

XI

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CHEMISTRY

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INTRODUCTION

The term “equilibrium” in physical sense is defined as the ‘no change of state of the body’. The state of the body can be either the state of rest or the state of uniform motion. Such static equilibrium can be further categorized into stable and unstable equilibriums.

You all must be acquainted with another well known equilibrium, equilibrium between liquid water and its vapour, $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{g})$. When $\text{H}_2\text{O}(\ell)$ is taken in a closed container, some water molecules go into the vapour phase (vaporization process) and simultaneously, water molecules return to the liquid phase (condensation process). Initially, the rate of vaporization is greater than the rate of condensation but after some time the rate of evaporation and the rate of condensation becomes equal. Thus, the number of water molecules leaving and the number of water molecules returning to the liquid phase are equal.

At this stage, both the processes takes place but it seems that the changes are not occurring, as the composition of the system does not change. Such processes in which forward and backward changes are occurring at the same rate are referred as *dynamic equilibrium*. This $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ equilibrium involving two phases of the same substance is called *physical equilibrium* because the changes that occur are physical changes.

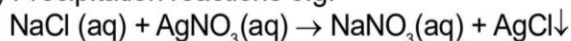
In this lesson, we will be more concerned with the state of equilibrium attained in chemical reactions. Most of the chemical reactions are reversible in nature (i.e., occurs in both the directions). At the start of a reversible process containing only reactants, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, theoretically the reverse process also begins to take place and reactant molecules are formed from product molecules

Types of chemical reactions

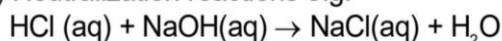
IRREVERSIBLE REACTION

The reaction which proceed in one direction only

(a) Precipitation reactions e.g.



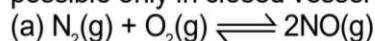
(b) Neutralization reactions e.g.



(c) Reactions in open vessels with one of the gaseous product

REVERSIBLE REACTION

Reactions which proceed in both the direction. These are possible only in closed vessel e.g.



TYPES OF CHEMICAL REACTIONS

Inversible reaction		Reversible reaction	
1.	The reaction which proceeds in one direction (forward direction) only	1.	The reaction which proceed in both the direction under the same set of experimental conditions
2.	Reactants are almost completely converted into products. Products do not react to form reactants again.	2.	Reactants form products and products also form reactants in backward direction. These are possible in closed vessels.
3.	Do not attain equilibrium state.	3.	Attain the equilibrium state and never go to completion.
4.	Such reactions are represented by single arrow (\rightarrow)	4.	Represented by double arrow (\rightleftharpoons) or (\rightleftharpoons)
5.	Examples – (a) Precipitation reactions e.g. $\text{NaCl(s)} + \text{AgNO}_3(\text{aq}) \rightarrow \text{NaNO}_3(\text{aq}) + \text{AgCl}\downarrow$ (b) Neutralization reactions e.g. $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(s)} + \text{H}_2\text{O}$ (c) $2\text{KClO}_3(\text{s}) \xrightarrow{\Delta} 2\text{KCl(s)} + 3\text{O}_2(\text{g})$ (d) Reactions in open vessels Even a reversible reaction will become irreversible if it is carried out in open vessel. Ex. $\text{CaCO}_3(\text{s}) \xrightarrow{\Delta} \text{CaO(s)} + \text{CO}_2(\text{g})$ $\text{NH}_4\text{HS(s)} \xrightarrow{\Delta} \text{NH}_3(\text{g}) + \text{H}_2\text{S(g)}$	5.	Examples – (a) Homogeneous reactions-only one phase is present (i) Gaseous phase $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI(g)}$ $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO(g)}$ [Birkland eyde process (HNO_3)] $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ (Haber's process) (ii) Liquid phase $\text{CH}_3\text{COOH}(\ell) + \text{C}_2\text{H}_5\text{OH}(\ell) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\ell) + \text{H}_2\text{O}(\ell)$ Heterogeneous reactions : More than one phases are present $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO(s)} + \text{CO}_2(\text{g})$ $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S(g)}$

Open

Closed

STATE OF CHEMICAL EQUILIBRIUM :

State of equilibrium means the balance of driving forces i.e. the factors taking the reaction in forward direction and the backward direction are balancing each other. The equilibrium state represents a compromise between two opposing tendencies.

- Tendency to minimise energy.
- Molecules try to maximise entropy.

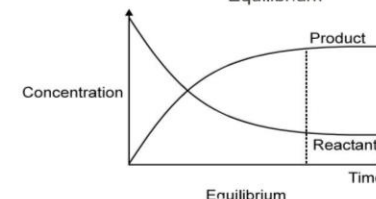
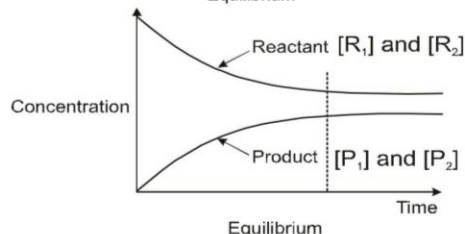
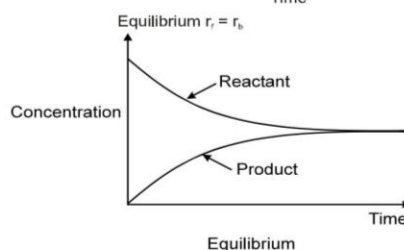
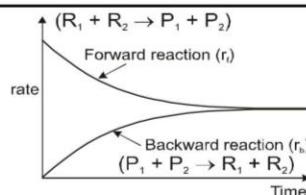
In a reversible reaction like–



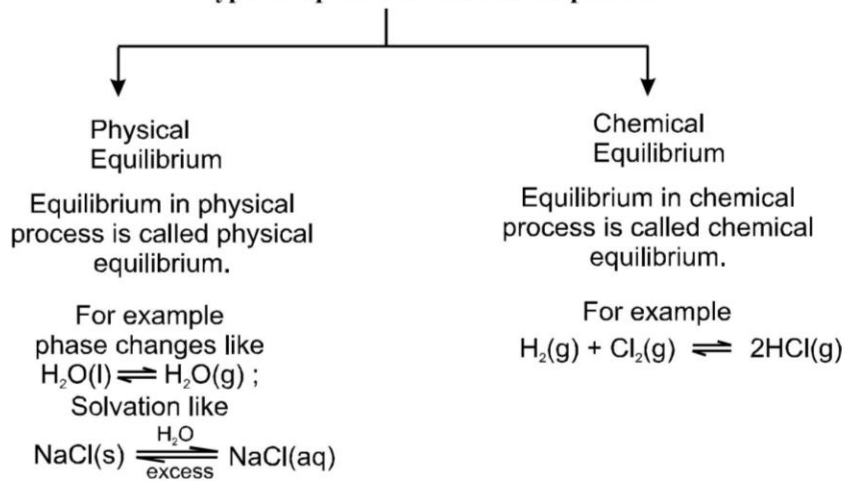
Initially only reactants are present. R_1 and R_2 combine to form P_1 and P_2 . As soon as P_1 and P_2 are formed, they start the backward reaction. As concentrations of R_1 and R_2 decrease rate of forward reaction decreases and rate of backward reaction increases. Ultimately a stage is reached when both the rates become equal. Such a state is known as “Chemical Equilibrium” or “state of Equilibrium”.

At equilibrium :

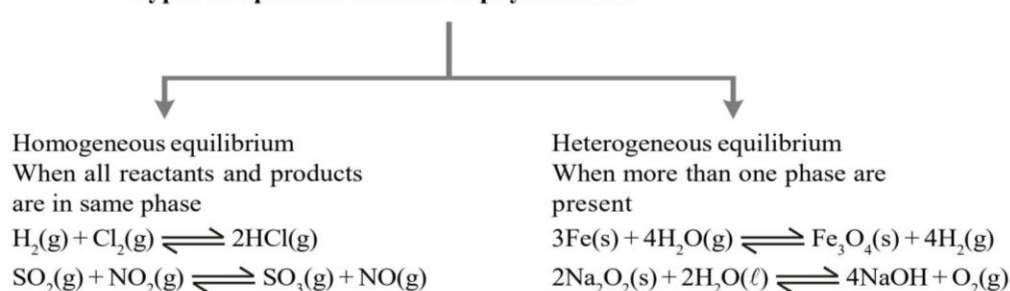
- Rate of forward reaction (r_f) = rate of backward reaction (r_b) (dynamic nature)
- All measurable parameters become constant with respect to time.



Types of equilibria on the basis of process



Types of equilibria on basis of physical state



CHARACTERISTICS OF CHEMICAL EQUILIBRIUM :

- The nature and the properties of the equilibrium state are the same regardless of the direction from which it is achieved. It can be achieved from both directions.
- Equilibrium is dynamic in nature. It means that at microscopic level reaction has not stopped. It appears that no change is occurring but both the opposing reactions are proceeding at the same rate. So there is no net change. Thus equilibrium is not static in nature.
- A catalyst can alter the rate of approach of equilibrium but does not change the state of equilibrium. By using catalyst, the equilibrium can be achieved in different (more/less) time, but the relative concentrations of reactants and products are same irrespective of the presence or absence of a catalyst.
- Equilibrium can be observed by constancy of some observable properties like colour, pressure, concentration, density, temperature, refractive index etc. which may be suitable in a given reaction.
- At equilibrium, free energy change $\Delta G = 0$
- Equilibrium state can be affected by altering factors like pressure, volume, concentration and temperature etc. (Le Chatelier's Principle).

- System moves toward an equilibrium state spontaneously even if it is disturbed. It will return to original state.

Law of mass action : [By Guldberg and Waage]

Rate at which a substance reacts \propto [Active Mass of the substance]^x

Active Mass = Molar concentration i.e. Moles/Litres

$$= \frac{\text{Wt of substance (gram)}}{\text{Molar wt.} \times \text{Vol. (Litre)}}$$

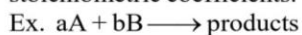
It is represented in square brackets i.e. [] e.g. [A], [N₂] etc.

● **For pure solids and pure liquids, although they have their own active masses but their concentration remain constant during a chemical change (reaction). Therefore, these are taken to be unity for the sake of convenience.**



$$K_c = [\text{CO}_2], \quad K_p = P_{\text{CO}_2}$$

The rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers of their stoichiometric coefficients.



Rate of reaction \propto [A]^a [B]^b

$$\text{Rate} = k [\text{A}]^a [\text{B}]^b,$$

where k is the rate constant of the reaction.

Example-1

Four vessel each of volume $V = 10$ Litres contains



Find the active masses in all the containers.

Sol. (A) $\Rightarrow [\text{CH}_4] = \frac{16}{16 \times 10} = 0.1 \text{ M}$

(B) $\Rightarrow [\text{H}_2\text{O}] = \frac{18}{18 \times 10} = 0.1 \text{ M}$

(C) $\Rightarrow [\text{Cl}_2] = \frac{35.5}{71 \times 10} = 0.05 \text{ M}$

(D) $\Rightarrow [\text{CO}_2] = \frac{44}{44 \times 10} = 0.1 \text{ M}$

EQUILIBRIUM CONSTANT (K) :

For a general reaction $aA + bB \rightleftharpoons cC + dD$,

Forward reaction rate $r_f = k_f[A]^a [B]^b$,

Backward reaction rate $r_b = k_b [C]^c [D]^d$,

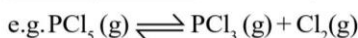
At equilibrium $r_f = r_b$

$$k_f [A]_{\text{eq}}^a [B]_{\text{eq}}^b = k_b [C]_{\text{eq}}^c [D]_{\text{eq}}^d$$

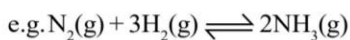
The concentrations of reactants & products at

equilibrium are related by $\frac{k_f}{k_b} = K_c = \frac{[C]_{\text{eq}}^c [D]_{\text{eq}}^d}{[A]_{\text{eq}}^a [B]_{\text{eq}}^b}$

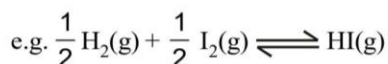
- K_c is a constant and is called the **equilibrium constant in terms of concentration**, where all the concentrations are at equilibrium and are expressed in moles/litre.



$$\Rightarrow K_c = \frac{[\text{PCl}_3]_{\text{eq}} [\text{Cl}_2]_{\text{eq}}}{[\text{PCl}_5]_{\text{eq}}}$$



$$\Rightarrow K_c = \frac{[\text{NH}_3]_{\text{eq}}^2}{[\text{N}_2] [\text{H}_2]_{\text{eq}}^3}$$

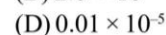
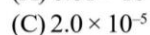
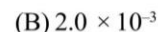
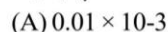
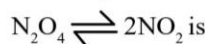


$$\Rightarrow K_c = \frac{[\text{HI}]_{\text{eq}}}{[\text{H}_2]_{\text{eq}}^{1/2} [\text{I}_2]_{\text{eq}}^{1/2}}$$

SOLVED EXAMPLE

Example-2

The decomposition of N_2O_4 to NO_2 was carried out in chloroform at 280°C . At equilibrium, 0.2 mol of N_2O_4 and 2×10^{-3} mole of NO_2 were present in 2L of solution. The equilibrium constant for the reaction



Ans. (A)



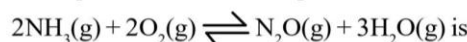
At equ. $\frac{0.2}{2} \quad \frac{2 \times 10^{-3}}{2}$ (2 Litre)

0.1 1×10^{-3}

$$K_c = \frac{(1 \times 10^{-3})^2}{0.1} = 10^{-5}$$

Example-3

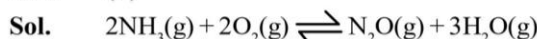
The equilibrium constant expression for the equilibrium



(A) $K_c = \frac{[\text{N}_2\text{O}][\text{H}_2\text{O}]^3}{[\text{NH}_3][\text{O}_2]}$ (B) $K_c = \frac{[\text{H}_2\text{O}]^3 [\text{N}_2\text{O}]}{[\text{NH}_3]^2 [\text{O}_2]^2}$

(C) $K_c = \frac{[\text{NH}_3]^2 [\text{O}_2]^2}{[\text{N}_2\text{O}][\text{H}_2\text{O}]^3}$ (D) $K_c = \frac{[\text{NH}_3][\text{O}_2]}{[\text{N}_2\text{O}][\text{H}_2\text{O}]}$

Ans. (B)

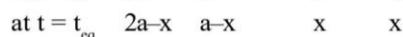
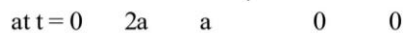
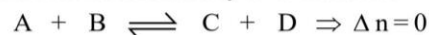


$$K_c = \frac{(\text{N}_2\text{O}) \times (\text{H}_2\text{O})^3}{(\text{NH}_3)^2 \times (\text{O}_2)^2}$$

Example-4

In a reaction $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g}) + \text{D}(\text{g})$, A, B, are mixed in a vessel at temperature T. The initial concentration of A was twice the initial concentration of B. After the equilibrium is reached, concentration of C was thrice the concentration of B. Calculate K_c .

Sol. Let concentration of B initially is 'a' mole/litre



Given that $x = 3(a-x) \Rightarrow x = \frac{3}{4}a$

$$K_c = \frac{[\text{C}]_{\text{eq}} [\text{D}]_{\text{eq}}}{[\text{A}]_{\text{eq}} [\text{B}]_{\text{eq}}}$$

$$K_c = \frac{x \cdot x}{(2a-x)(a-x)} \Rightarrow K_c = \frac{\left(\frac{3a}{4}\right)^2}{\left(2a - \frac{3a}{4}\right)\left(a - \frac{3a}{4}\right)}$$

$$\Rightarrow K_c = \frac{9}{5} = 1.8$$

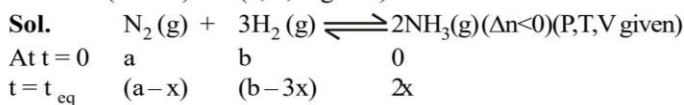
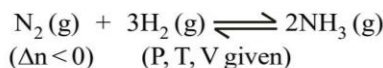
- **$K_p \rightarrow$ Equilibrium constant in terms of partial pressure.** It is defined for the equilibrium reaction which contains gaseous component. If component other than gas is present its active mass must be one. e.g. $aA(g) + bB(g) \rightarrow cC(g) + dD(g)$

$$K_p = \frac{[P_C]_{eq}^c [P_D]_{eq}^d}{[P_A]_{eq}^a [P_B]_{eq}^b}$$

where various pressures are the partial pressures of various gases substances.

