CHEMICAL EQUILIBRIUM

1. INTRODUCTION

Equilibrium represents the state of a process in which the proprties like temperature, pressure, concentration of the system do not show any change with the passage of time.

If the opposing processes involve only physical changes, the equilibrium is called physical equilibrium. If the opposing processes involve chemical changes, i.e., the opposing processes are chemical reactions, the equilibrium is called chemical equilibrium.

2. EQUILIBRIA IN CHEMICAL PROCESSES

2.1 Reversible Reactions

A reaction in which not only the reactants react to form the products under certain conditions but also the products react to form reactants under the same conditions is called a reversible reaction. In other words a reaction which takes place not only in the forward direction but also in the backward direction under the same conditions is called a reversible reaction.

A reversible reaction between A and B to form C and D is represented as :
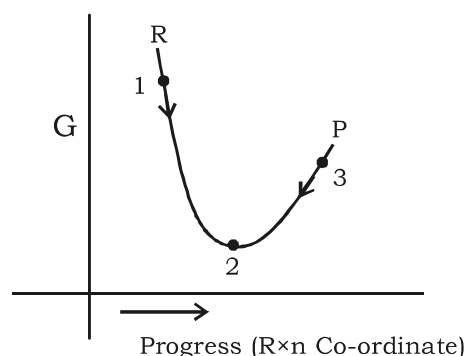
$$A + B \rightleftharpoons C + D$$
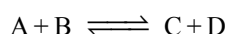
2.2 Irreversible Reactions

If a reaction cannot take place in the reverse direction, i.e., the products formed do not react to give back the reactants under the same conditions, it is called an irreversible reaction.

$$A + B \longrightarrow C + D$$

2.3 Concept of Chemical Equilibrium


Progress (R×n Co-ordinate)

- It is the state of minimum Gibb's energy

- $dG = 0$ and $\Delta G = 0$ at this state

- Rate of forward reaction = Rate of backward reaction

- This equilibrium is dynamic and stable in nature

Dynamic Nature of Chemical Equilibrium

In the Haber's process, starting with definite amounts of N_2 and H_2 and carrying out the reaction at a particular temperature, when equilibrium is attained, the concentrations of N_2, H_2 and NH_3 become constant. If the experiment is repeated by taking deuterium (D_2) in place of H_2 but with the same amounts and exactly similar conditions as before, equilibrium is attained containing D_2 and ND_3 in place of H_2 and NH_3 but in the same amounts. Now, if the two reaction mixtures are mixed, then after some time, it is found that the concentrations of ammonia and hydrogen are same except that now all forms of ammonia (i.e., NH_3, NH_2D, NHD_2, ND_3) and all forms of hydrogen (i.e., H_2, HD, $_2$) are present. This shows that at equilibrium, the reaction is still going on, i.e., equilibrium is dynamic in nature.
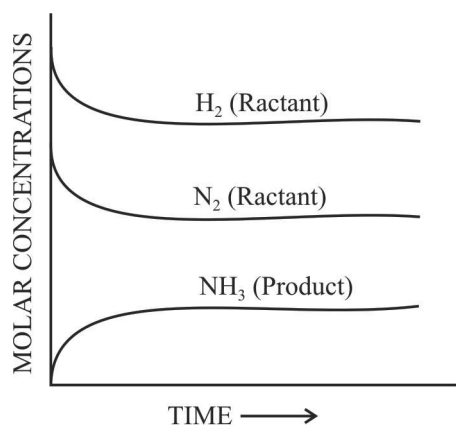
Representing the attainment of equilibrium for the reaction
$N_2(g) + 3H_2(g) \rightleftharpoons NH_3(g)$

2.4 Characteristics of Chemical Equilibrium

(i) At equilibrium, the concentration of each of the reactants and the products becomes constant.

(ii) At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction and hence the equilibrium is dynamic in nature.

(iii) A chemical equlibrium can be established only if none of the products is allowed to escape out or separate out as a solid.

e.g. if CO_2 gas escapes out in case of decomposition of $CaCO$, the reaction will no longer remain reversible.

Similarly, the reaction is irreversible if one of the products separates out as solid,

$$AgNO_3 + KCl \longrightarrow AgCl\downarrow + KNO$$
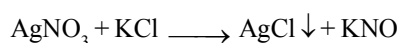
(iv) Chemical equilibrium can be attained from either direction, i.e., from the direction of the reactants as well as from the direction of the products.

