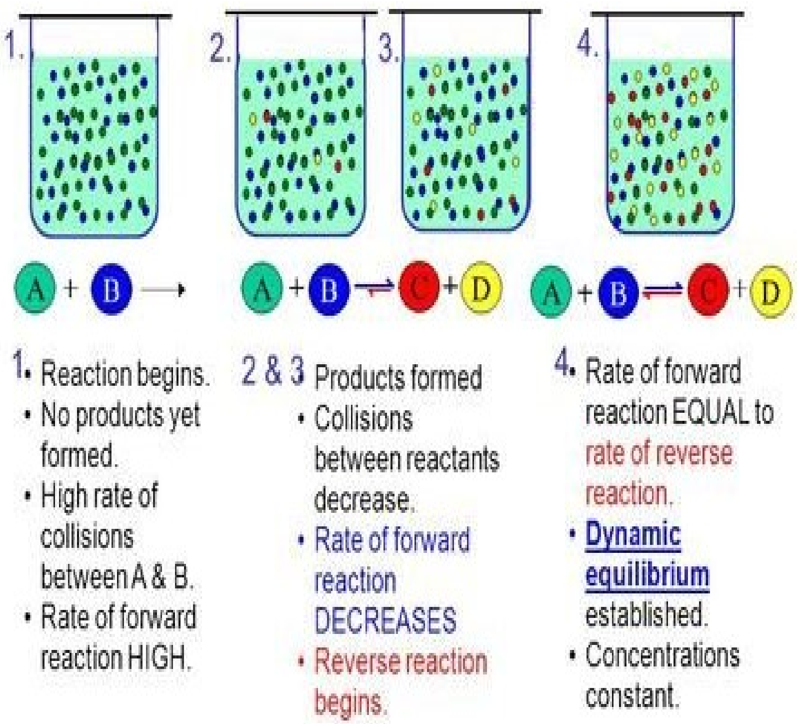


Fig:1 Chemical Equilibrium

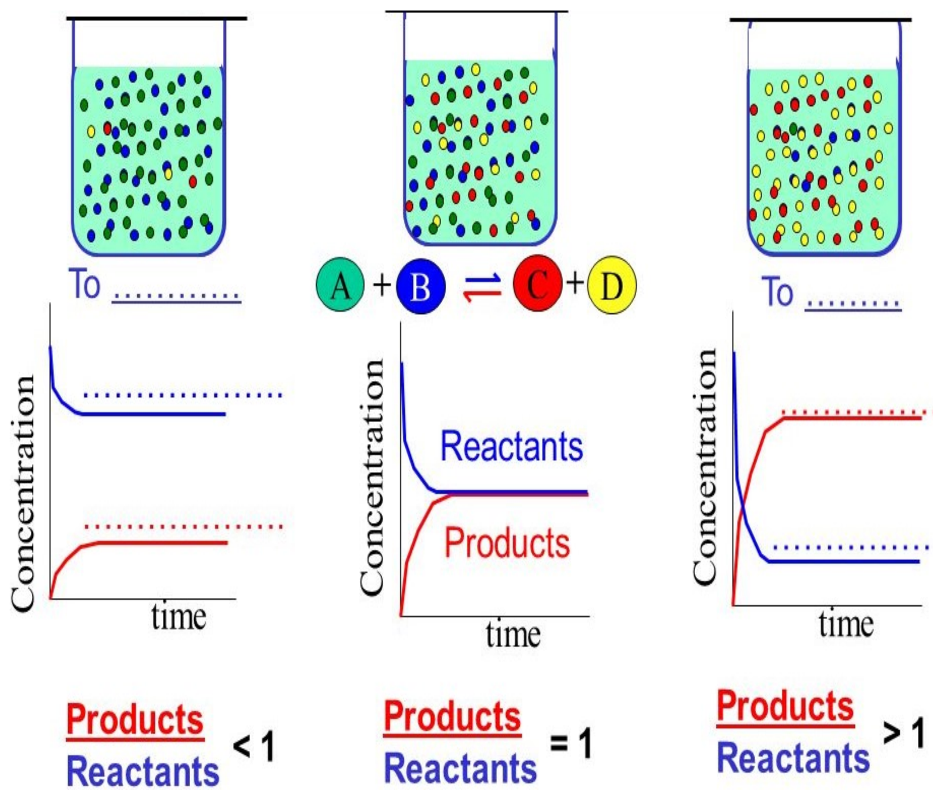


Fig:2 Shift of Equilibrium Position

Reversible reaction

Reversible chemical reactions

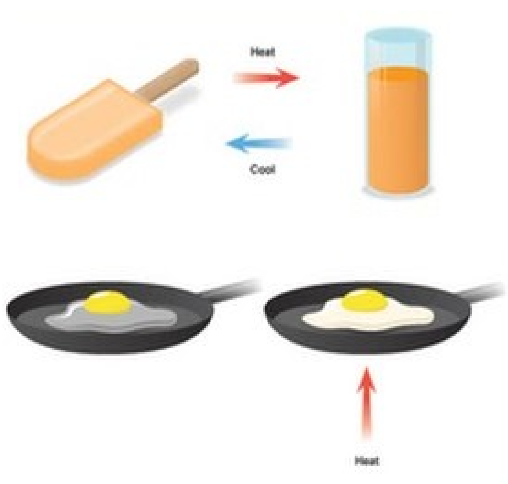
- It can occur in both directions   Denoted by $\rightleftharpoons$
- infinite changes can occur in the system
- The reactants can change to the products, and the products can also change back to the reactants.
- As the reactants react with other reactants to form products, the products are reacting with other products to form reactants i.e product donot react to form the reactant
- Equilibrium between initial and final state of the system

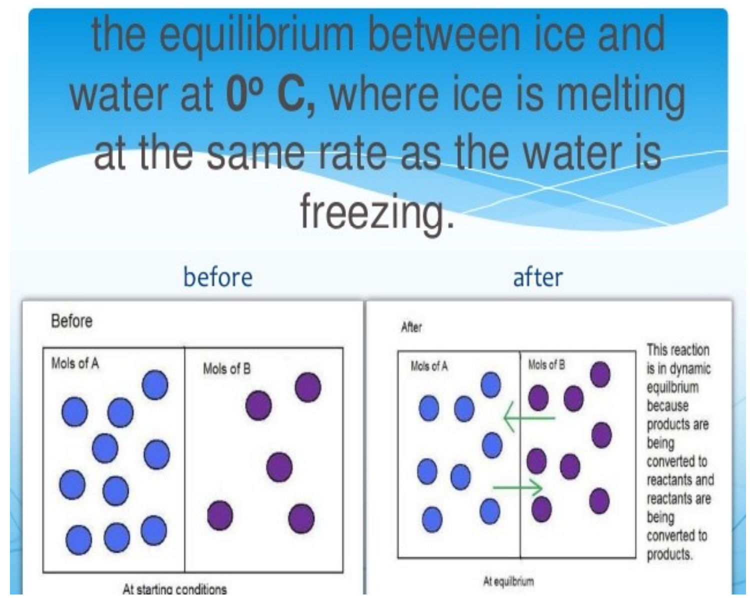
Irreversible reaction

Irreversible chemical reactions

- It can occur in only one direction Denoted by $\longrightarrow$
- Finite changes can occur in the system
- The reactants can change to the products, but the products cannot change back to the reactants.
- Irreversible reactions only proceed in one direction, so the reaction can never be at equilibrium.
- No equilibrium in the system

Reversible and irreversible reaction





Reversible reaction

Example:

$$N_2 + O_2 \rightleftharpoons 2NO$$

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$$NH4Cl \rightleftharpoons NH_3 + HCl$$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Irreversible reaction

Example:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

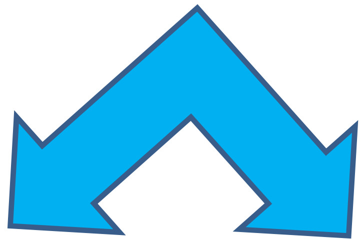
$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

$$Cl_2(g) + 2OH^-(aq) \rightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$$

Law of Mass action