Example-5

Calculate the expression for K_c and K_p if initially a moles of N_2 and b moles of H_2 is taken for the following reaction.



$$[N_2] = \frac{a-x}{V}, [H_2] = \frac{b-3x}{V}, [NH_3] = \frac{2x}{V}$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$$

Total no. of moles at equilibrium = $a + b - 2x$

$$[P_{N_2}] = \frac{(a-x)}{a+b-2x} \cdot P, [P_{H_2}] = \frac{(b-3x)}{a+b-2x} \cdot P,$$

$$[P_{NH_3}] = \frac{(2x) \cdot P}{a+b-2x}$$

$$\therefore K_p = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{\left(\frac{2x}{a+b-2x} \cdot P\right)^2}{\left[\left(\frac{a-x}{a+b-2x}\right) \cdot P\right] \left[\left(\frac{b-3x}{a+b-2x}\right) \cdot P\right]^3}$$

$$K_p = \frac{4x^2 \cdot P^2}{P^4 \cdot \frac{(a+b-2x)^2}{(a+b-2x)^4}} = \frac{(a+b-2x)^2 \cdot 4x^2}{P^2 (a-x)(b-3x)^3}$$

- **Relation between K_p & K_c**

$$PV = nRT \text{ or } P = \frac{n}{V} RT$$

$$P = CRT \text{ where } C = \frac{n}{V} = (\text{moles per litre})$$

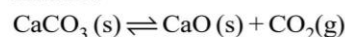
$$P_C = [C] RT; P_D = [D] RT; P_A = [A] RT; P_B = [B] RT$$

$$\Rightarrow K_p = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)}$$

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

Where $\Delta n_g = (c+d) - (a+b)$, calculation of Δn involves only gaseous components.

$\Rightarrow \Delta n_g =$ sum of the number of moles of gaseous products – sum of the number of moles of gaseous reactants. Δn_g can be positive, negative, zero or even fraction.



$\Delta n_g = 1$ (because there is only one gas component in the products and no gas component in the reaction)

$$\Rightarrow K_p = K_c (RT)$$

Unit of Equilibrium constants :

- Unit of K_p is $(\text{atm})^{\Delta n}$
- Unit of K_c is $(\text{mole/Lit})^{\Delta n} = (\text{conc.})^{\Delta n}$

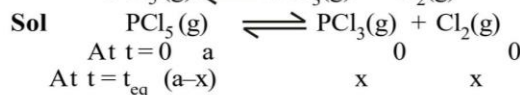
Note

In fact, equilibrium constant does not carry any unit because it is based upon the activities of reactants and products and activities are unitless quantities. Under ordinary circumstances, where activities are not known, above types of equilibrium constant and their units are employed.

SOLVED EXAMPLE

Example-6

Calculate K_p and K_c if initially a moles of PCl_5 is taken



$$[PCl_5] = \frac{a-x}{V}, [PCl_3] = \frac{x}{V}, [Cl_2] = \frac{x}{V}$$

$$K_c = \frac{\left(\frac{x}{V}\right)^2}{\left(\frac{a-x}{V}\right)}$$

Total no. of moles = $a - x + x + x = a + x$

$$[P_{PCl_5}] = \frac{(a-x)P}{a+x}, [P_{PCl_3}] = \frac{x \cdot P}{a+x},$$

$$[P_{Cl_2}] = \frac{x \cdot P}{a+x}$$

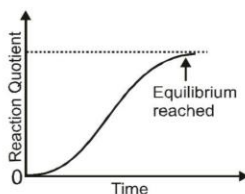
$$K_p = \frac{\left(\frac{xP}{a+x}\right) \cdot \left(\frac{xP}{a+x}\right)}{\left(\frac{a-xP}{a+x}\right)} = \frac{x^2 P}{a^2 - x^2}$$

● **Applications of Equilibrium constant :
 Predicting the direction of the reaction
 Reaction Quotient (Q)**

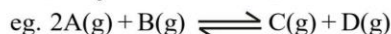
At each point in a reaction, we can write a ratio of concentration terms having the same form as the equilibrium constant expression. This ratio is called the reaction quotient denoted by symbol Q.

It helps in predicting the direction of a reaction.

The expression $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ at any time during reaction is called reaction quotient. The concentrations [C], [D], [A], [B] are not necessarily at equilibrium.



- The reaction quotient is a variable quantity with time.
- It helps in predicting the direction of a reaction.
- If $Q > K_c$ reaction will proceed in backward direction until equilibrium is reached.
- If $Q < K_c$ reaction will proceed in forward direction until equilibrium is established.
- If $Q = K_c$ Reaction is at equilibrium.



Q_c = Reaction quotient in terms of concentration

$$Q_c = \frac{[C][D]}{[A]^2[B]}$$

$$K_c = \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}^2[B]_{eq}} \quad [\text{Here all the conc. are at equilibrium}]$$

SOLVED EXAMPLE

Example-7

For the reaction $NOBr(g) \rightleftharpoons NO(g) + \frac{1}{2} Br_2(g)$

$K_p = 0.15$ atm at $90^\circ C$. If $NOBr$, NO and Br_2 are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 0.2 atm respectively, will Br_2 be consumed or formed?

Sol. $Q_p = \frac{[P_{Br_2}]^{1/2} [P_{NO}]}{[P_{NOBr}]} = \frac{[0.2]^{1/2} [0.4]}{[0.50]} = 0.36$

$K_p = 0.15$

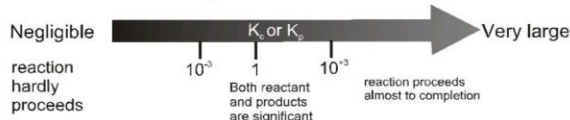
$\therefore Q_p > K_p$

Hence, reaction will shift in backward direction

$\therefore Br_2$ will be consumed

● **Predicting the extent of the reaction**

$$K = \frac{[\text{Product}]_{eq}}{[\text{Reactant}]_{eq}}$$



Case-I

If K is large ($K > 10^3$) then product concentration is very very larger than the reactant ($[\text{Product}] \gg [\text{Reactant}]$) Hence concentration of reactant can be neglected with respect to the product. In this case, the reaction is product favourable and equilibrium will be more in forward direction than in backward direction.

Case-II

If K is very small ($K < 10^{-3}$)

$[\text{Product}] \ll [\text{Reactant}]$

Hence concentration of Product can be neglected as compared to the reactant.

In this case, the reaction is reactant favourable.

Example-8

The K_p values for three reactions are 10^{-5} , 20 and 300 then what will be the correct order of the percentage composition of the products.

Sol. Since K_p order is $10^{-5} < 20 < 300$ so the percentage composition of products will be greatest for $K_p = 300$.

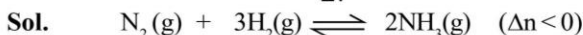
● **Calculating equilibrium concentrations**

The concentration of various reactants and products can be calculated using the equilibrium constant and the initial concentrations.

Example-9

1 mole of N_2 and 3 moles of H_2 are placed in 1L vessel. Find the concentration of NH_3 at equilibrium, if equilibrium pressure is 1 atm and the equilibrium

constant at 400K is $\frac{4}{27}$



1mol 3 mol 0
 (1-x) (3-3x) 2x

$P_{eq} = 1$ atm, $T = 400$ K

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2x)^2}{(1-x)(3-3x)^3} = \frac{4}{27}$$

$$\frac{x^2}{(1-x)^4} = 1 \Rightarrow x = (1-x)^2 \Rightarrow x^2 - 3x + 1 = 0$$

$$\Rightarrow x = \frac{3 \pm \sqrt{9-4}}{2} \Rightarrow x = \frac{3 \pm \sqrt{5}}{2}$$

$$x = \frac{3+2.24}{2} \text{ or } x = \frac{3-2.24}{2}$$

$$x = \frac{5.24}{2} = 2.62 \text{ or } x = \frac{0.76}{2}$$

$\Rightarrow x = 0.38$ (since x cannot be greater than 1)

$$\therefore [\text{NH}_3] = 0.38 \times 2 = 0.76$$

CHARACTERISTICS OF EQUILIBRIUM CONSTANT & FACTORS AFFECTING IT :

- Equilibrium constant does not depend upon concentration of various reactants, presence of catalyst, direction from which equilibrium is reached
- The equilibrium constant does not give any idea about time taken to attain equilibrium.
- **Equilibrium constant is dependent only on the temperature.**

It means K_p and K_c will remain constant at constant temperature no matter how much changes are made in pressure, concentration, volume or catalyst.

- However if temperature is changed,

$$\log \frac{k_2}{k_1} = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]; \Delta H = \text{Enthalpy of reaction}$$

If $T_2 > T_1$ then $K_2 > K_1$ provided $\Delta H = +ve$ (endothermic reaction)

$K_2 < K_1$ if $\Delta H = -ve$ (exothermic reaction)

In the above equation, the unit of R and $\Delta H/T$ should be same.

- **Theoretically K depends on the stoichiometry of the reaction.**
- If two chemical reactions at equilibrium having equilibrium constants K_1 and K_2 are added then the resulting equation has equilibrium constant $K = K_1 \cdot K_2$

Equation constant



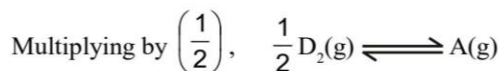
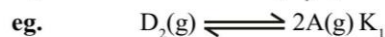
On adding $A(g) \rightleftharpoons C(g) K = K_1 \cdot K_2$

- If the reaction having eq. constant K_1 is reversed then resulting equation has eq. constant $\frac{1}{K_1}$



On reversing, $C(g) + D(g) \rightleftharpoons A(g) + B(g) K = \frac{1}{K}$

- If a chemical reaction having equilibrium constant K_1 is multiplied by a factor n then the resulting equation has equilibrium constant $K = (K_1)^n$, n can be fraction

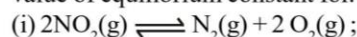


$$K = (K_1)^{1/2} = \sqrt{K_1}$$

SOLVED EXAMPLE

Example-10

The value of K_c for the reaction, $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ at a certain temperature is 400. calculate the value of equilibrium constant for.



- Sol.** Equilibrium constant (K_c) for the reaction $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ is

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2} = 400$$



$$K'_c = \frac{[\text{N}_2][\text{O}_2]^2}{[\text{NO}_2]^2} = \frac{1}{K_c}$$

$$K'_c = \frac{1}{400} = 0.0025 \text{ mole litre}^{-1}$$



$$K''_c = \frac{[\text{NO}_2]}{[\text{N}_2]^{1/2}[\text{O}_2]} = \sqrt{K_c}$$

$$\Rightarrow K''_c = \sqrt{400} = 20 \text{ litre}^{-1/2} \text{ mole}^{-1/2}$$

- **Relation between equilibrium constant & standard free energy change.**

$$\Delta G^\circ = -2.303 RT \log K$$

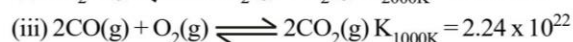
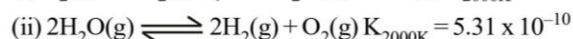
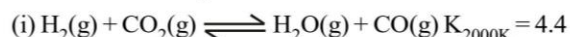
Where ΔG° = standard free energy change

T = Absolute temperature,

R = universal gas constant.

Example-11

From the following data :



State whether the reaction (iii) is exothermic or endothermic?

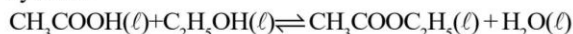
- Sol.** Equation (iii) = $-[2 \times (i) + (ii)]$

$$\therefore K_{2000K(iii)} = \frac{1}{K_1^2 K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

$\therefore T \uparrow K \downarrow \Rightarrow$ reaction is exothermic.

Homogeneous liquid system : Formation of ethyl acetate :

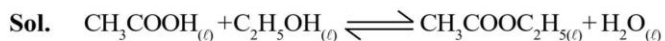
The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.



$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

Example-12

In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at T°C, the equilibrium mixture on analysis shows that 54.3% of the acid is esterified. Calculate the equilibrium constant of this reaction.



Initial	1	1	0	1
At eq.	1-x	1-x	x	1+x
	1-0.543	1-0.543	0.543	1+0.543

$$(54.3\% \text{ of } 1 \text{ mole}) = \frac{1 \times 54.3}{100} = 0.543 \text{ mole}$$

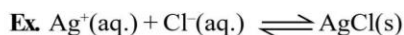
Hence given x = 0.543 mole

Applying law of mass action :

$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{0.543 \times 1.543}{0.457 \times 0.457} = 4.0$$

● **EQUATION INVOLVING IONS :**

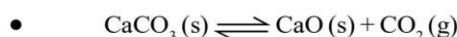
Equilibrium involving ions always take place in aqueous medium . In case of expression of K_c concentration of ion is taken.



$$K_c = \frac{1}{[\text{Ag}^+][\text{Cl}^-]}$$

Heterogenous Equilibrium :

For pure solid and pure liquid, active mass is taken to be unity i.e. 1 as their concentration remain constant throughout the reaction



$$K_p = (P_{\text{CO}_2})_{\text{eq}}, K_c = [\text{CO}_2(\text{g})]_{\text{eq}}$$

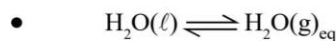
$$[\text{CaCO}_3(\text{s})] = \frac{\text{moles}}{\text{volume}} = \frac{W_{\text{CaCO}_3}}{M_{\text{CaCO}_3} V} = \frac{\text{density CaCO}_3}{M_{\text{CaCO}_3}}$$

= constant

$$K = \frac{[\text{CaO}(\text{s})]_{\text{eq}} [\text{CO}_2(\text{g})]_{\text{eq}}}{[\text{CaCO}_3(\text{s})]_{\text{eq}}}$$

$$\frac{K \cdot [\text{CaCO}_3(\text{s})]_{\text{eq}}}{[\text{CaO}(\text{s})]_{\text{eq}}} = [\text{CO}_2(\text{g})]_{\text{eq}}$$

$$K_c = [\text{CO}_2(\text{g})]_{\text{eq}}$$



$$K_p = (P_{\text{H}_2\text{O}(\text{g})})_{\text{eq}}, K_c = [\text{H}_2\text{O}(\text{g})]_{\text{eq}}$$

[For pure solid and pure liquid active mass is taken as unity i.e. = 1]

DEGREE OF DISSOCIATION (α) :

It is the fraction of one mole dissociated into the products.

(Defined for one mole of substance)

So, α = no. of moles dissociated / initial no. of moles taken

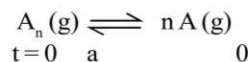
= fraction of moles dissociated out of 1 mole.

Note : % dissociation = $\alpha \times 100$

Suppose 5 moles of PCl_5 is taken and if 2 moles of PCl_5

$$\text{dissociated then } \alpha = \frac{2}{5} = 0.4$$

Let 1 mole of gas A_n dissociates to give n moles of A as follows-



$$t=0 \quad a \quad \quad \quad 0$$

$$t=t_{\text{eq}} \quad a-x \quad \quad \quad n \cdot x \quad \quad \quad \alpha = \frac{x}{a} \Rightarrow x = \alpha a$$

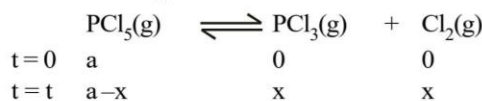
Total number of moles = $a - a\alpha + n \cdot a\alpha$

$$= [1 + (n-1)\alpha] a$$

SOLVED EXAMPLE

Example-13

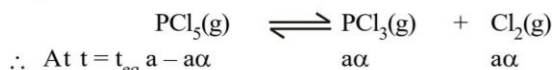
Calculate the degree of dissociation and K_p for the following reaction.



Since for a mole, x moles are dissociated

Sol. ∴ For 1 mole, $\frac{x}{a}$ moles = α are dissociated

$$\therefore x = a\alpha$$



∴ At $t=t_{\text{eq}}$ $a - a\alpha$ $a\alpha$ $a\alpha$
 Total no. of moles at equilibrium = $a + a\alpha = a(1 + \alpha)$

$$P_{\text{PCl}_5} = \frac{a(1-\alpha)P}{a(1+\alpha)}, P_{\text{PCl}_3} = \frac{a\alpha \cdot P}{a(1+\alpha)}, P_{\text{Cl}_2} = \frac{a\alpha}{a(1+\alpha)} \cdot P$$

$$K_p = \frac{\left(\frac{\alpha P}{1+\alpha}\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\right)P}$$

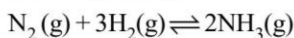
$$K_p = \frac{\alpha^2 \cdot P}{1-\alpha^2} \text{ (Remember)}$$

EXTERNAL FACTORS AFFECTING EQUILIBRIUM

(LE CHATELIER'S PRINCIPLE):

If a change is applied to the system at equilibrium, then equilibrium will be shifted in that direction in which it can minimise the effect of change applied and the equilibrium is established again under new conditions.

- **Effect of concentration :** If the concentration of a component is increased, reaction shifts in a direction which tends to decrease its concentration. e.g. In the following example.



[reactant] ↑ Forward shift

[Product] ↑ Backward shift

- If concentration of reactant is increased at equilibrium then reaction shifts in the forward direction .
- If concentration of product is increased then reaction shifts in the backward direction

Note :

The addition of any solid component does not affect the equilibrium.

- **Effect of pressure :**

On increasing pressure, equilibrium will shift in the direction in which pressure decreases i.e. no. of moles in the reaction decreases and vice versa.