3. RATE OF A REACTION

Average Rate = Change in concentration/Time taken
$= \Delta c/\Delta t$
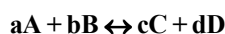
Δc = Final Concentration – Initial concentration

3.1 Instantaneous rate

Lim $\Delta c/\Delta t = dc/dt$

$\Delta t \rightarrow 0$

Units of rate : conc/time or mol/Ls

3.2 Overall rate of a reaction

aA + bB ↔ cC + dD

Overall Rate =

$-(1/a)\,\Delta A/\Delta t = -(1/b)\,\Delta B/\Delta t = +(1/c)\,\Delta C/\Delta t = +(1/d)\,\Delta D/\Delta t$

Overall rate :

Rate of forward reaction – Rate of backward reaction

"At equilibrium the overall rate of a reversible reaction becomes zero".
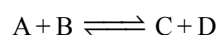
4. EQUILIBRIUM CONSTANT (K)

4.1 Law of Mass Action

The rate of a reaction is proportional to the product of the active masses of the reactants, each raised to the power equal to its stoichiometric coefficient as represented by the balanced chemical equation.

$$aA + bB + cC + ... \longrightarrow Products$$

$$\text{Rate of reaction} \propto [A]^a [B]^b [C]^c .....$$

Law of Chemical Equilibrium is a result obtained by applying the Law of Mass Action to a reversible reaction in equilibrium.

$$A + B \rightleftharpoons C + D$$

Rate of the forward reaction $\propto [A][B] = k_f[A][B]$

Rate of the backward reaction $\propto [C][D] = k_b[C][D]$

At equilibrium,

Rate of forward reaction = Rate of backward reaction

$$k_f[A][B] = k_b[C][D] \quad \text{or} \quad \frac{[C][D]}{[A][B]} = \frac{k_f}{k_b} = K$$

At constant temperature, as k_f and k_b are constant, therefore,

$\dfrac{k_f}{k_b} = K$ is also constant at constant temperature and is called 'Equilibrium constant'.

The product of the molar concentrations of the products, each raised to the power equal to its stoichiometric coefficient divided by the product of the molar concentrations of the reactants, each raised to the power equal to its stoichiometric coefficient is constant at constant temperature and is called Equilibrium constant.

4.2 Characteristics of Equilibrium Constant

(i) The value of the equilibrium constant for a particular reaction is always constant depending only upon the temperature of the reaction and is independent of the concentrations of the reactants with which we start or the direction from which the equilibrium is approached.

(ii) If the reaction is reversed, the value of the equilibrium constant in inversed.

(iii) If the equation (having equilibrium constant K) is divided by 2, the equilibrium constant for the new equation is the square root of K (i.e., $\sqrt{K}$).

(iv) If the equation (having equilibrium constant K) is multiplied by 2, the equilibrium constant for the new equation is the square of K (i.e., K^2)

(v) If the equation (having equilibrium constant K) is written in two steps (having equilibrium constant K_1 and K_2) then $K_1 \times K_2 = K$.

(vi) The value of the equilibrium constant is not affected by the addition of a catalyst to the reaction.

This is because the catalyst increases the speed of the forward reaction and the backward reaction to the same extent.
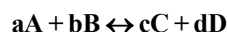
4.3 Extent of Reaction

High value of Kc $(K_c > 10^3) \rightarrow$ At equilibrium reaction is forward dominant

Low value of Kc $(K_c < 10^{-3}) \rightarrow$ At equilibrium reaction is backward dominant

Moderate value of K_c (between 10^3 and 10^{-3}) $\rightarrow$ At equilibrium neither direction dominates
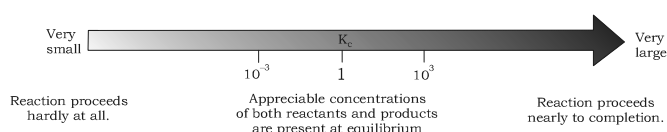
4.4 Reaction Quotient (Q)

$aA + bB \leftrightarrow cC + dD$

$Q = [C]^c [D]^d / [A]^a [B]^b$

$Q > K_c$: Reaction will tend towards backward direction

$Q > K_c$: Reaction will tend towards forward direction

$Q > K_c$: Reaction will be at equilibrium

Note :

Q is a variable which always approaches K_{eq} which is a constant.