- Law state that the rate of any chemical reaction is proportional to the product of the masses of the reacting substances, with each mass raised to a power equal to the coefficient that occurs in the chemical equation
- The rate of the chemical reaction is directly proportional to the product of the activities or concentrations of the reactants.
- It explains and predicts behaviors of solutions in dynamic equilibrium.
- A chemical reaction mixture that is in equilibrium, the ratio between the concentration of reactants and products is constant in a reaction equilibrium mixture.

Two aspects are involved in the initial formulation of the law:



Equilibrium aspect ,composition of a rxn mix. at equilibrium

Kinetic aspect,concerning the rate equations for elementary reactions

Kinetic derivation for law of mass action

Rate law:

It is an equation that shows the dependence of the reaction rate on the concentration of each reactant.

$$aA + bB \longrightarrow \text{Products}$$

$$\text{rate} \ \alpha \ [A]^m [B]^n$$

$$\text{rate} = k[A]^m [B]^n$$

where k is the rate constant

Rate law for elementary reaction

- Law of mass action applies

Rate of reaction α Product of active masses of reactants

Active mass molar concentration raised to power of number of species

Examples:

$$A \longrightarrow P+Q \quad rate=K_1[A]$$

$$A \longrightarrow P+Q \quad rate=K_2[A]^1[B]^2$$

$$2A + B \longrightarrow E+F+G \quad rate=K_3[A]^2[B]^1$$

Calculation of the equilibrium constant

For the reaction

$$aA + bB \rightleftharpoons cC + dD$$

The relationship between the value of the equilibrium constant k and the concentrations of reactant and product is given by

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

K_c is fixed value for a particular rxn at Sp.Temp.