∴ $P \propto$ no. of moles

(i) For $\Delta n_g = 0 \rightarrow$ No. effects

(ii) For $\Delta n_g > 0$, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$Q_p = \frac{(X_{PCl_3} P) \cdot (X_{Cl_2} P)}{(X_{PCl_5} \cdot P)} \Rightarrow Q_p \propto P[X = \text{mole fraction}]$$

$P \downarrow ; Q_p \downarrow ;$ (Forward shift)

$P \uparrow ; Q_p \uparrow ;$ (Backward shift)

(iii) For $\Delta n < 0$, eg. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_p = \frac{[(X_{NH_3})P]^2}{[(X_{N_2})P][(X_{H_2})P]^3} \Rightarrow Q_p \propto \frac{1}{P^2}$$

$P \uparrow ; Q_p \downarrow ;$ (Forward shift) ; $P \downarrow ; Q_p \uparrow ;$ (Backward shift)

- **Effect of volume :**

- If volume is increased, pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.

- If volume is increased then, for

$\Delta n_g > 0$ reaction will shift in the forward direction

$\Delta n_g < 0$ reaction will shift in the backward direction

$\Delta n_g = 0$ reaction will not shift.

eg. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (No effect)

Explanation :

(i) $\Delta n_g > 0$, eg. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$Q_c = \frac{\frac{(n_{Cl_2})}{V} \times \frac{(n_{PCl_3})}{V}}{\frac{(n_{PCl_5})}{V}} \Rightarrow Q_c \propto \frac{1}{V} \text{ for } \Delta n_g > 0$$

On increasing V, Q_c , decreases.

Now, for $Q_c < K_c$ reaction will shift in forward direction.

Thus, if, Volume ↑ Q_c ↓ (Forward shift)

Volume ↓ Q_c ↑ (Backward shift)

(ii) $\Delta n_g < 0$, eg. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_c = \frac{\left\{\frac{(n_{NH_3})}{V}\right\}^2}{\left\{\frac{(n_{N_2})}{V}\right\} \left\{\frac{(n_{H_2})}{V}\right\}^3}$$

$\Rightarrow Q_c \propto V^2$ for $\Delta n_g < 0$

$V \uparrow Q_c \uparrow$ (Backward shift) ; $V \downarrow Q_c \downarrow$ (Forward shift)

- **Effect of catalyst :**

Due to catalyst, the state of equilibrium is not affected i.e. no shift will occur as catalyst lowers the activation energy of both the forward & reverse reaction by same amount, thus altering the forward & reverse rate equally and hence, the equilibrium will be attained faster i.e time taken to reach the equilibrium is less.

- **Effect of inert gas addition :**

(i) At constant volume :

Inert gas addition has no effect at constant volume

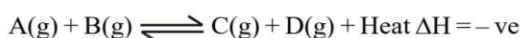
(ii) At constant pressure :

If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed

- (i) $\Delta n_g > 0$, reaction will shift in the forward direction
 (ii) $\Delta n_g < 0$, reaction will shift in the backward direction
 (iii) $\Delta n_g = 0$, no effect

● **Effect of temperature :**

(i) **Exothermic reaction :** The reaction in which heat is evolved



$T \uparrow \Rightarrow K'$ will decrease

$$\log \frac{K_1}{K_2} = \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \text{ (from vant' hoff equation)}$$

$$\log \frac{K_1}{K_2} < 0 \Rightarrow \log K_1 - \log K_2 > 0$$

$$\Rightarrow \log K_1 > \log K_2$$

$$\Rightarrow K_1 > K_2$$

Reaction will shift in backward direction.

$T \downarrow \Rightarrow K$ will increase.

Reaction will shift in forward direction.

(ii) **Endothermic reaction :** energy consumed.



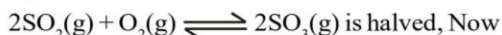
$$\therefore \Delta H = +ve$$

$T \uparrow \Rightarrow K \uparrow \Rightarrow$ Forward ; $T \downarrow \Rightarrow K \downarrow \Rightarrow$ Backward

SOLVED EXAMPLE

Example-14

The volume of a closed reaction vessel in which the equilibrium.



- (A) The rates of forward and backward reactions will remain the same.
 (B) The equilibrium will not shift.
 (C) the equilibrium will shift to the right.
 (D) The rate of forward reaction will become double that of reverse reaction and the equilibrium will shift to the right.

Sol. (D) In the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

In this reaction three moles (or volumes) of reactants are converted into two moles (or volumes) of products i.e. there is a decrease in volume and so if the volume of the reaction vessel is halved the equilibrium will be shifted to the right i.e. more product will be formed and the rate of forward reaction will increase i.e. double that of reverse reaction.

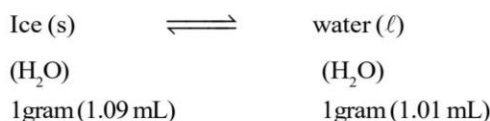
Special point :- Le-Chatelier's principle is applicable for both chemical and physical equilibrium.

PHYSICAL EQUILIBRIUM:

Physical reaction : Those reaction in which change in only and only state of substance takes place without any chemical change is called physical reaction.

(a) **Ice-water system (melting of ice) :**

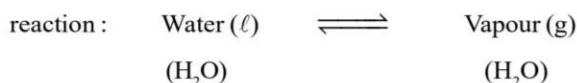
Melting of ice is accompanied by absorption of heat (endothermic) and decrease in volume



Hence both increase of temperature and pressure will favour the melting of ice into water.

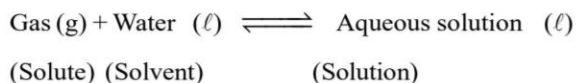
(b) **Water-water vapour system (Vapourisation of water):**

Vapourisation of water is an endothermic and condensation of vapour into water is an exothermic



- The equilibrium shifts towards right side when the temperature is increased so rise in temperature will increase the vapour.
- The equilibrium shifts towards left side when the pressure is increased (i.e. volume is decreased) so increase in pressure will favour the rate of condensation of vapour into water.
- Thus favourable conditions for conversion of water into vapour are high temperature and low pressure.

(c) **Solubility of gases :**



- Effect of pressure \rightarrow Solubility of gases which dissolve in a solvent increases with a decrease in volume, and with increasing pressure.

Example-15

On applying pressure to the equilibrium $\text{ice} \rightleftharpoons \text{water}$, which phenomenon will happen :

- (1) More ice will be formed
- (2) More water will be formed
- (3) Equilibrium will not be disturbed
- (4) Water will evaporate

Ans. (2)

Example-16

Which of the following conditions should be more favourable for increasing the rate of forward reaction in the equilibrium $H_2(g) \rightleftharpoons H(g) + H(g)$ ($\Delta H = +ve$) ?

- (1) 2000° C temperature and 760 mm pressure.
- (2) 3500° C temperature and 100 cm pressure.
- (3) 3500° C temperature and 1 mm pressure.
- (4) All are wrong.

Ans. (3)

Sol. In $H_2 \rightleftharpoons H + H$, heat has to be provided to dissociate H_2 into H. Therefore, the reaction is endothermic (ΔH will positive). So, temperature should be high. Since, one mole of H_2 forms two atoms of H, so volume is increasing (Δn is positive) so pressure should be low for increasing the rate of forward reaction.

Example-17

Assertion:- $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) + \text{heat}$

Forward reaction is favoured at low temperature and low pressure.

Reason :- Reaction is exothermic.

- 1.Assertion is correct & Reason is incorrect
- 2.Both assertion and reason are correct
- 3.Assertion is incorrect & reason is correct
4. Both assertion and reason are correct.

Ans. (1)

THERMODYNAMICS OF EQUILIBRIUM :

For a general reaction, $mA + nB \rightleftharpoons pC + qD$, ΔG is given by-

$$\Delta G = \Delta G^0 + 2.303 RT \log_{10} Q$$

where ΔG = Gibb's Free energy change

ΔG^0 = Standard Gibb's Free energy change

Q = reaction quotient

Since, at equilibrium, $Q = K$

Here K is thermodynamic equilibrium constant replacing K_c or K_p

$$K = \frac{(a_C)^p (a_D)^q}{(a_A)^m (a_B)^n} ; \text{Here } a_x \text{ denotes the activity of X.}$$

In fact, ' a_x ' is the ratio of the activity of substance at equilibrium and its activity in standard condition. That is why it is unitless and K is also unitless.

- Note :**
- (i) Thermodynamic equilibrium constant is unitless since activity is unitless.
 - (ii) For pure solids & pure liquids, activity is unity.
 - (iii) For gases (ideal behaviour), the activity is its partial pressure (in atm).
 - (iv) For components in solution, activity is molar concentration.

At equilibrium, $\Delta G = 0$

$$\Rightarrow \Delta G^0 = -2.303 RT \log_{10} K$$

$$\text{Now since, } \Delta G^0 = \Delta H^0 - T\Delta S^0$$

where ΔH^0 = Standard enthalpy change of the reaction

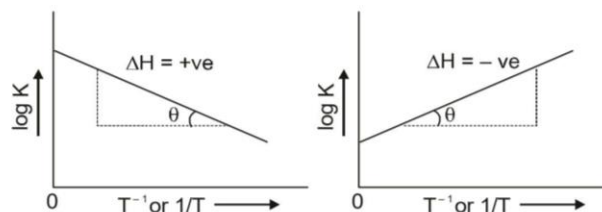
ΔS^0 = Standard entropy change

$$\Rightarrow -2.303 RT \log_{10} K = \Delta H^0 - T\Delta S^0$$

$$\Rightarrow \log_{10} K = -\frac{\Delta H^0}{2.303} \cdot \frac{1}{RT} + \frac{\Delta S^0}{2.303R}$$

If plot of $\ln k$ vs $\frac{1}{T}$ is plotted then it is a straight line

with slope = $-\frac{\Delta H^0}{R}$, and intercept = $\frac{\Delta S^0}{R}$



Endothermic reaction

Exothermic reaction

$$\text{Slope} = \frac{-\Delta H^0}{2.303R} = \tan \theta, \text{ y intercept} = \frac{\Delta S^0}{2.303R}$$

If at temperature T_1 , equilibrium constant is K_1 and at T_2 , it is K_2 then ;

$$\log_{10} K_1 = \frac{-\Delta H^0}{2.303R} \cdot \frac{1}{T_1} + \frac{\Delta S^0}{2.303R} \dots\dots\dots (i)$$

$$\log_{10} K_2 = \frac{-\Delta H^0}{2.303R} \cdot \frac{1}{T_2} + \frac{\Delta S^0}{2.303R} \dots\dots\dots (ii)$$

[Assuming ΔH^0 and ΔS^0 remains constant in this temperature range.]

Subtract eq. (ii) from (i) we get **Vant Hoff**

$$\text{equation-} \log \left(\frac{K_1}{K_2} \right) = \frac{\Delta H^0}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Note :

- ΔH should be substituted with sign.
- Unit of $\Delta H/T$ and gas constant R should be same.
- For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature
- For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature

Condition for Spontaneity : $\Delta G < 0$ for spontaneous process or reaction.

Since, $\Delta G = \Delta H - T\Delta S$

$\Rightarrow \Delta H - T\Delta S < 0 \Rightarrow T > \Delta H/\Delta S$

- $\Delta G > 0$ for non-spontaneous process or reaction.
- $\Delta G = 0$ for equilibrium.

SOME IMPORTANT POINTS

Calculation of Degree of dissociation from vapour density:

Ex. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

$$\alpha = \frac{D_T - D_0}{D_0} \text{ or } \frac{D - d}{d}$$

Where : D_T or D = Principle or theoretical vapour density

D_0 or d = Observed or practical vapour density

α = Degree of dissociation

$$\text{Vapour density} = \frac{\text{Molecular weight}}{2}$$

Reversible reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

Total moles Volume at NTP V a p o u r
 density

Let initial moles 1 0 0

1 $V_T = 22.4$ $D_T \propto \frac{1}{V_T}$

Moles at equilibrium $(1-\alpha)$ α α

$1+\alpha$ $V_0 = 22.4(1+\alpha)$ $D_0 \propto \frac{1}{V_0}$

If α is the degree of dissociation

$$\frac{D_T}{D_0} = \frac{V_0}{V_T} = \frac{22.4(1+\alpha)}{22.4}$$

$$\frac{D_T}{D_0} = 1 + \alpha \text{ or } \alpha = \frac{D_T}{D_0} - 1 \text{ or } \alpha = \frac{D_T - D_0}{D_0}$$

So for a general reversible reaction $n_1A \rightleftharpoons n_2B + n_3C$

$$\alpha = \frac{n_1 \left(\frac{D_T - D_0}{D_0} \right)}{\Delta n}$$

When &

- (i) $\Delta n > 0$ then $D_T > D_0$
- (ii) $\Delta n = 0$ then $D_T = D_0$

(iii) $\Delta n < 0$ then $D_T < D_0$

Reaction Quotient (Q) :

Consider a general homogeneous reversible reaction :



Reaction Quotient (Q) = $\frac{[C][D]}{[A][B]}$, (Applied in any

condition)

Equilibrium constant $K = \frac{[C][D]}{[A][B]}$, (Applied only in

equilibrium state)

- (i) When $Q = K$ then reaction is in equilibrium state.
- (ii) When $Q < K$ then rate of forward reaction increases.
- (iii) When $Q > K$ then rate of backward reaction increases.

Example-18

The vapour density of undecomposed N_2O_4 is 46. When heated, vapour density decreases to 24.5 due to its dissociation to NO_2 . The percentage dissociation of N_2O_4 at the final temperature is -

- (1) 87
- (2) 60
- (3) 40
- (4) 70

Ans. (1)

Example-19

If PCl_5 is 80% dissociated at 250°C then its vapour density at room temperature will be

- (1) 56.5
- (2) 104.25
- (3) 101.2
- (4) 52.7

Ans. (2)

Sol. $D_T = \frac{\text{Molecular weight}}{2} = \frac{208.5}{2} = 104.25$

Vapour density at room temperature (D_T) is 104.25, which is fixed.

Example-20

Assertion: For a reaction concentration quotient Q is

equal to K when the reaction is in equilibrium.

Reason: If a catalyst is added to the reaction at equilibrium, the value of Q remains no longer equal to K.

Ans. (C)

SOLVED EXAMPLE

Example-21

For the reaction $H_2 + I_2 \rightleftharpoons 2HI$

The value of equilibrium constant is 9.0. The degree of dissociation of HI will be –

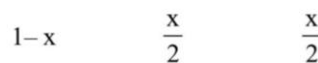
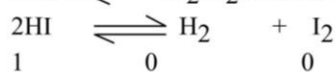
- (A) 2 (B) 2/5 (C) 5/2 (D) 1/2

Ans. (B)

Sol. Equilibrium constant of the reaction



So the equilibrium constant for the dissociation of HI i.e. $2HI \rightleftharpoons H_2 + I_2$ will be 1/9.



$$K_C = \frac{x}{2} \times \frac{x}{2} \times \frac{1}{(1-x)} \times \frac{1}{(1-x)}$$

$$\frac{1}{9} = \frac{x^2}{2 \times 2(1-x)^2}; \frac{1}{3} = \frac{x}{2(1-x)}$$

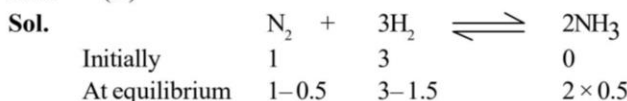
$$\text{or } 2 - 2x = 3x \quad 5x = 2 \quad x = 2/5$$

Example-22

For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, N_2 & H_2 were taken in the molar ratio of 1 : 3. Up to the point of equilibrium 50% each reactant has been reacted. If total pressure at equilibrium is P. The partial pressure of ammonia would be –

- (A) P/3 (B) P/6 (C) P/4 (D) P/8

Ans. (A)



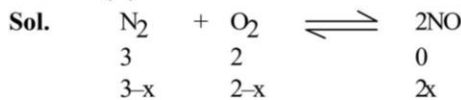
$$\text{Total moles} = (1 - 0.5) + (3 - 1.5) + 1 = 3; P_{NH_3} = \frac{1}{3} P$$

Example-23

In a reaction vessel of 2 litre capacity 3 moles of N_2 reacts with 2 moles of O_2 to produce 1 mole of NO. What is the molar concentration of N_2 at equilibrium?

- (A) 1.25 (B) 1.50 (C) 0.75 (D) 2.0

Ans. (A)



$$\therefore 2x = 1; x = 0.5$$

$$[N_2] = \frac{3-0.5}{2} = 1.25$$

Example-24

van't Hoff's equation giving the effect of temperature on chemical equilibrium may be represented as -

(A) $\frac{d}{dT} \ln K_p = \frac{\Delta H^\circ}{RT^2}$

(B) $\frac{d}{dT} \ln K_c = \frac{\Delta H^\circ T^2}{R}$

(C) $\frac{d}{dT} \ln K_p = \frac{\Delta H^\circ T^2}{R}$

(D) $\frac{d}{dT} \ln K_p = \frac{RT^2}{\Delta H^\circ}$

Ans. (A)

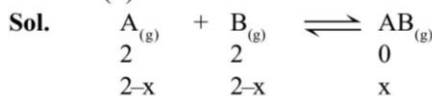
Sol. This is differential form of van't Hoff's equation

Example-25

For reaction; $A_{(g)} + B_{(g)} \rightleftharpoons AB_{(g)}$, we start with 2 moles of A and B each. At equilibrium 0.8 moles of AB is formed. Then how much of A changes to AB.