4.5 Calculating Equilibrium Concentrations

Suppose we are given the following data :

1. The balanced reaction and value of K_c

2. The initial concentration of the reactants, or the initial moles

3. Volume of the container

And we need to find the final equilibrium concentration of the reactants and products. Then we can follow the following steps :

Step-1

Write down the balanced chemical equation for the reaction

Step-2

Under every reactant and product, write down the initial moles/concentration

Step-3

Subtract the amount reacting and add the amount produced in terms of a variable x and note down the equilibrium concentration in terms of x. If we are dealing in moles then we will need to divide the moles by volume to obtain concentrations.

Step-4

Substitute the equilibrium concentration in the expression of K_c and equate it to the value of K_c.

Step-5

Solve the above equation and calculate the value of x and in case of multiple solutions select the value which is sensible from reaction point of view. Then back substitute

the value of x in the equilibrium concentration expression and obtain the actual value of the same.

4.6 Equilibrium constant K_p

aA + bB ↔ cC + dD
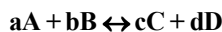
$K_p = (P_C^c \times P_D^d)/(PAa \times P_B^b)$

where P_C, P_D, P_A, P_B are partial pressures of A, B, C and D respectively.

$K_p = K_c (RT)^{\Delta n}$

$R = 0.0821$ L atm/mol–K

4.7 Relationship of K_{eq} and ΔG

For any reaction :

$\Delta G = \Delta G° + RT \ln Q$ Where Q is the reaction quotient.

At equilibrium $\Delta G = 0$

$\Delta G° = -RT \ln K_{eq} = -2.303 RT \log_{10} K_{eq}$

where K_{eq} is generally taken as K_p. It depends on the definition of standard values to define $\Delta G°$.

If the standard active masses are taken as 1 M each then we will take $K_{eq} = K_C$ and if they are taken as 1 atm each then we will take $K_{eq} = K_p$.

4.8 Dependence of K_{eq} on temperature

Van't Hoff Equation :

$\ln (K_2/K_1) = (\Delta H/R)(1/T_1 - 1/T_2)$ or

$\log 10 (K_2/K_1) = (\Delta H/2.303R)(1/T_1 - 1/T_2)$

Exothermic Reactions

ΔH = negative

On increasing the temperature the equilibrium constant will decrease i.e. The reaction will become more backward dominant.

Endothermic Reaction

ΔH = possitive

On increasing the temperature the equilibrium constant will increase. The reaction will become more forward dominant.

POINTS TO REMEBER

Whether the reaction is exothermic or endothermic on increasing the temperature, it will tend towards endothermic direction.
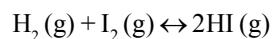
5. HOMOGENOUS EQUILIBRIA

Reactions in which all reactants and products are in the same phase Homogenous Reactions can further be divided into three sub-categoreis :
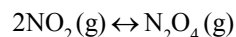
5.1 Those reactions where gaseous moles increase $(\Delta n = +ve)$

$$PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$$

5.2 Those reactions where gaseous moles remain the same $(\Delta n = 0)$

$$H_2(g) + I_2(g) \leftrightarrow 2HI(g)$$

5.3 Those reactions where gaseous moles decrease $(\Delta n = -ve)$

$$2NO_2(g) \leftrightarrow N_2O_4(g)$$

6. DEGREE OF DISSOCIATION, α

It is defined as the fraction of molecules dissociating. For example, if 100 molecules are present and only 40 dissociate then the degree of dissociation is 0.4 or 40%.

7. HETEROGENEOUS EQUILIBRIA

Category of reactions where various phases/states exist in the same reaction.

In presence of gases the activity of solids and excess liquids is constant. Therefore we can assume the active masses of solids and excess liquids as constant.

$CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)}$
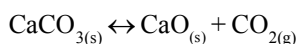
$K_c = [CO_2]$

$Kp = P_{CO_2}$

8. LE CHATELIER'S PRINCIPLE

If a distrubance is introduced in an equilibrium mixture it will behave so as to undo the distrubance and re-establish equilibrium.

8.1 Effect of Change of Concentration

If in a reaction in equilibrium, the concentration of any reactant is increased, the equilibrium shifts in the forward direction. On the other hand, if the concentration of any product is increased, the equilibrium shifts in the backward direction. The reverse happens if the concentrations are decreased.

8.2 Effect of change of temperature

Exothermic reactions are favoured by low temperature whereas endothermic reations are favoured by high temperature.

8.3 Effect of change of pressure

Low pressure favours those reactions which are accompanied by increase in total number of moles and high pressure favours those reactions which take place with decrease in total number of moles. However, pressure has no effect on an equilibrium reaction which proceeds with no change in total number of moles.