The equilibrium NO_2 Conc. is x M and N_2O_4 is y M:

Calculation of the equilibrium constant

$$K = \frac{[N_2O_4]}{[NO_2]} = \frac{[x]}{[y]^2}$$

Note: K is unitless and only temperature changes the value of K_c

K is measured from the ratio of products to reactants at equilibrium on

Homogeneous equilibrium & Heterogeneous equilibrium

K = Reactants at equilibrium/Products at equilibrium

Homogeneous equilibrium

- substances are in the same phase
- Rxn involving only gases or solution

Heterogeneous equilibrium

- substances are in different phases
- Rxn involving only(s,l, g,aq) of matter.

Homogeneous equilibria:

Ex: $N_2O_{4(g)} \rightleftharpoons 2\ N_2O_{(g)}$ $=0.212$ at $100\ ^0c$

$$K = \frac{[N_2O_4]}{[NO_2]} = \frac{[x]}{[y]^2}$$

Ex: $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ at 500^0c

lime

Heterogeneous equilibrium $K_{c/eq} = [CO_2]$

$K_p = P\ CO_2$

Relationship between Kc, Kp and Kx

Relationship between Kp ,Kc, Kx and Kn

Kp=Equilibrium constant in terms of partial pressure.

Kc=Equilibrium constant in terms of concentration.

Kx=Equilibrium constant in terms of mole fraction.

Kn=Equilibrium constant in terms of number of moles.

Kp and Kc are related as $\mathbf{K_P = K_C\,(RT)^{\Delta n}}$ ....(eq 1)

Relationship between K_P and K_n

$$K_p = \frac{P_C^{\ c} \times P_D^{\ d}}{P_A^{\ a} \times P_B^{\ b}}$$ ....(eq 2)

From ideal gas equation, $PV=nRT$

$$\Rightarrow P=n(RT/V)$$

Where, **n** is the number of moles

So, $\mathbf{P_A = n_A(RT/v), P_B = n_B(RT/V), P_C = n_C(RT/V)}$ **and** $\mathbf{P_D = n_D(RT/V)}$

Replacing equation 2 by the above value we get that,

$$K_p = \frac{[n_C(RT/V)]^c \cdot [n_D(RT/V)]^d}{[n_A(RT/V)]^a \cdot [n_B(RT/V)]^b}$$

$$\Rightarrow K_p = \frac{n_C^c \cdot n_D^d}{n_A^a \cdot n_B^b} \cdot (RT/V)^{(c+d)-(a+b)}$$

$$=> K_p = K_n \cdot (RT/V)^{\Delta n}$$

$$=> K_p = K_n \cdot (P_T/n_T)^{\Delta n}$$

Δn=number of gaseous moles of product – number of gaseous moles of reactant

Relation between Kp and Kx

$$K_p = \frac{P_C{}^c \times P_D{}^d}{P_A{}^a \times P_B{}^b}.$$

From above (eq….. 2)

Partial pressure(P) = Mole fraction(x) . Total pressure(P_T)

So, $P_A = \mathbf{x_A \, . \, P_T}$

$P_B = \mathbf{x_B \, . \, P}$

$P_C = \mathbf{x_C \, . \, P_T}$

$P_D = \mathbf{x_D \, . \, P_T}$

Putting the values in whole equation:

$$K_P = \frac{(\mathbf{x_C \, . \, P_T})^c \, . \, (\mathbf{x_D \, . \, P_T})^d}{(\mathbf{x_A \, . \, P_T})^a \, . \, (\mathbf{x_B \, . \, P_T})^b}$$

$$= \frac{\mathbf{x_C}^c \, . \, \mathbf{x_D}^d}{\mathbf{x_A}^a \, . \, \mathbf{x_B}^b} \; P_T^{(c+d) - (a+b)}$$

$$\Rightarrow \quad \mathbf{K_P = K_x \, (P_T)^{\Delta n}}$$

Kp=**Kc**$(RT)^n$ where R is the gas constant, T is the Temperature and n is the change in no. of gaseous moles in the **reaction**.

Q1. Calculate $K_{c\ and}$ K_x for the given reaction

$N_2O_4(g)=2NO_2(g)$ Hints: Kp=0.157

Q2. a) What is the difference between homogeneous and heterogeneous equilibria?

b) List the examples.

Q3. Under what conditions are the values of KC and KP for a given gas phase equilibrium the same?

Q4. What is the relation between KP KC and KX?