- (A) 20% (B) 40%
 (C) 60% (D) 4%

Ans. (B)



$$\therefore x = 0.8$$

Thus % of A changed into

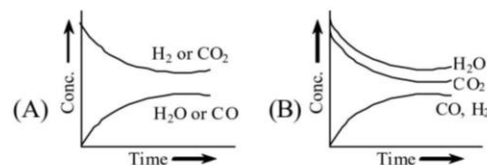
$$AB = \frac{0.8}{2} \times 100 = 40\%$$

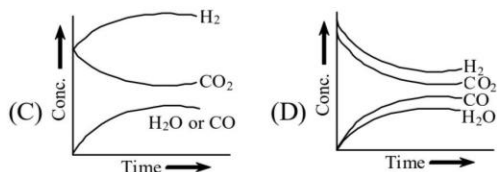
Example-26

Which of the following graphs are correct for the given reaction;



Assume initially only H_2 and CO_2 are present -





Ans. (A)

Sol. Concentration of reactants decrease with time whereas concentration of products increase with time.

Example-27

Which oxide of nitrogen is the most stable -

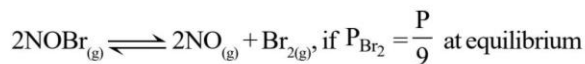
- (A) $2\text{NO}_{2(g)} \rightleftharpoons \text{N}_{2(g)} + 2\text{O}_{2(g)}$; $K = 6.7 \times 10^{16} \text{ mol litre}^{-1}$
- (B) $2\text{NO}_{(g)} \rightleftharpoons \text{N}_{2(g)} + \text{O}_{2(g)}$; $K = 2.2 \times 10^{30} \text{ mol litre}^{-1}$
- (C) $2\text{N}_2\text{O}_{5(g)} \rightleftharpoons 2\text{N}_{2(g)} + 5\text{O}_{2(g)}$; $K = 1.2 \times 10^{34} \text{ mol}^{-5} \text{ litre}^{-5}$
- (D) $2\text{N}_2\text{O}_{(g)} \rightleftharpoons 2\text{N}_{2(g)} + \text{O}_{2(g)}$; $K = 3.5 \times 10^{33} \text{ mol litre}^{-1}$

Ans. (A)

Sol. Greater is the value of K, more will be the tendency to show forward reaction.

Example-28

For the reaction equilibrium,



and P is total pressure, the ratio $\frac{K_p}{P}$ is equal to -

- (A) 1/9 (B) 1/81 (C) 1/27 (D) 1/3

Ans. (B)

Example-29

An example of a reversible reaction is :

- (A) $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\text{NaI}(\text{aq}) \rightleftharpoons \text{PbI}_2(\text{s}) + 2\text{NaNO}_3(\text{aq})$
- (B) $\text{AgNO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightleftharpoons \text{AgCl}(\text{s}) + \text{HNO}_3(\text{aq})$
- (C) $2\text{Na}(\text{s}) + \text{H}_2\text{O}(\ell) \rightleftharpoons 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$
- (D) $\text{KNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightleftharpoons \text{KCl}(\text{aq}) + \text{NaNO}_3(\text{aq})$

Ans. (D)

Sol. Precipitation reactions, acid base reactions and reactions in which gases are liberated and are taking place in open container will be irreversible reactions.

Example-30

For the reaction, $\text{A} + \text{B} \rightleftharpoons 3\text{C}$, if 'a' mol/litre of each 'A' & 'B' are taken initially then at equilibrium the

incorrect relation is :

- (A) $[\text{A}] - [\text{B}] = 0$ (B) $3[\text{B}] + [\text{C}] = 3a$
- (C) $3[\text{A}] + [\text{C}] = 3a$ (D) $[\text{A}] + [\text{B}] = 3[\text{C}]$

Ans. (D)

Sol. At equilibrium :

$$[\text{A}] = [\text{B}]$$

$$[\text{A}] + \frac{1}{3}[\text{C}] = a$$

Example-31

The equilibrium constant for the decomposition of water $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ is given by : (α = degree of dissociation of $\text{H}_2\text{O}(\text{g})$; p = Total equilibrium pressure)

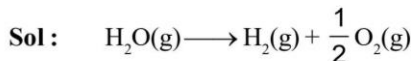
$$(A) K = \frac{\alpha^2 p^{1/2}}{(1+\alpha)(2-\alpha)^{1/2}}$$

$$(B) K = \frac{\alpha^{3/2} p^{1/2}}{(1+\alpha)(2+\alpha)^{1/2}}$$

$$(C) K = \frac{\alpha^3 p^{1/2}}{\sqrt{2}}$$

$$(D) K = \frac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$$

Ans. (B)



$$\begin{matrix} 1 & 0 & 0 \\ 1-\alpha & \alpha & \alpha/2 \end{matrix}$$

Total moles at equilibrium = $1-\alpha + \alpha + \alpha/2 = 1 + \alpha/2$

Let the total pressure at equilibrium be = p

$$\text{So, } p_{\text{H}_2\text{O}} = \frac{1-\alpha}{1+\alpha/2} \times p$$

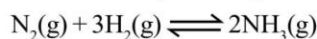
$$p_{\text{H}_2} = \frac{\alpha}{1+\alpha/2} \times p$$

$$p_{\text{O}_2} = \frac{\alpha/2}{1+\alpha/2} \times p$$

$$\text{So } K_p = \frac{(p_{\text{O}_2})^{1/2} (p_{\text{H}_2})}{(p_{\text{H}_2\text{O}})}$$

Example-32

The reaction quotient Q for :



is given by $Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$. The reaction will proceed

in backward direction, when:

- (A) $Q = K_c$ (B) $Q < K_c$
 (C) $Q > K_c$ (D) $Q = 0$

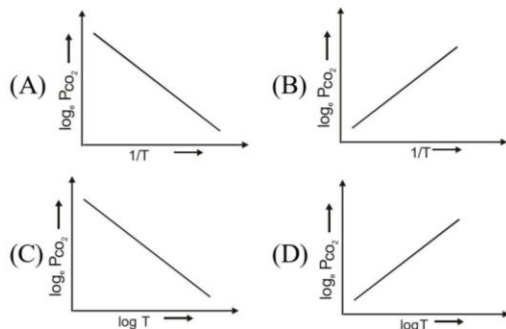
Ans. (C)

Sol. When $Q > K$, reaction will favour backward direction and when $Q < K$, it will favour forward direction.

Example-33

For the chemical equilibrium, $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

ΔH_f° can be determined from which one of the following plots ?



Ans. (A)

Sol. $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

$$K_p = P_{\text{CO}_2}$$

$$\log K_p = \log A - \frac{\Delta H_f^\circ}{2.303RT}$$

$$\log P_{\text{CO}_2} = \log A - \frac{\Delta H_f^\circ}{2.303} \frac{1}{RT} \quad \dots\dots (i)$$

Graph (a) represents (i) and its slope will be used to determine the heat of the reaction.

Equilibrium, Reaction Quotient and Equilibrium constant (K_p & K_c)

Example-34

A chemical reaction $X \rightleftharpoons Y$ is said to be in equilibrium when -

- (A) 50% of the conversion has taken place
 (B) only 10% conversion of X to Y has taken place
 (C) the rate of transformation of X to Y is equal to the rate of transformation of Y to X in the system
 (D) there is change in the concentration of either x or y

Sol. (C) $r_f = r_b$

Example-35

For which of the following K_p is less than K_c ?

- (A) $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$
 (B) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
 (C) $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$
 (D) $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$

Ans. (B)

Sol. $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
 $K_p = K_c (RT)^{\Delta n}$
 $\Delta n = P_{\text{mole}} - R_{\text{mole}}$
 $\Delta n = (2 - 4) = -2$
 $K_p = K_c (RT)^{-2}$
 $K_p < K_c$

Example-36

For homogeneous gas reaction $4\text{NH}_3 + 5\text{O}_2 \rightleftharpoons 4\text{NO} + 6\text{H}_2\text{O}$. The equilibrium constant K_c has the unit of -

- (A) (concentration)¹ (B) (concentration)⁻¹
 (C) (concentration)⁹ (D) (concentration)¹⁰

Ans. (A)

Sol. $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

at equ. x x x x

$$K_c = \frac{(x)^4 \times (x)^6}{(x)^4 \times (x)^5}$$

$$K_c = (x)$$

Example-37

The decomposition of N_2O_4 to NO_2 was carried out in chloroform at 280°C . At equilibrium, 0.2 mol of N_2O_4 and 2×10^{-3} mole of NO_2 were present in 2L of solution. The equilibrium constant for the reaction

$\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is

- (A) 0.01×10^{-3} (B) 2.0×10^{-3}
 (C) 2.0×10^{-5} (D) $.01 \times 10^{-5}$

Ans. (A)

Sol. $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$

At equ. $\frac{0.2}{2}$ $\frac{2 \times 10^{-3}}{2}$ (2 Litre)

$$0.1 \quad 1 \times 10^{-3}$$

$$K_c = \frac{(1 \times 10^{-3})^2}{0.1} = 10^{-5}$$

Example-38

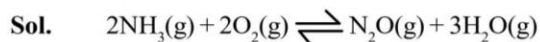
The equilibrium constant expression for the equilibrium

$2\text{NH}_3(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}(\text{g}) + 3\text{H}_2\text{O}(\text{g})$ is

$$(A) K_c = \frac{[N_2O][H_2O]^3}{[NH_3][O_2]} \quad (B) K_c = \frac{[H_2O]^3[N_2O]}{[NH_3]^2[O_2]^2}$$

$$(C) K_c = \frac{[NH_3]^2[O_2]^2}{[N_2O][H_2O]^3} \quad (D) K_c = \frac{[NH_3][O_2]}{[N_2O][H_2O]}$$

Ans. (B)



$$K_c = \frac{(N_2O) \times (H_2O)^3}{(NH_3)^2 \times (O_2)^2}$$

$$K_c = \frac{\left(\frac{2.4}{5}\right)^2}{\left(\frac{0.4}{5}\right)\left(\frac{0.4}{5}\right)}$$

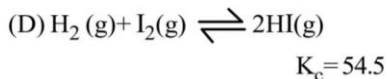
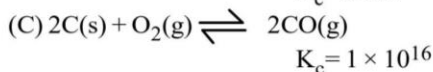
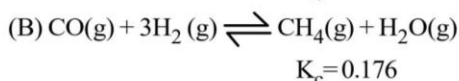
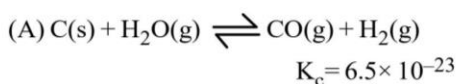
$$K_c = \frac{2.4 \times 2.4}{0.4 \times 0.4}$$

$$K_c = \frac{5.76}{0.16}$$

$$K_c = 36$$

Example-39

Assuming that the system is at equilibrium, which of the following reactions goes most nearly to 100% completion -



Ans. (C)

Sol. Fast rate for completion.

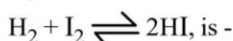
K_c must be greater value.

$$K_c = \frac{\text{Product concentration}}{\text{Reactant concentration}}$$

More product concentration, more value of K_c , so, reaction goes to fast completion.

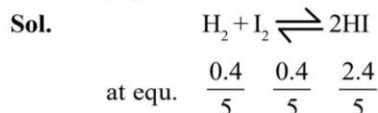
Example-40

An equilibrium system for the reaction between hydrogen and iodine to give hydrogen iodide at 765K in a 5 litre volume contains 0.4 mole of hydrogen, 0.4 mole of iodine and 2.4 moles of hydrogen iodide. The equilibrium constant for the reaction is



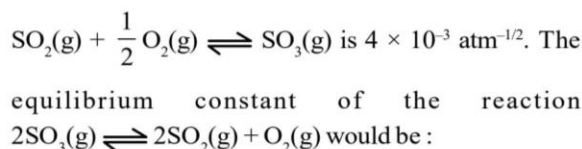
- (A) 36.0 (B) 15.0
 (C) 0.067 (D) 0.028

Ans. (A)



Example-41

The equilibrium constant of the reaction

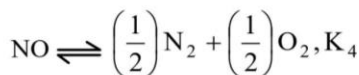
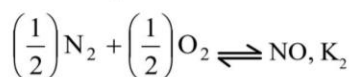


- (A) 250 atm (B) 4×10^3 atm
 (C) 0.25×10^4 atm (D) 6.25×10^4 atm

Ans. (D)

Sol. $k_p = \left[\frac{1}{4 \times 10^{-3}} \right]^2$

Example-42



Correct relation between K_1, K_2 and K_4 is :

- (A) $K_1 \times K_3 = 1$ (B) $\sqrt{K_1} \times K_4 = 1$
 (C) $\sqrt{K_3} \times K_2 = 1$ (D) All of these

Ans. (D)

Sol. $K = 2 = \sqrt{k_1}, K_2 = \frac{1}{K_4}, K_1 = \frac{1}{K_3}$

$\therefore K_1 K_3 = 1, \sqrt{K_1} K_4 = 1 \sqrt{K_3} = 1$

Example-43

The value of K_p for the reaction.

$2\text{H}_2\text{O}(\text{g}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 4\text{HCl}(\text{g}) + \text{O}_2(\text{g})$
 is 0.03 atm at 427°C, when the partial pressure are expressed in atmosphere, then the value of K_c for the same reaction is -

- (A) 5.23×10^{-4} (B) 7.34×10^{-4}
 (C) 3.2×10^{-3} (D) 5.43×10^{-5}

Ans.

(A)

Sol. $\Delta n_g = 4 + 1 - (2 + 2) = 1$

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

$$0.03 = K_c (0.082 \times 700)^1$$

$$K_c = 523 \times 10^{-4}$$

Example-44

For the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 $K_c = 66.9$ at 350°C and $K_c = 50.0$ at 448°C. The reaction has -

- (A) $\Delta H = +ve$ (B) $\Delta H = -ve$
 (C) $\Delta H = \text{zero}$ (D) $\Delta H = \text{Not found the signs}$

Ans.

(B)

Sol. K decreases as increase in temp. hence exothermic $\Delta H < 0$

Example-45

For the equilibrium $2\text{NOBr}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$,
 calculate the ratio $\frac{K_p}{P}$, where P is the total pressure

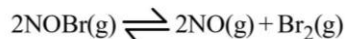
and $P_{\text{Br}_2} = \frac{P}{9}$ at a certain temperature -

- (A) $\frac{1}{9}$ (B) $\frac{1}{81}$ (C) $\frac{1}{27}$ (D) $\frac{1}{3}$

Ans.

(B)

Sol.



$$\text{At equ. } P - \frac{3P}{9} \quad \frac{2P}{9} \quad \frac{P}{9}$$

$$P_T = \frac{6P}{9} + \frac{2P}{9} + \frac{P}{9} = P$$

$$K_p = \frac{\left(\frac{2P}{9}\right)^2 \times \left(\frac{P}{9}\right)}{\left(\frac{6P}{9}\right)^2} = \frac{K_p}{P} = \frac{1}{81}$$

Example-46

28g of N_2 and 6g of H_2 were mixed. At equilibrium 17g NH_3 was produced. The weight of N_2 and H_2 at equilibrium are respectively -

- (A) 11g, 0g (B) 1g, 3g
 (C) 14g, 3g (D) 11g, 3g

Ans. (C)

Sol.



$$\text{Initial } \frac{28}{28} \quad \frac{6}{2} \quad 0$$

$$\frac{1}{\text{mole}} \quad \frac{3}{\text{mole}} \quad \frac{0}{\text{mole}}$$

$$\text{at equ. } t = ? \quad 1-x \quad 3-3x \quad 2x$$

$$2x = \frac{17}{17} \quad 2x = 1 \quad x = 1/2$$

$$\text{Final } 1/2 \quad 3/2 \quad 1$$

$$\text{weight} = 14 \text{ g } \quad 3 \text{ g}$$

Degree of dissociation, Vapour Density & Effective Molar Mass Le-Chatelier Principle

Example-47

For the gas phase reaction
 $\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$, $\Delta H = -32.7 \text{ kcal}$ carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by -

- (A) increasing the temperature
 (B) Increasing concentration of H_2
 (C) Decreasing temperature
 (D) Increasing pressure

Ans.

(A)

Sol.



$$\Delta n = P_{\text{mole}} - R_{\text{mole}} = 1 - 2 = -1$$

$$\Delta H = -ve \text{ Exothermic reaction } \downarrow x \propto \frac{1}{T} \uparrow$$

Temperature increases Reaction goes toward reactant.

Thus, concentration of C_2H_4 increases.

Example-48

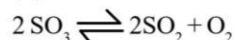
In a vessel containing SO_3 , SO_2 and O_2 at equilibrium, some helium gas is introduced so that the total pressure increases while temperature and volume remains constant. According to Le-Chatelier principle, the dissociation of SO_3 -

- (A) increase (B) decrease
 (C) remain unaltered (D) changes unpredictable

Ans.