### 8.4 Effect of change in volume

The effect of decrease of volume is equivalent to the effect of increase of pressure.

hence the effect of decrease in volume will be to shift the equilibrium in the direction in which the number of moles decreases.

8.5 Effect of a Catalyst

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

eg contact process,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); K_c = 1.7 \times 10^{26}$$
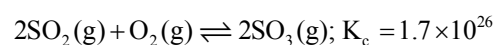
Practically the oxidation of SO_2 to SO_3 is very slow. Thus, platinum or divanadium penta-oxide (V_2O_5) is used as catalyst to increase the rate of the reaction.

8.6 Effect of adding an inert gas to a reaction mixture in equilibrium.

(a) If the reaction takes place at constant volume addition of an inert gas will not change the molar concentrations of the reactants and products. Hence, the state of equilibrium will remain unaffected.

(b) If the reaction takes place at constant pressure, addition of inert gas must accompany in increase in the total volume to keep pressure constant. Thus, reaction shifts towards larger number of moles.

IONIC EQUILIBRIUM

Ionic equilibrium is the study of equilibrium in the reactions where formation of ions take place in aqueous solution.

1. ELECTROLYTES

Electrolytes are those compounds which on dissolving in polar solvents like water break into ions. The solution of electrolytes conducts electricity because of the presence of ions.

1.1. Classification of electrolytes

1.1.1 Electrolytes can be classified on the basis of their strength into two categories:

Strong electrolytes : Those electrolytes which easily break into ions and give almost complete dissociation. Eg. HCl, NaOH, NaCl, HNO_3, $HClO_4$, H_2SO_4, $CaCl_2$ etc

Weak electrolytes : Those electrolytes which dissociate partially. Eg. CH_3COOH, NH_4OH, HCN, $H_2C_2O_4$, and all organic acids and bases etc.

1.1.2 Electrolytes can be further classified on the basis of the kind of compound they are.
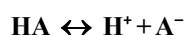
○ **Acids**
○ **Bases**
○ **Salts**

1.2 Acids and Bases

The definition of acids and bases varies from theory to theory:

1.2.1 Arrhenius theory

This theory defines acids and bases from the perspective of water as a solvent.

Arrhenius acids: Those compounds which will increase H^+ ion concentration in water. Eg HCl, H_2SO_4, CH_3COOH etc

HA ↔ H⁺ + A⁻

Arrehenius bases: Those compounds which will increase OH^- ion concentration in water. Eg. NaOH, $Ca(OH)_2$, NH_4OH etc

The major drawback of this theory is that the basis of all definitions is water.
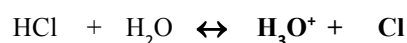
BOH ↔ B⁺ + OH⁻
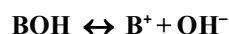
1.2.2 Bronsted-Lowry concept

Acids : Those compounds which can transfer protons that is H^+ to other compounds

Bases: Those compounds which can accept protons.

That is, Bronsted acids are "proton donors" and Bronsted bases are "Proton acceptors".

HCl + H_2O ↔ H_3O^+ + Cl

Acid-1   Base-1   Acid-2   Base-2

Conjugate Acid-Base pairs: Pairs which are separated by a proton and exhibit opposite behaviours in the two directions of the same reaction. Eg. In the above reaction HCl and Cl⁻ are conjugate acid-base pairs.

Note : In a conjugate pair if acid is strong the base is weak and vice-versa.
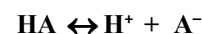
1.2.3 Lewis Concept

Acid: A compound which can accept a pair of electrons.

Base: is a compound which can transfer its lone pair of electrons.

Eg. $BF_3 + NH_3 ↔ H_3N → BF_3$
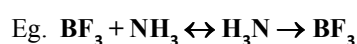
In the above reaction BF_3 is a lewis acid and NH_3 is a lewis base.

2. DISSOCIATION OF WEAK ACIDS AND BASES

HA ↔ H⁺ + A⁻

$K_a = c\alpha^2/(1-\alpha)$

K_a is called "ionisation constant" or the "Dissociation constant" of the acid.

For low dissociation : $1 - \alpha \approx 1$

$K_a = c\alpha^2$

$\Rightarrow \alpha = \sqrt{(K_a/C)}$ This expression will be valid only when $\alpha < 0.05$ (5%)

$[H^+] = c\alpha = \sqrt{cK_a} = [A^-]$

Similarly for a Weak base $K_a = c\alpha^2/(1-\alpha)$

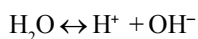K_b is called "ionisation constant" or "dissociation constant" for the base.