(C)

Sol.



$\Delta H = +ve$ endothermic reaction

Inert gas doesn't show reaction with the reacting mixture it show effect only due to it's volume.

At constant volume doesn't effect of inert gas. Thus dissociation of SO_3 unchanged.

$$V = \text{constant} = \Delta n = 0$$

No effect of inert gas.

Example-49

In the system $AB(s) \rightleftharpoons A(g) + B(g)$ doubling the quantity of $AB(s)$ would -

- (A) increase the amount of A to double its value
 (B) increase the amount B to double its value
 (C) increase the amount of both A & B to double their values
 (D) cause no change in the amounts of A and B

Ans.

(D)

Sol. $AB(s) \rightleftharpoons A(g) + B(g)$

Active mass for Solid = 1 unity

$K_c = (x)(x)$.

Amount of $AB(s)$ doesn't appear in K_c , K_p

So, no change in amount of A and B

Example-50

Given a system in equilibrium, an increase in concentration of the product is always produced by a rise in temperature when the reaction is -

- (A) Gas phase (B) Spontaneous
 (C) Endothermic (D) First order

Ans.

(C)

Sol. $A \rightleftharpoons 2B$ $T \uparrow$ Product concentration increases.

$\Delta n = 2 - 1 = 1$.

So, endothermic reaction.

Endothermic reaction $T \uparrow$ $P \downarrow$ - For forward reaction $\uparrow x \propto T \uparrow$

Example-51

Nitrogen gas was injected into an equilibrium mixture of $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$? The pressure is increased from 1.0 atm to 10 atm. Which of the following statements is correct -

- (A) The concentration of the reacting gases are unchanged.
 (B) $[SO_3]$ increases
 (C) $[SO_2]$ increases
 (D) $[O_2]$ increases

Ans.

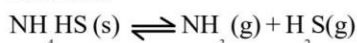
(A)

Sol. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

Nitrogen gas doesn't react with reacting mixture. Thus concentration of the reacting gases are unchanged.

Example-52

Consider the heterogeneous equilibrium in a closed container



If more NH_4HS is added to the equilibrium

- (A) Partial pressure of NH_3 increases
 (B) Partial pressure of H_2S increases
 (C) Total pressure in the container increases
 (D) No effect on partial pressure of NH_3 and H_2S .

Ans.

(D)

Sol. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

$K_p = NH_3(g) \times H_2S(g)$

Partially pressure of NH_3 and H_2O doesn't affected by $NH_4HS(s)$ because $NH_4HS(s)$ is solid for solid active mass unity.

Example-53

According to Le-Chatelier's principle, adding heat to a solid to liquid in equilibrium will causes the -

- (A) Temperature to increase
 (B) Temperature to decrease
 (C) Amount of liquid to increase
 (D) Amount of solid to increase

Ans.

(C)

Sol. Solid $\xrightarrow{\text{Heat}}$ liquid

ice

(More volume) less volume

Amount of liquid increases. Thus reaction goes toward less volume.

Thermodynamics of Equilibrium

Example-54

For the reaction,

$A(g) + B(g) \rightleftharpoons C(g) + D(g)$ at 298K, the values of ΔH° and ΔS° are -29.8 kcal and -0.1 kcal K^{-1} respectively. The values of ΔG° and equilibrium constant K_c are -

- (A) 1, 2 respectively (B) 0, 2 respectively
 (C) 0, 1 respectively (D) 0, 0 respectively

Ans.

(C)

Sol. $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ $\Delta H^\circ = -29.8 \times 10^3 \text{ Cal}$

$\Delta S^\circ = -0.1 \times 10^3 \text{ Cal}$

$\Delta G^\circ = -29.8 \times 10^3 - [-0.1 \times 10^3 \times 298]$

$\Delta G^\circ = \Delta G + 2.303 RT \log_{10} K_c$.

$\Delta G = \text{zero At equilibrium}$

$\Delta G^\circ = -2.303 n RT \log_{10} K_c$

$K_c = 1$

$$\log_{10} K_c = \frac{-\Delta G^\circ}{2.303 \times RT}$$

$$= \frac{0}{2.303 \times 8.314 \times 298}$$

$$\log_{10} K_c = 0 \quad K_c = 1$$

Example-55

For the reaction,
 $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$,
 the values of ΔH° and ΔS° at 298K are 77.2 kJ mol⁻¹ and 122 JK⁻¹ mol⁻¹ respectively. The standard equilibrium constant at the same temperature is -

- (A) 0.695×10^{-8} (B) 6.95×10^{-8}
 (C) 69.5×10^{-8} (D) 695×10^{-8}

Ans. (B)

Sol. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
 $= 77.2 \times 10^3 - 298 \times 122$
 $= 77.2 \times 10^3 - 36356$
 $= 40844$

at equ. $\Delta G^\circ = -2.303 RT \log_{10} K_c$
 $40844 = -2.303 \times 2477.58 \log_{10} K_c$
 $= -5634.4737 \log_{10} K_c$

$= -\frac{40844}{5634.4737} = \log_{10} K_c$

Antilog $= -7.2489468 = \log K_c$

$0.76 \times 10^{-8} = K_c$

$K_c = 6.95 \times 10^{-8}$

Trick

for (-ve) Antilog before decimal digit one power increases

$= 7.24$

After decimal digit subtract from (1)

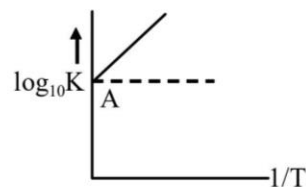
$1 - 0.24$

$= -\frac{0.76 \times 10^{-8}}{\log}$

$= 6.9 \times 10^{-8}$

Example-56

Variation of $\log_{10} K$ with $\frac{1}{T}$ is shown by the following graph in which straight line is at 45°, hence ΔH° is :



- (A) + 4.606 cal (B) - 4.606 cal
 (C) 2 cal (D) - 2 cal

Ans. (B)

Sol. $\Delta H^\circ = -2.303 R = -4.606 \text{ cal.}$

IONIC EQUILIBRIUM

INTRODUCTION

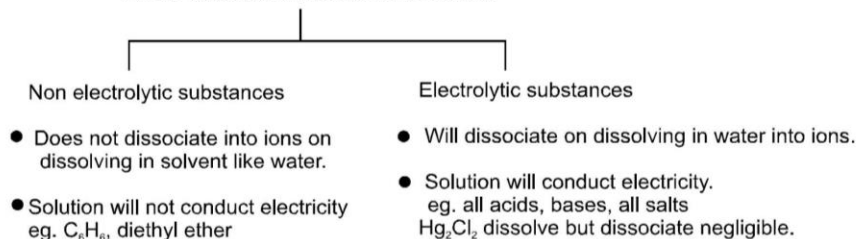
Ionic Equilibrium :

Weak electrolytes are partially ionised in aqueous solution and an equilibrium is situated between the ionised and unionised electrolyte. This type of equilibrium is known as ionic equilibrium.

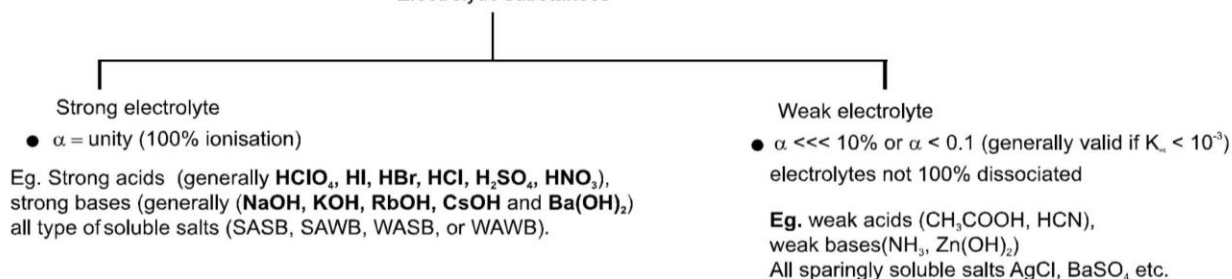
Let us consider an acid HA which when dissolved in water, an equilibrium will setup between ionised and unionised acid molecule as below -



All the substances can be classified into

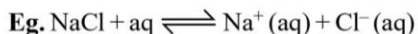


Electrolytic substances



Degree of dissociation

- When an electrolyte is dissolved in a solvent (H_2O), it spontaneously dissociates into ions.
- It may dissociate partially ($\alpha \ll 1$) or sometimes completely ($\alpha \cong 1$)



- The degree of dissociation of an electrolyte (α) is the fraction of one mole of the electrolyte that has dissociated under the given conditions.

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{No. of moles taken initially}}$$

The value of α depends

(a) Nature of electrolyte :

Strong electrolyte dissociate completely where as weak electrolytes dissociate partially.

(b) Nature of solvent :

A solvent having high value of **dielectric constant** will favour dissociation.

(c) Dilution :

For weak electrolytes degree of dissociation will increase by dilution (**Ostwald's dilution law**)

(d) Temperature :

On increasing temperature generally degree of dissociation increases.

(e) Presence of other solute :

When a substance is present it may effect the solubility of the another solute. Generally presence of common ion supresses degree of dissociation of weak electrolyte.

Arrhenius theory of Electrolytic Dissociation or Ionization

- When an electrolyte dissociates into water, it gives two types of charged particles called ions.
- Ions which carry (+) ve charge and move towards cathode are called as '**Cations**' while ions carrying (-) ve charge and moving towards anode called as '**anion**'.
- Every electrolytic solution is always neutral in nature.

- (d) Quantity or part of electrolyte which is ionized or decomposed or dissociate called as “**Degree of Ionisation**”.
- (e) Electrolyte which gives H^+ ions after dissociation in the aqueous solution is called as acid while that which gives OH^- after dissociation in the aqueous solution is called as base.

OSTWALD'S DILUTION LAW :

This law deals with the application of the law of mass action to the equilibrium between the ions and unionized molecules in aqueous solutions of weak binary electrolytes such as acetic acid, propionic acid, HCN, NH_4OH , etc.

Consider a dilute solution of a weak binary electrolyte AB containing c moles in 1 litre. At any given temperature, there will be equilibrium between the unionized molecules of AB and the ions A^+ and B^- . Let ' α ' be the degree of dissociation of AB at equilibrium.



Initial conc. c 0 0
 Conc. at. equilb. $c(1-\alpha)$ $c\alpha$ $c\alpha$

Then according to the law of mass action, the equilibrium constant K_{eq} will be given by

$$K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha}$$

This expression “ $K_{eq} = \frac{\alpha^2 c}{1-\alpha}$ ” is called **Ostwald's**

dilution law. K_{eq} is called the dissociation (or ionization) constant of the weak electrolyte. α has a very small value for a weak electrolyte and is therefore negligible in comparison with unity.

$$\therefore 1 - \alpha \approx 1. \quad \therefore K_{eq} = \alpha^2 c$$

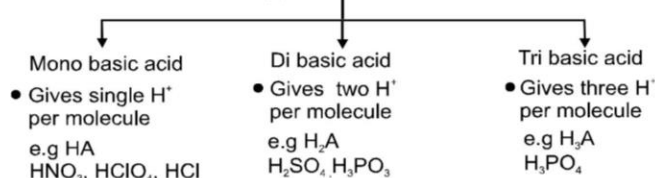
$$\alpha = \sqrt{\frac{K_{eq}}{c}} \quad \alpha \propto \sqrt{V}$$

This law is valid only for weak electrolytes that too in dilute solutions. It is not applicable for strong electrolytes.

ACIDS BASES AND SALTS :

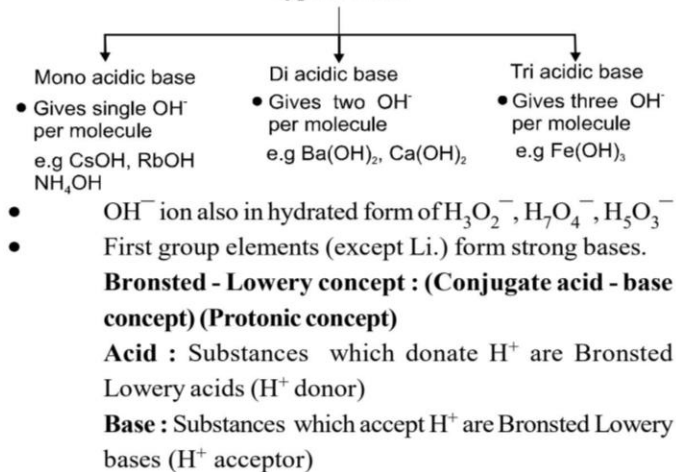
- Arrhenius concept :**
Arrhenius Acid : Substance which gives H^+ ion on dissolving in water (H^+ donor)
 eg. HNO_3 , $HClO_4$, HCl , HI , HBr , H_2SO_4 , H_3PO_4 etc.

Types of acids



- H_3BO_3 is not Arrhenius acid.
- H^+ ion in water is extremely hydrated (in form of H_3O^+ , $H_5O_2^+$, $H_7O_3^+$) and high charge density.
- The structure of solid $HClO_4$ is studied by X-ray, It is found to be consisting of H_3O^+ and ClO_4^- .
 $HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-$ (better representation)
Arrhenius base : Any substance which releases OH^- (hydroxyl) ion in water (OH^- ion donor)

Types of base



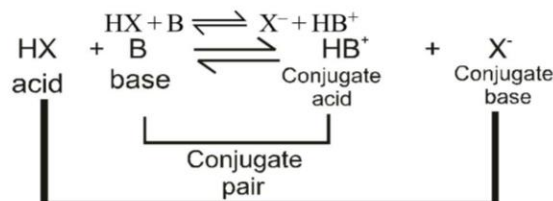
Bronsted - Lowry concept : (Conjugate acid - base concept) (Protonic concept)

Acid : Substances which donate H^+ are Bronsted Lowry acids (H^+ donor)

Base : Substances which accept H^+ are Bronsted Lowry bases (H^+ acceptor)

Conjugate acid - base pairs

In a typical acid base reaction



- Forward reaction – Here HX , being a proton donor, is an acid B , being a proton acceptor, is a base.
- Backward reaction – Here HB^+ , being a proton donor, is an acid X^- , being a proton acceptor, is a base.

Acid	Base	Conjugate Acid	Conjugate Base
HCl	$+ H_2O$	$\rightleftharpoons H_3O^+$	$+ Cl^-$
HSO_4^-	$+ NH_3$	$\rightleftharpoons NH_4^+$	$+ SO_4^{2-}$
$[Fe(H_2O)_6]^{3+}$	$+ H_2O$	$\rightleftharpoons H_3O^+$	$+ [Fe(H_2O)_5(OH)]^{2+}$

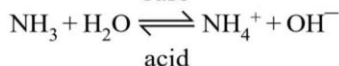
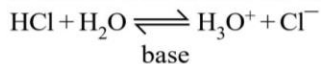
- Conjugate acid - base pair differ by only one proton
- Strong acid will have weak conjugate base and vice versa
- Reaction will always proceed from strong acid to weak acid or from strong base to weak base.

e.g.

Acid	Conjugate base	Base	Conjugate acid
HCl	Cl^-	NH_3	NH_4^+
H_2SO_4	HSO_4^-	H_2O	H_3O^+



Amphoteric (amphiprotic) : substances which can act as acid as well as base are known as amphoteric



SOLVED EXAMPLE

Example-57

In which of the following reactions does NH_3 act as an acid?

- (A) $\text{NH}_3(\text{aq}) + \text{H}^+(\text{aq}) \longrightarrow \text{NH}_4^+$
 (B) $\text{NH}_3(\text{l}) + \text{Na}(\text{s}) \longrightarrow \text{NaNH}_2(\text{aq}) + \frac{1}{2}\text{H}_2(\text{g})$
 (C) $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{s})$
 (D) None of these

Sol.

In the following reaction, NH_3 changes to NaNH_2 which contains NH_2^- ion. This means that NH_3 has donated a proton to Na and hence acts as an acid.

Properties of Water :

- Amphoteric (amphiprotic) Acid/base nature:**
 Water acts as an acid as well as base according to Arrhenius and Bronsted-Lowry theory but according to Lewis concept it can be generally taken as base.
In pure water $[\text{H}^+] = [\text{OH}^-]$ so it is Neutral.
- Molar concentration / Molarity of water :**

$$\text{Molarity} = \frac{\text{No. of moles}}{\text{litre}} = \frac{1000\text{gm / litre}}{18\text{gm / mole}}$$

$$= 55.55 \text{ mole / litre} = \mathbf{55.55 \text{ M}}$$
 (density = 1 gm/cc)
- Ionic product of water :** According to Arrhenius concept
 $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ so, ionic product of water,
 $\mathbf{K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ at } 25^\circ \text{ (exp.)}$
- dissociation of water, is endothermic, so on increasing temperature K_{eq} increases
 : - The value of K_w increases with the increase in temperature i.e. the ionisation of water increases with increase in temperature and finally the concentration of H^+ and OH^- ion increases.
 (a) Values of K_w at various temperature :-

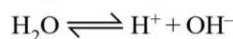
Temperature ($^\circ\text{C}$)	Value of K_w
(1) 20-35 or 25 $^\circ$	1×10^{-14} (Room temp.)
(2) 90	1×10^{-12}

 K_w increases with increase in temperature.

Now $\text{pH} = -\log[\text{H}^+] = 7$ and $\text{pOH} = \log[\text{OH}^-] = 7$ for water at 25 $^\circ$ (experimental)

$\text{pH} = 7 = \text{pOH} \Rightarrow$ neutral
 $\text{pH} < 7$ or $\text{pOH} > 7 \Rightarrow$ acidic
 $\text{pH} > 7$ or $\text{pOH} < 7 \Rightarrow$ Basic } at 25 $^\circ\text{C}$

- Ionic product of water is always a constant whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.**
- Degree of dissociation of water :**



$$\Rightarrow \alpha = \frac{\text{no. of moles dissociated}}{\text{total no. of moles initially taken}}$$

$$= \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7}\%$$

ACIDITY AND pH SCALE :

- Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water.
 So greater the tendency to give H^+ , more will be the acidic strength of the substance.
- Basic strength means the tendency of a base to give OH^- ions in water.
 So greater the tendency to give OH^- ions, more will be basic strength of the substance.
- The concentration of H^+ ions is written in a simplified form introduced by Sorenson known as pH scale.
 pH is defined as negative logarithm of activity of H^+ ions.
 $\therefore \text{pH} = -\log a_{\text{H}^+}$ (where a_{H^+} is the activity of H^+ ions)
- Activity of H^+ ions is the concentration of free H^+ ions or H_3O^+ ions in a dilute solution.
- The pH scale was marked from 0 to 14 with central point at 7 at 25 $^\circ\text{C}$ taking water as solvent.
- If the temperature and the solvent are changed, the pH range of the scale will also change. For **Example**

0-14	at 25 $^\circ\text{C}$
Neutral point, pH = 7	
0-13	at 80 $^\circ\text{C}$ ($K_w = 10^{-13}$)
Neutral point, pH = 6.5	
- pH can also be negative or > 14

pH CALCULATIONS OF DIFFERENT TYPES OF SOLUTIONS

(a) Strong acid Solution :

(i) If concentration is greater than 10^{-6} M

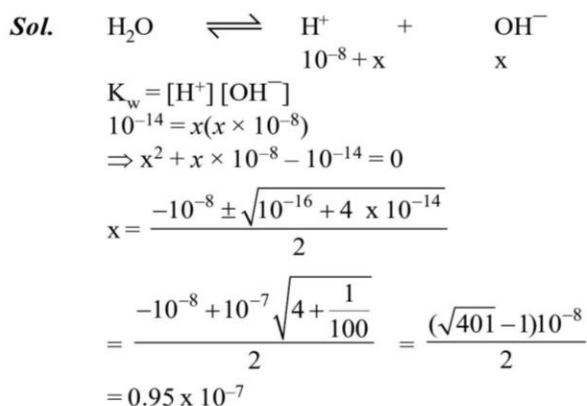
In this case H^+ ions coming from water can be neglected, so $[\text{H}^+] =$ normality of strong acid solution.

(ii) If concentration is less than 10^{-6} M
 In this case H^+ ions coming from water cannot be neglected,
 So $[H^+] =$ normality of strong acid + H^+ ions coming from water in presence of this strong acid

SOLVED EXAMPLE

Example-58

Calculate pH of 10^{-8} M HCl solution.



$[H^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7} M$

$pH = 7 - \log 1.05 \approx 6.98$

for 10^{-9} M HCl $pH \approx 7$

for 10^{-12} M HCl $pH \approx 7$

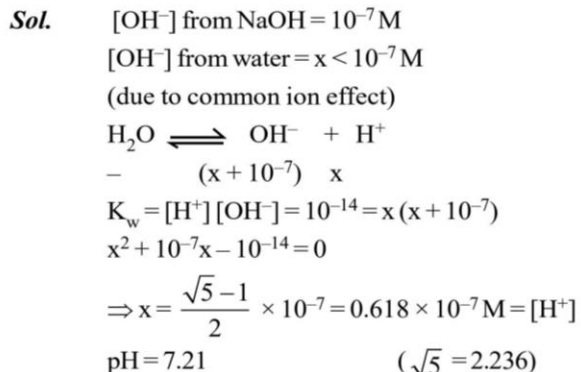
(b) Strong base Solution :

Calculate the $[OH^-]$ which will be equal to normality of the strong base solution and then use

$K_w = [H^+] \times [OH^-] = 10^{-14}$, to calculate $[H^+]$.

Example-59

Calculate pH of 10^{-7} M of NaOH solution.



(c) pH of mixture of two strong acids :

If V_1 volume of a strong acid solution of normality N_1 is

mixed with V_2 volume of another strong acid solution of normality N_2 , then

equi. of H^+ ions from I-solution = $N_1 V_1$

equi. of H^+ ions from II-solution = $N_2 V_2$

If final normality is N and final volume is V , then

$NV = N_1 V_1 + N_2 V_2$

$[H^+] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$

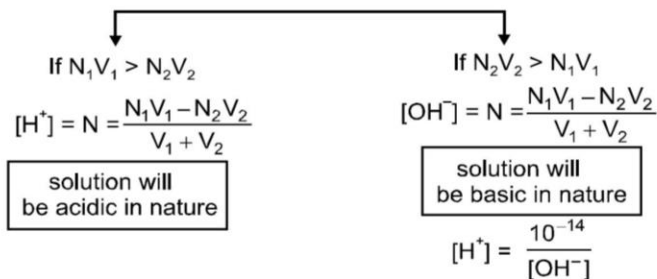
(d) pH of mixture of two strong bases :

similar to above calculation

$[OH^-] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$ & $[H^+] = \frac{10^{-14}}{[OH^-]}$

(e) pH of mixture of a strong acid and a strong base :

- Acid Base neutralisation reaction will take place.
- The solution will be acidic or basic depending on which component has been taken in excess.
- If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of a strong base solution of normality N_2 , then
 Number of eq. H^+ ions from I-solution = $N_1 V_1$
 Number of eq. OH^- ions from II-solution = $N_2 V_2$



SOLVED EXAMPLE

Example-60

Calculate pH of mixture of (400ml, $\frac{1}{200}$ M $Ba(OH)_2$) + (400ml, $\frac{1}{50}$ M HCl) + (200ml of Water)

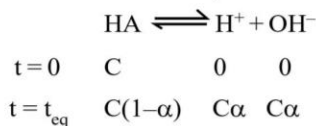
Sol. $[H^+] = \frac{(400 \times \frac{1}{50}) - (400 \times \frac{1}{200} \times 2)}{1000} = 4 \times 10^{-3} M$,

so $pH = 3 - 2 \log 2 = 2.4$

(f) pH of a weak acid(monoprotic) Solution :

- Weak acid does not dissociated 100% therefore we have to calculate the percentage dissociation using K_a dissociation constant of the acid.

- We have to use Ostwald's Dilution law (as we have been derived earlier)



$$K_a = \frac{[\text{H}^+][\text{OH}^-]}{[\text{HA}]} = \frac{C\alpha^2}{1-\alpha}$$

$$\text{If } \alpha \ll 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2$$

$$\Rightarrow \alpha = \sqrt{\frac{K_a}{C}} \quad (\text{is valid if } \alpha < 0.1 \text{ or } 10\%)$$

$$[\text{H}^+] = C\alpha = C \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C}$$

$$\Rightarrow \text{So pH} = \frac{1}{2}(\text{p}K_a - \log C)$$

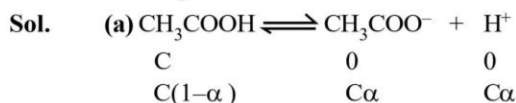
on increasing dilution
 $\Rightarrow C \downarrow \Rightarrow \alpha \uparrow$ and $[\text{H}^+] \downarrow \Rightarrow \text{pH} \uparrow$

Example-61

Calculate pH of



Take $K_a = 2 \times 10^{-5}$.



$$K_a = \frac{C\alpha^2}{1-\alpha}$$

$$\Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}} \quad (\alpha \ll 0.1)$$

$$\text{So, } [\text{H}^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow \text{pH} = 3 - \frac{1}{2} \log 2 = 2.85$$

$$\text{(b) } \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-3}}} = \sqrt{2 \times 10^{-2}} \quad (\alpha > 0.1)$$

So we have to do the exact calculations

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow 2 \times 10^{-5} = \frac{10^{-3} \times \alpha^2}{1-\alpha} \Rightarrow \alpha = 13.14\%$$

$$[\text{H}^+] = 10^{-3} \times 0.1314 = 1.314 \times 10^{-4} \Rightarrow \text{pH} = 4 - \log(1.314) \approx 3.8 \text{ Ans.}$$

(c) If approximation is used then,

$$\alpha = \sqrt{\frac{2 \times 10^{-5}}{10^{-6}}} = \sqrt{20} > 1,$$

so we have to do the exact calculation,

$$2 \times 10^{-5} = 10^{-6} \frac{\alpha^2}{1-\alpha}$$

$$\Rightarrow \alpha \approx 0.95 \text{ or } 95\%$$

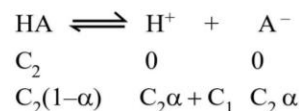
$$[\text{H}^+] = 0.95 \times 10^{-6} = 9.5 \times 10^{-7}$$

$$\Rightarrow \text{pH} = 7 - \log(9.5) = 6.022 \text{ Ans.}$$

(g) pH of a mixture of weak acid(monoprotic) and a strong acid Solution :

- Weak acid and Strong acid both will contribute H^+ ion.
- For the first approximation we can neglect the H^+ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.
- To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.

If $[\text{SA}] = C_1$ and $[\text{WA}] = C_2$, then $[\text{H}^+]$ from $\text{SA} = C_1$ the weak acid will dissociate as follows.



$$K_a = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)} \quad (\alpha \ll \ll 1)$$

(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

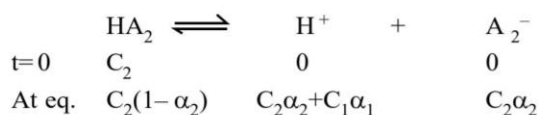
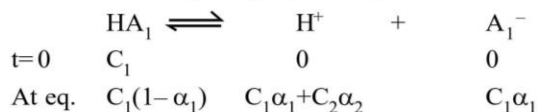
$$K_a = (C_2\alpha + C_1)\alpha$$

$$\text{Total } \text{H}^+ \text{ ion concentration} = C_1 + C_2\alpha$$

- If the total $[\text{H}^+]$ from the acid is greater than 10^{-6} M , then contribution from the water can be neglected at 25°C temp., if not then we have to take $[\text{H}^+]$ from the water also.

(h) pH of a mixture of two weak acid (both monoprotic) solutions :

- Both acids will dissociate partially.
- Let the acid are HA_1 & HA_2 and their concentrations in the mixture are C_1 & C_2 respectively, then



$$K_{a1} = \frac{C_1\alpha_1(C_1\alpha_1 + C_2\alpha_2)}{C_1(1-\alpha_1)} \quad K_{a2} = \frac{(C_2\alpha_2 + C_1\alpha_1)C_2\alpha_2}{C_2(1-\alpha_2)}$$

(Since α_1, α_2 both are small in comparison to unity)

$$K_{a1} = (C_1\alpha_1 + C_2\alpha_2)\alpha_1; K_{a2} = (c_1\alpha_1 + c_2\alpha_2)\alpha_2$$

$$\Rightarrow \frac{K_{a1}}{K_{a2}} = \frac{\alpha_1}{\alpha_2}$$

$$[H^+] = C_1\alpha_1 + C_2\alpha_2$$

$$= \frac{C_1K_{a1}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} + \frac{C_2K_{a2}}{\sqrt{C_1K_{a1} + C_2K_{a2}}}$$

$$\Rightarrow [H^+] = \sqrt{C_1K_{a1} + C_2K_{a2}}$$

- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

$$\text{So, } [H^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$$

SOLVED EXAMPLE

Example-62

Calculate pH of solution obtained by mixing equal volume of 0.02 M HOCl & 0.2 M CH₃COOH solutions. given that K_{a1}(HOCl) = 2 × 10⁻⁴ K_{a2}(CH₃COOH) = 2 × 10⁻⁵ also calculate [OH⁻], [OCl⁻], [CH₃COO⁻] at equilibrium.

Sol. Volume of final solution become double.

So concentration become half

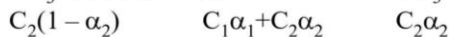
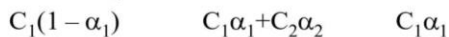
$$C_1 = 0.01 \text{ M, } C_2 = 0.1 \text{ M}$$

$$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$$

$$= \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1}$$

$$= \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3} \text{ M}$$

$$\text{pH} = 3 - \log 2 = 2.7$$



$$\alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 0.1 \quad \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 0.01$$

$$[\text{OCl}^-] = C_1\alpha_1$$

$$= 0.01 \times 10^{-1}$$

$$= 1 \times 10^{-3} \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = C_2\alpha_2$$

$$= 0.1 \times 10^{-2}$$

$$= 1 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12} \text{ M}$$

- All these steps can be followed for the calculation of pOH for weak base and their mixtures (we just have to replace K_a with K_b).

(k) pH of a mixture of a weak acid/ weak base with

weak/strong base/acid respectively.

For this type of mixtures there can be two cases in general,

- if the acids and bases are mixed in equal amounts (equivalents)
- if the acids and bases are mixed in different amounts (equivalents)

First case will lead to phenomenon of **SALT HYDROLYSIS** and second case will lead to formation of **BUFFER SOLUTIONS**.

Salts :

- Species formed by the reaction of neutralization of acid and base is called as salt.
- salt formation is the exothermic process and released energy by this reaction is called as the heat of neutralization for 1 eq. monoacidic base and 1 eq. monobasic acid.
- The value of heat of neutralization is equal to 13.6 kcal.
- Salts are generally crystalline solid.
- Salts are classified into following four types.

Simple Salts :

These salts formed by the neutralisation process, which are of three types.

- Normal Salt :** These salts are formed by the neutralization reaction of simple acid and simple base, like - NaCl, NH₄Cl, CH₃COONa, KNO₃ etc.
- Acid Salt :** It is formed by the incomplete neutralization reaction of acid with the base is called the acidic salt and gives proton in aqueous solution. Like - NaHCO₃, NaHSO₄, Na₂HPO₄.



- Basic salt :** Salt which is formed by the incomplete neutralization reaction of base with acid called the basic salt and gives OH⁻ ion in aqueous solution. Like- Zn(OH)Cl, Mg(OH)Cl, Fe(OH)₂Cl etc.



1mol Basic salt



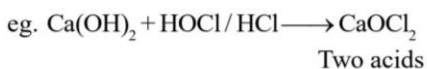
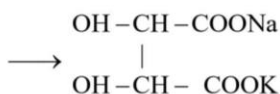
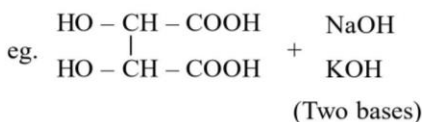
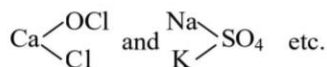
1mol Basic salt



1mol Basic salt

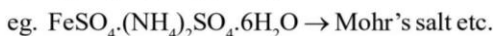
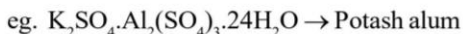
Mixed Salts :

Salts which are formed by the neutralisation reaction of more than two different acids and bases are called mixed salt. Or Salts which furnish more than one cation or more than one anion when dissolved in water are also as mixed salt. **Like Rochelle salt,**



Double salts :

Salts which are formed by the addition of two or more simple salts are called as double salt.



Complex salts : -

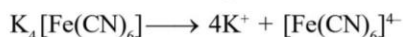
(a) Salt which are formed by the donation of electron pair by the ligand molecule with the metal ion are called as complex salts. Or salts which are formed by the combination of simple salts or molecular compounds.

(b) Complex salts are stable in solid state.

(c) On dissolving the water, complex salts. Give minimum one complex ion -



or all coordination compound



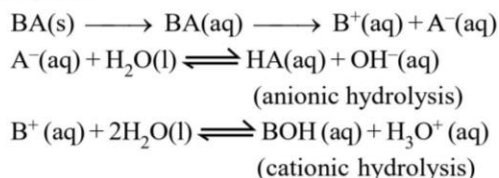
SALT HYDROLYSIS (REVERSE OF NEUTRALISATION)



When acids and bases are mixed in equal amounts (equivalents), then we will be having salt solutions only in the water and we have to calculate pH of salt solutions.