$\alpha = \sqrt{(K_b/C)}$ This expression will be valid only when $\alpha < 0.05$ (5%)

$[B^+] = [OH^-] = \sqrt{cK_b}$

Note :

α weak electrolytes increase on dilution

3. SELF-IONISATION OF WATER

$H_2O \leftrightarrow H^+ + OH^-$

$K_w = [H^+][OH^-]$

K_w is called ionic product of water.

For pure water: $[H^+] = [OH^-]$

At 25° C we know that $[H^+][OH^-] = 10^{-14}$

$[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7} M$

Acidic: $[H_3O^+] > [OH^-]$

Neutral: $[H_3O^+] = [OH^-]$

Basic: $[H_3O^+] < [OH^-]$

Note: K_w increases as temperature increases.

4. pH SCALE

$pH = -\log_{10}[H^+]$

$pH + pOH = pK_w = 14$ (at 25°)

At 25°C

$pH < 7$ Acidic

$pH > 7$ Basic

$pH = 7$ Neutral

5. MIXTURE OF TWO WEAK ACIDS
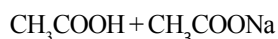
$[H^+] = (x + y) = \sqrt{c_1K_1 + c_2K_2}$

6. BUFFER SOLUTIONS

Solutions which can resist any change in pH on addition of small amount of acid or base.

Buffer solutions are of three types:
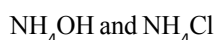
6.1 Acidic Buffer Eg.

$CH_3COOH + CH_3COONa$

Henderson-Hasselbalch equation

$pH = pK_a + \log [salt]/[acid]$

6.1.1 Buffer Range:

$pK_a - 1 \leq pH \leq pK_a + 1$

6.2 Basic Buffer Eg.

NH_4OH and NH_4Cl

$pOH = pK_b + \log [salt]/[base]$

6.2.1 Buffer range:

$pK_b - 1 \leq pOH \leq pK_b + 1$

6.3 Mixed Buffer Eg.

CH_3COONH_4

Note :

O   pH of a buffer solution does not change on dilution.

O   For any acid-conjugate base pair $K_a.K_b = K_w$

7. POLYPROTIC ACIDS

Those acids which can furnish more than one H^+ permolecule. Eg. H_2SO_4, H_2CO_3, H_3PO_4

For any polyprotic acid : $\mathbf{K_1 > K_2 > K_3 ....so on}$

For dissociation of H_2A $\mathbf{[A2^-] \approx K}$

i.e. The concentration of the second ion of a polyprotic acid is almost equal to the second dissociation constant.

8. SALT HYDROLYSIS

Depending on the nature of the parent acid and base there can be 4 type of salts:

8.1 Salt of strong acid and strong base (NaCl)

This type of salt do not get hydrolysed.

Neutral solution with pH = 7

8.2 Salt of weak acid and strong base (CH_3COONa)

This type of salt give acidic solution on hydrolysis.

$K_h = C\alpha_h^2/(1 - \alpha_h) = K_w/K_a$; $pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} \log C$

8.3 Salt of Strong acid and weak base (NH_4Cl)

This type of salt give basic solution on hydrolysis.

$K_h = C\alpha_h^2/(1 - \alpha_h) = K_w/K_b$; $pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log C$
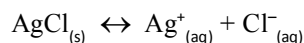
8.4 Salt of weak acid and weak base (CH_3COONH_4)

This type of salt may give acidic, basic or neutral solution.

$K_h = \alpha_h^2/(1 - \alpha_h)^2 = K_w/(K_a \times K_b)$; $pH = 7 + \frac{1}{2} pK_b - \frac{1}{2} pK_b$

9. SPARINGLY SOLUBLE SALTS & PRECIPITATION

When a salt is dissolved in water then it starts breaking into ions and after sometime the solubility process attains equilibrium.

$AgCl_{(s)} \leftrightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$

$K_{sp} = [Ag^+][Cl^-] = Q = I.P.$

I.P. $< K_{sp} \Rightarrow$ forward reaction, more salt can be dissolved

I.P. $= K_{sp} \Rightarrow$ saturation, no more salt can be dissolved

I.P. $> K_{sp} \Rightarrow$ backward reaction, precipitation of solid salt will take place