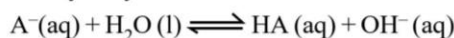
When a salt is added to water, the solid salt first dissolves and breaks into ions completely (unless otherwise specified). The ions of the salt may or may not react with water, the cations when react with water will produce H_3O^+ ions and the anions on reaction with

water will produce OH^- ions. Depending on the extent of hydrolysis and on the amounts of H_3O^+ and OH^- ions the solution can be acidic, basic or neutral. If salt is BA, then



ANIONIC HYDROLYSIS

Anions can function as a base on reaction with water and hydrolyse as follows :



The extent of hydrolysis of a given anion depends on its basic strength

(a) Complete hydrolysis

The anions, which are stronger base than OH^- and the conjugate acids of the anions are weaker acid than H_2O , they will show complete hydrolysis in aqueous medium.



(b) Hydrolysis to a limited extent

The anions, which are weaker base than OH^- and the conjugate acids are stronger acid than H_2O but weaker acid than H_3O^+ will hydrolyse to a limited extent in aqueous medium



Other **Examples** are CH_3COO^- , NO_2^- , S^{2-} etc.

(c) No hydrolysis

The anions that are weaker base than OH^- and the conjugate acids are stronger than both H_2O and H_3O^+ do not hydrolyse at all.



Other **Examples** include SO_4^{2-} , NO_3^- , ClO_4^- etc.

CATIONIC HYDROLYSIS

Cations can function as acid on reaction with water and hydrolyze as follows.



The extent of hydrolysis of a given cation depends on its acidic strength.

(a) Complete hydrolysis

The cations, which are stronger acid than H_3O^+ and their conjugate bases are very much weaker than H_2O will show complete hydrolysis. **Example** is PH_4^+ ion.



(b) Hydrolysis to a limited extent

The cations, which weaker acid than H_3O^+ ion and their conjugate bases are stonger than H_2O but weaker than OH^- , show hydrolysis to a limited extent. For **Example**



Other ions showing hydrolysis to limited extent are $C_6H_5NH_3^+$, $CH_3NH_3^+$ etc.

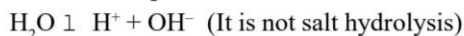
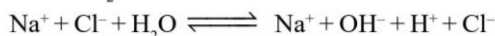
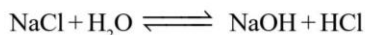
(c) No hydrolysis

The cations, which are weaker acid than H_3O^+ and their conjugate bases are stronger than both H_2O and OH^- do not hydrolyze at all. **Example** is alkali and alkaline earth metal ions.



A. Hydrolysis of strong acid and strong base [SA – SB] types of salt –

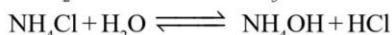
Ex. $NaCl$, $BaCl_2$, Na_2SO_4 , $KClO_4$, $BaSO_4$, $NaNO_3$, KBr , KCl etc.



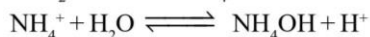
- (i) Hydrolysis of salt of [SA – SB] is not possible.
- (ii) Aqueous solution of these type of salt is neutral in nature. ($pH = pOH = 7$)
- (iii) pH of the solution is 7.
- (iv) No effect on litmus paper.

B. Hydrolysis of strong acid and weak base [SA - WB] types of salt –

Ex. $CaSO_4$, NH_4Cl , $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$, $AgCl$, AgI , $AgNO_3$ etc



WB SA



- (i) In this type of salt hydrolysis, cation reacts with H_2O therefore called as cationic hydrolysis.
- (ii) Solution is acidic in nature as $[H^+]$ is increased.
- (iii) pH of the solution is less than 7.
- (iv) Solution turns blue litmus paper red.

K_h = Hydrolysis constant

K_w = Ionic product of water

K_a = Ionisation constant of acid

K_b = Ionisation constant of base

h = Degree of hydrolysis

C = Concentration of salt (concentration of ions)

(a) Relation between K_h , K_w and K_b



Hydrolysis constant $[K_h]$

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \quad \dots\dots(1)$$

For weak Base $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \dots\dots(2)$$

For water $H_2O \rightleftharpoons H^+ + OH^-$

$$K_w = [H^+][OH^-] \quad \dots\dots(3)$$

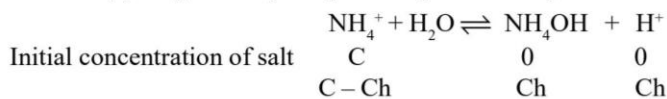
Now mutiplying Eq. (1) and (2) = Eq. (3)

$$\frac{[NH_4OH][H^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} = [H^+][OH^-]$$

i.e. $K_h \times K_b = K_w$

$$K_h = \frac{K_w}{K_b} \quad \dots\dots(4)$$

(b) Degree of hydrolysis – Represented by h



$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2h^2}{C(1-h)} = \frac{Ch^2}{(1-h)}$$

Since $h \ll 1$ then $(1-h) \approx 1$

$$\therefore K_h = Ch^2 \quad \dots\dots(5)$$

$$h^2 = \frac{K_h}{C} \Rightarrow h = \sqrt{\frac{K_h}{C}} \quad \dots\dots(6)$$

$$\therefore K_h = \frac{K_w}{K_b} \Rightarrow h = \sqrt{\frac{K_w}{K_b \times C}}$$

$$h = \sqrt{\frac{K_w}{K_b \times C}} \quad \dots\dots(7)$$

(c) pH of the solution : $pH = -\log [H^+]$

$$[H^+] = Ch = C \sqrt{\frac{K_w}{K_b \times C}} \Rightarrow [H^+] = \sqrt{\frac{K_w \times C}{K_b}} \quad \dots\dots(8)$$

taking – log on both sides

$$-\log [H^+] = -\log \sqrt{\frac{K_w \times C}{K_b}} \Rightarrow pH = -\log \left(\frac{K_w \times C}{K_b} \right)^{\frac{1}{2}}$$

$$\text{pH} = -\frac{1}{2} [\log K_w + \log C - \log K_b]$$

$$\text{pH} = -\frac{1}{2} \log K_w - \frac{1}{2} \log C - \frac{1}{2} (-\log K_b)$$

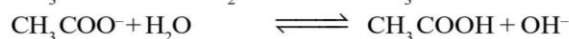
$$\text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \log C - \frac{1}{2} \text{p}K_b$$

$$\boxed{\text{pH} = 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C} \quad \text{.....(9)}$$

C. Hydrolysis of weak acid and strong base [WA-SB] types of salt -

Ex.

CH₃COONa, HCOONa, KCN, NaCN, K₂CO₃, BaCO₃, K₃PO₄ etc.



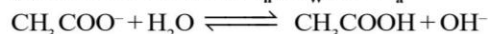
(i) In this type of salt hydrolysis, anion reacts with water therefore called as anionic hydrolysis.

(ii) Solution is basic in nature as [OH⁻] increases.

(iii) pH of the solution is greater than 7.

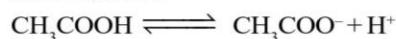
(iv) Solution turns red litmus paper blue.

(a) Relation between K_h, K_w and K_a



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad \text{.....(1)}$$

For weak acid



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{.....(2)}$$

For water



$$K_w = [\text{H}^+][\text{OH}^-] \quad \text{.....(3)}$$

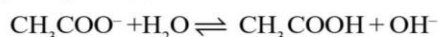
Now multiply eq. (1) × eq. (2) = eq. (3)

$$\frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \times \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = [\text{H}^+][\text{OH}^-]$$

$$K_h \times K_a = K_w$$

$$\boxed{K_h = \frac{K_w}{K_a}} \quad \text{.....(4)}$$

(b) Degree of hydrolysis (h):



Initial concentration of salt	C	0	0
	C - Ch	Ch	Ch

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{\text{Ch} \times \text{Ch}}{\text{C} - \text{Ch}} = \frac{\text{C}^2 \text{h}^2}{\text{C}(1-h)}$$

$$K_h = \frac{\text{Ch}^2}{(1-h)}$$

Since $h \ll 1$ then $(1-h) \approx 1$

$$\therefore \boxed{K_h = \text{Ch}^2} \quad \text{.....(5)}$$

$$\text{h}^2 = \frac{K_h}{C} \quad \text{or} \quad \text{h} = \sqrt{\frac{K_h}{C}} \quad \text{.....(6)}$$

$$\boxed{\text{h} = \sqrt{\frac{K_w}{K_a \times C}}} \quad \text{.....(7)}$$

(c) pH of the solution

$$[\text{OH}^-] = \text{Ch}$$

$$[\text{OH}^-] = C \times \sqrt{\frac{K_w}{K_a \times C}} \quad \text{or} \quad [\text{OH}^-] = \sqrt{\frac{K_w \times C}{K_a}}$$

$$\therefore K_w = [\text{OH}^-][\text{H}^+]$$

$$\therefore [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{K_w}{\sqrt{\frac{K_w \times C}{K_a}}}$$

$$\boxed{[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{C}}} \quad \text{.....(8)}$$

taking - log on both sides

$$-\log [\text{H}^+] = -\log \sqrt{\frac{K_w \times K_a}{C}}$$

$$\text{pH} = -\log \left(\frac{K_w \times K_a}{C} \right)^{\frac{1}{2}}$$

$$\text{pH} = -\frac{1}{2} [\log K_w + \log K_a - \log C]$$

$$\text{pH} = -\frac{1}{2} \log K_w - \frac{1}{2} \log K_a + \frac{1}{2} \log C$$

$$\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$$

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C \quad \text{.....(9)}$$

D. Hydrolysis of weak acid and weak base (WA - WB)

type of salt :

Ex. $\text{CH}_3\text{COONH}_4$, AgCN , NH_4CN , CaCO_3 , $[\text{NH}_4]_2\text{CO}_3$,
 ZnHPO_3 etc.



• Solution is almost neutral but it may be acidic or basic depending upon the nature of acid and base and pH of the solution is near to 7.

(a) Relation between K_h , K_w , K_a and K_b



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \quad \text{.....(1)}$$

For weak base



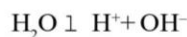
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \text{.....(2)}$$

For weak acid



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{.....(3)}$$

For water



$$K_w = [\text{H}^+][\text{OH}^-] \quad \text{.....(4)}$$

Multiply Eq. (1) \times Eq. (2) \times Eq. (3) = Eq. (4)

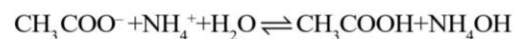
$$\frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$\times \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = [\text{H}^+][\text{OH}^-]$$

$$K_h \times K_b \times K_a = K_w$$

$$K_h = \frac{K_w}{K_a \times K_b} \quad \text{.....(5)}$$

(b) Degree of hydrolysis (h) –



Initial concentration of salt C C 0 0
 C - Ch C - Ch Ch Ch

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} = \frac{\text{Ch} \times \text{Ch}}{(\text{C} - \text{Ch})(\text{C} - \text{Ch})}$$

$$= \frac{\text{C}^2 \text{h}^2}{\text{C}(1 - \text{h}) \times \text{C}(1 - \text{h})}$$

Since $h \ll \ll \ll 1$ then $(1 - h) \approx 1$

$$\therefore K_h = h^2 \quad \text{.....(6)}$$

$$\text{or } h^2 = \frac{K_w}{K_a \times K_b} \text{ or } h = \sqrt{\frac{K_w}{K_a \times K_b}} \quad \text{.....(7)}$$

(c) pH of the solution

from equation (3)

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{K_a \times \text{Ch}}{\text{C} - \text{Ch}} = \frac{K_a \times h}{1 - h}$$

Since $h \ll \ll \ll 1$ then $(1 - h) \approx 1$

$[\text{H}^+] = K_a \times h$ [Now put the value of h from eq. (5)]

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{K_b}} \quad \text{.....(8)}$$

taking -log on both sides $-\log [H^+] = -\log \left(\frac{K_w \times K_a}{K_b} \right)^{1/2}$

$$pH = -\frac{1}{2} [\log (K_w \times K_a) - \log K_b]$$

$$pH = -\frac{1}{2} [\log K_w + \log K_a - \log K_b]$$

$$pH = -\frac{1}{2} [\log K_w] - \frac{1}{2} [\log K_a] - \frac{1}{2} [-\log K_b]$$

$$pH = +\frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b \quad \dots\dots(9)$$

Note : Degree of hydrolysis of weak acid and weak base [WA - WB] type salt does not depend on the concentration of salt.

For WA - WB types of salt :

	$K_a > K_b$	
$K_b > K_a$	$K_a = K_b$	
1. Hydrolysis	Cationic-anionic	
Anionic-cationic	Neutral hydrolysis	
2. Nature	Acidic	
Basic	Neutral	
3. pH	pH < 7	
pH > 7	pH = 7	

Summary :

Type of salts	$K_h = \frac{K_w}{\text{weak}}$	$h = \sqrt{\frac{K_h}{C}}$
---------------	---------------------------------	----------------------------

[H ⁺]	pH
-------------------	----

SA SB

-7

WA SB	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_w}{K_a \times C}}$
-------	-------------------------	---------------------------------------

$$\sqrt{\frac{K_w \times K_a}{C}} \quad 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

SA WB	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_w}{K_b \times C}}$
-------	-------------------------	---------------------------------------

$$\sqrt{\frac{K_w \times C}{K_b}} \quad 7 - \frac{1}{2} pK_b - \frac{1}{2} \log C$$

WA WB	$K_h = \frac{K_w}{K_a \times K_b}$	$h = \sqrt{\frac{K_w}{K_a \times K_b}}$
-------	------------------------------------	---

$$\sqrt{\frac{K_w \times K_a}{K_b}} \quad 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

BUFFER SOLUTIONS

Buffer Solutions are those, which resist a change in pH upon addition of small amount of acid or base. this does not mean that the pH will not change, and all it means is that the pH change would be less than the change that would have occurred had it not been a buffer.

- (i) In certain applications of chemistry and biochemistry we require solutions of constant pH. Such solution are called buffer solution.
- (ii) A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H⁺ ions) or a base (OH⁻ ions) is called buffer solution.
- (iii) Buffer solutions are also called solutions of reverse acidity or alkalinity.
- (iv) Following are the characteristics of buffer solutions

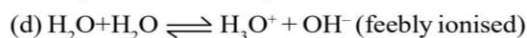
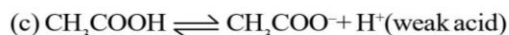
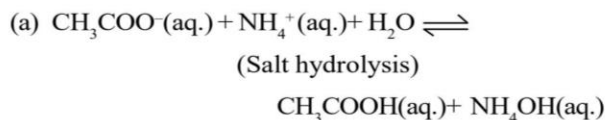
- (a) It must have appro.constant pH.
- (b) Its pH should not be changed on long standing
- (c) Its pH should not be changed on dilution.
- (d) It pH should not be changed to any great extent on addition of small quantity of acid or base.
- (v) Buffer solutions can be classified as follows.

- (A) Simple buffer (B) Mixed buffer

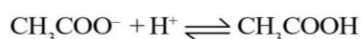
Simple buffer

- (i) It is a solution of one compound i.e. salts of WA + WB (Refer salt hydrolysis.)
- (ii) Buffer action of such solution can be explained as follows,

In the salt solution of CH₃COONH₄ following equilibria will be there,



on addition of small amount of acid the $[\text{H}^+]$ in solution will increase and



(from acid) (very less ionised)

equilibria will shift in forward direction. Similarly on addition of small amount of base, the $[\text{OH}^-]$ in solution will increase



(from base) (very less ionised)

equilibria will shift in forward direction Hence one can conclude that there will be no change (almost) in the pH of the solution.

(iii) Simple buffer solutions have very little significance since $\text{pH} = 7 + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b$, so solution of desired pH can not be prepared.

Mixed buffer

Mixed buffers are solutions of more than one compounds. They can be further classified as

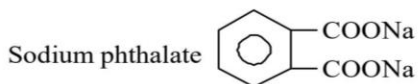
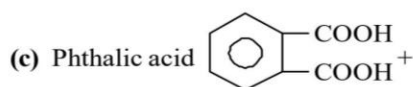
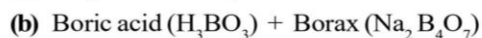
(a) Acidic buffer

(b) Basic buffer

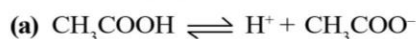
Acidic buffer

(i) These are the mixture of a weak acid and its salt with strong base.

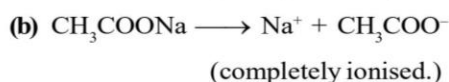
e.g.



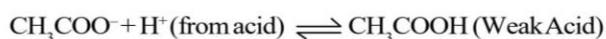
(ii) Buffer action of acidic buffer can be explained with following equilibria,



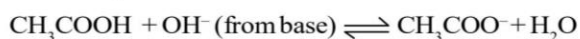
(Feebly ionised.)



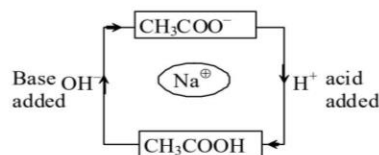
When a strong acid is added in the solution $[\text{H}^+]$ increases, which will combine with CH_3COO^- to form feebly ionised CH_3COOH , which is also suppressed by common ion effect,



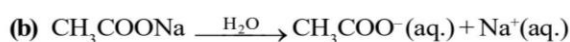
Again when strong base is added in the solution it will attack on unionised acid CH_3COOH to form feebly ionised H_2O molecules



(iii) One can remember the buffer action of acidic buffer with the help of following figure -



(iv) pH of such acidic buffer can be calculated as follows.



CH_3COOH is feebly ionised and its ionisation is also suppressed by presence of common ion (CH_3COO^-). So one can fairly assume $[\text{CH}_3\text{COO}^-] = [\text{salt}]$ and $[\text{CH}_3\text{COOH}] = [\text{Acid}]$ taken initially in buffer solution.

so $K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$

or $[\text{H}^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$

$\log[\text{H}^+] = \log K_a + \log[\text{CH}_3\text{COOH}] - \log[\text{CH}_3\text{COO}^-]$
 $-\log[\text{H}^+] =$
 $-\log K_a - \log[\text{CH}_3\text{COOH}] + \log[\text{CH}_3\text{COO}^-]$

$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$

$\text{pH} = \text{pK}_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$

or
$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Above equation called Henderson's equation.

- If we increase the concentration of given salt in acidic buffer, pH will also increases.
- If we increase the concentration of acid in acidic buffer, pH will decreases.
- If conc. and volume are given for salt and acid then the pH is given by the following formula-

$$\text{pH} = \text{p}K_a + \log \frac{[N_2V_2]}{[N_1V_1]}$$

Where N_2V_2 = normality & volume of salt

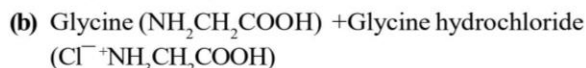
N_1V_1 = normality & volume of acid

Note : Mixture of weak acid and strong base solution can also act as an acidic buffer, if value of N_1V_1 of weak acid is greater than the value of N_2V_2 of strong base.

Basic Buffer

(i) These are the mixture of a weak base and its salt with strong acid.

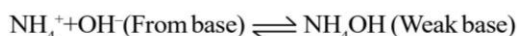
e.g.



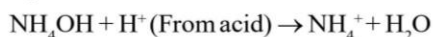
(ii) Buffer action of basic buffer can be explained with the help of following equilibria



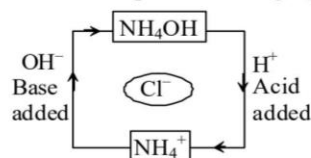
When a strong base is added in the solution $[\text{OH}^-]$ increases, which will combine with NH_4^+ to form feebly ionised NH_4OH , which is also suppressed by common ion effect.



Again when strong acid is added in the solution it will attack on unionised base NH_4OH to form feebly ionised H_2O molecules.



(iii) One can remember the buffer action of basic buffer with the help of following figure -



(iv) p^{H} of such basic buffer can be calculated from

Henderson - Hasselbalch equation as follows.



NH_4OH is feebly ionised and its ionisation is also suppressed by presence of common ion (NH_4^+). So one can fairly assume $[\text{NH}_4^+] = [\text{Salt}]$ and $[\text{NH}_4\text{OH}] = [\text{Base}]$ taken initially in buffer solution.

$$\text{so } K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

$$\text{or } [\text{OH}^-] = \frac{K_b[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = \frac{K_b[\text{Base}]}{[\text{Salt}]}$$

or $\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$ This is known as the **Henderson's equation of a buffer.**

or $\text{pH} = 14 - \text{pOH}$

Buffer Capacity

- The property of a buffer solution to resist alteration in its pH value is known as buffer capacity.
- Buffer capacity is number moles of acid or base added in one litre of solution as to change the pH by unity, i.e.

$$\text{Buffer capacity } (\phi) = \frac{\text{Number of moles acid or base added to 1 lit. sol.}}{\text{Change in pH}}$$

Maximum buffer capacity :

It can be proved that the maximum buffer is achieved when the salt and acid or base concentration is equal.

SOLVED EXAMPLE

Example-63

The pH of a blood stream is maintained by a proper balance of H_2CO_3 and NaHCO_3 . What volume of 5 M NaHCO_3 **Solution** should be mixed with 10ml of a sample of **Solution** which is 2.5 M in H_2CO_3 (assume no NaHCO_3), in order to maintain a $\text{pH} = 7.4$. ($\text{p}K_a$ for $\text{H}_2\text{CO}_3 = 6.7$, $\log 2 = 0.3$)

Sol.
$$\text{pH} = \text{p}K_a + \log \frac{\text{salt}}{\text{base}}$$

$$\Rightarrow 7.4 = 6.7 + \log \frac{\text{salt}}{\text{base}} \Rightarrow \frac{\text{salt}}{\text{base}} = 5$$

$$\Rightarrow 5 \times 2.5 \times 10 \times 10^{-3} = 5 \times V$$

$$\Rightarrow \text{required volume} = 25 \text{ ml}$$

Example-64

Calculate the buffer capacity of 1lt of

- (i) 0.1M CH₃COOH and 0.1M CH₃COONa
 (ii) 0.2M CH₃COOH and 0.2M CH₃COONa
 pK_a CH₃COOH = 4.74
 which will be a better buffer

Sol. $\frac{\delta x}{dpH} = \frac{2.303(a+x)(b-x)}{a+b}$

$\frac{2.303 ab}{a+b}$ $x \ll a, b$

(i) Buffer capacity = $\frac{0.1 \times 0.1 \times 2.303}{0.1 + 0.1} = 0.11515$

(ii) Buffer capacity = $\frac{0.2 \times 0.2 \times 2.303}{0.2 + 0.2} = 0.2303$

Second buffer **Solution** can be said better buffer

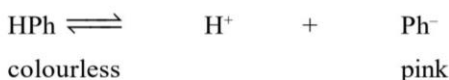
INDICATOR

INTRODUCTION

- Definition :-** Those compound or substance which indicate the nature of solution by changes their self colour.
- Types of indicators :**

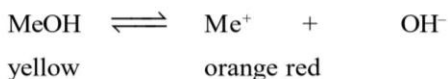
(a) Acidic indicator (HIn)

Ex. Phenolphthalein (HPh)



(b) Basic indicator (InOH)

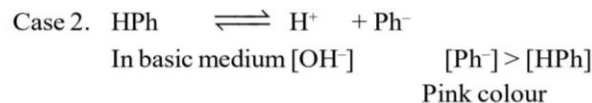
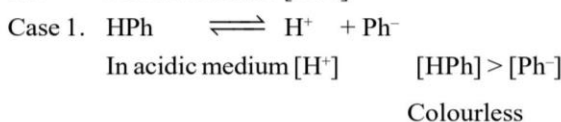
Ex. Methyl orange (MeOH)



2. OSTWALD THEORY OF INDICATORS

- (i) According to this theory, all the indicators are weak organic acid or base.
- (ii) Every indicator has light colour in its unionised form and dark colour in ionised form.
- (iii) Every indicator works in opposite medium (it means if it is acidic then it will work in basic medium and vice versa) it means colour change in opposite medium due to their unionised form is change in ionised form.

Ex. Acidic indicator [HPh]



(a) pH of acidic indicator -



$$K_1 = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

$$[\text{H}^+] = \frac{K_1[\text{HIn}]}{[\text{In}^-]}$$

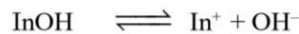
Taking - log on both sides

$$pH = pK_1 - \log [\text{HIn}] + \log [\text{In}^-]$$

$$pH = pK_1 + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$pH = pK_1 + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$$

(b) pOH of basic indicator -



$$K_1 = \frac{[\text{In}^+][\text{OH}^-]}{[\text{InOH}]}$$

$$pOH = pK_1 + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$$

(c) pH range of acidic indicator :

[HIn]	:	[In ⁻]
1	:	10
10	:	1

$$pH = pK_1 \pm 1$$

(d) pOH range of basic indicator :

[InOH]	:	[In ⁺]
1	:	10
10	:	1

$$pOH = pK_1 \pm 1$$

(e) Neutral condition for indicators (No working condition)

For acidic indicator		For basic indicators	
[HIn]	:	[InOH]	:
1	:	1	:
1	:	1	:

$$pH = pK_1$$

$$pOH = pK_1$$

S.No.	Name of indicator	Colour in acidic medium	Colour in basic medium	Working pH range of indicators
1.	Methyl orange (MeOH)	Orange red	Yellow	3.1 to 4.5
2.	Methyl red	Red	Yellow	4.2 to 6.2
3.	Phenol red	Yellow	Red	6.2 to 8.2
4.	Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

3. ACID-BASE TITRATION

S.No.	Type of titration	pH range of titration	Suitable indicators
1.	SA/SB.	3 – 11	All indicators (MeOH, HPh etc.)
2.	SA/WB	3 – 7	Methyl orange (MeOH) and methyl red
3.	WA/SB	7 – 11	Phenolphthalein (HPh)
4.	WA/WB	6.5 – 7.5	Phenol red

SOLUBILITY AND SOLUBILITY PRODUCT (K_{sp})

SOLUBILITY

(a) Definition

(i). At constant temperature the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of solution (i.e. saturated solution) is called solubility.

$$S(M) = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}} \quad S = \frac{x}{M_w \times V_L} \text{ mol L}^{-1}$$

(ii). The maximum weight of solute which can be dissolved in a given amount of solvent is known as solubility.

(b) Important points :-

Solubility does not depend on amount of substances and volume of solution where as depends on the following –

- Temperature
- Presence of common ion
- Nature of solvent

(Molecular wt. of $\text{AgCl} = 143.5$)

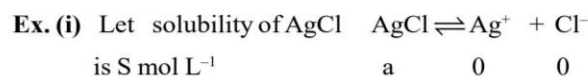
(Molecular wt. of $\text{BaSO}_4 = 233$)

Solubility can be expressed in terms of molarity.

SOLUBILITY PRODUCT (K_{sp}):

(a) At constant temperature equilibrium state, the product of concentrations of ions in a saturated solution of substance is called solubility product of that substance. (Saturated solution is that solution in which

further dissolution of even a small amount of salt is not possible).



According to L.M.A.

Solubility product at saturation in terms of concentration of ions $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$

Solubility product in terms of solubility $K_{sp} = (S)(S)$

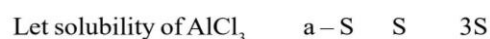
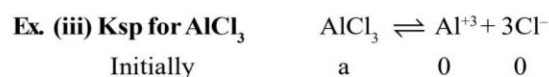
$$K_{sp} = S^2$$



Solubility product in terms of concentration of ions
 $K_{sp} = [\text{Ca}^{+2}][\text{Cl}^-]^2$

In terms of solubility $K_{sp} = (S)(2S)^2$

$$K_{sp} = 4S^3$$



is $S \text{ mol L}^{-1}$

Solubility product in terms of concentration of ions

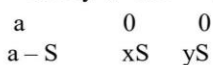
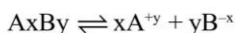
$$K_{sp} = [Al^{+3}][Cl^-]^3$$

In terms of solubility

$$K_{sp} = (S)(3S)^3$$

$$K_{sp} = 27S^4$$

(b) General form



$$K_{sp} = [A^{+y}]^x [B^{-x}]^y = [xS]^x \times [yS]^y = x^x \cdot s^x \cdot y^y \cdot s^y$$

$$K_{sp} = x^x y^y S^{(x+y)}$$

Ex. (i) $Al_2(SO_4)_3$

$$K_{sp} = 2^2 \times 3^3 \times (S)^{2+3} = 4 \times 27 \times S^5 = 108 S^5$$

(ii) Na_2KPO_4

$$K_{sp} = 2^2 \times 1^1 \times 1^1 (S)^{2+1+1} = 4S^4$$

(iii) $NaKRbPO_4$

$$K_{sp} = 1^1 \times 1^1 \times 1^1 \times 1^1 \times (S)^{1+1+1+1} = S^4$$

Example-65

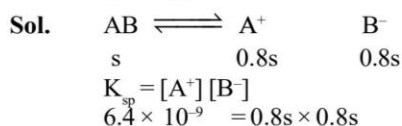
If solubility product of the base $M(OH)_3$ is 2.7×10^{-11} , the concentration of OH^{-1} will be

- (1) 3×10^{-3} (2) 3×10^{-4}
 (3) 10^{-3} (4) 10^{-11}

Ans. (1)

Example-66

Compound AB gets 80% ionised. What should be the solubility of AB, calculate if its solubility product is 6.4×10^{-9} ?



$$0.64 s^2 = 6.4 \times 10^{-9} \text{ or } s^2 = \frac{6.4 \times 10^{-9}}{0.64} = 10^{-8}$$

$$\therefore s = 10^{-4}$$

Example-67

Assertion : For a sparingly soluble salt, K_{sp} is the maximum dissolved value of solute in a solution.

Reason : K_{sp} corresponds to the ionic product of the salt in a saturated solution.

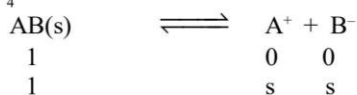
Ans. (A)

APPLICATION OF SOLUBILITY PRODUCT (K_{sp})

- To find out the solubility (S) :

(i) K_{sp} of AB (Mono-mono, di-di, tri-tri valency) type salt -

Ex. NaCl, $BaSO_4$, CH_3COONa , $CaCO_3$, NaCN, KCN, NH_4CN , NH_4Cl etc.

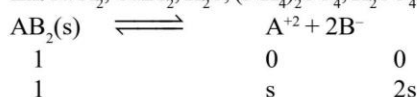


$$K_{sp} = [A^+][B^-]$$

$$K_{sp} = s^2 \text{ or } s = \sqrt{K_{sp}}$$

(ii) K_{sp} of AB_2 or A_2B (Mono-di or di-mono valency) type salt -

Ex. $CaCl_2$, $CaBr_2$, K_2S , $(NH_4)_2SO_4$, K_2SO_4 , K_2CO_3 etc.



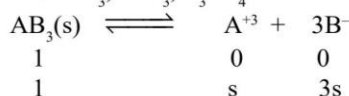
$$K_{sp} = [A^{+2}][B^-]^2$$

$$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$$

$$s = \left(\frac{K_{sp}}{4} \right)^{1/3}$$

(iii) K_{sp} of AB_3 or A_3B (Mono-tri or tri-mono valency) type salt -

Ex. $FeCl_3$, $AlCl_3$, K_3PO_4 etc.

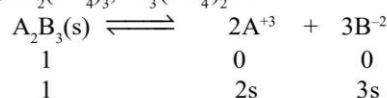


$$K_{sp} = [A^{+3}][B^-]^3 = s \times (3s)^3 = 27s^4$$

$$s = \left(\frac{K_{sp}}{27} \right)^{1/4}$$

(iv) K_{sp} of A_2B_3 or A_3B_2 (Di-tri or tri-di valency) type salt -

Ex. $Al_2(SO_4)_3$, $Ba_3(PO_4)_2$ etc.



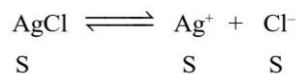
$$K_{sp} = [A^{+3}]^2 [B^{-2}]^3 = 2s \times 2s \times 3s \times 3s \times 3s = 108s^5$$

$$s = \left(\frac{K_{sp}}{108} \right)^{1/5}$$

Common ion effect on solubility :

Important point :- Solubility of substances always decreases in the presence of common ion.

Ex. (i) Find out the solubility of AgCl in the presence of C NaCl solution ?

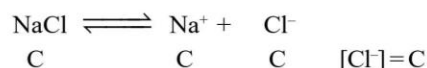


(Let solubility of AgCl is S mol L⁻¹)

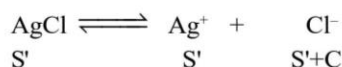
$$K_{sp} = [Ag^+][Cl^-]$$

$$K_{sp} = S^2$$

In NaCl solution



Let solubility of AgCl in the presence of NaCl solution is S' mol L^{-1} .



According to L.M.A.

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

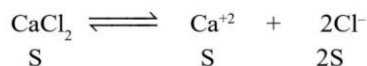
$$K_{sp} = S' (S' + C) = S'^2 + S'C$$

(Neglecting the higher power terms of S')

$$K_{sp} = S' C$$

$$S' = \frac{K_{sp}}{C}$$

Ex. (ii) Find out the solubility of CaCl_2 solution in the presence of C NaCl solution ?



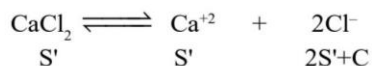
[Let solubility of CaCl_2 is S mol L^{-1}]

$$K_{sp} = [\text{Ca}^{+2}][\text{Cl}^-]^2 = 4S^3$$

For NaCl solution



Let solubility of CaCl_2 in the presence of NaCl solution is S' mol L^{-1} .



According to L.M.A.

$$K_{sp} = [\text{Ca}^{+2}][\text{Cl}^-]^2$$

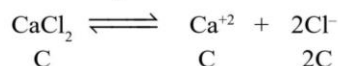
$$K_{sp} = S' (2S' + C)^2 = S' (4S'^2 + 4S'C + C^2)$$

$$K_{sp} = 4S'^3 + 4S'^2C + S'C^2$$

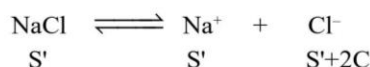
(Neglecting the higher power terms of S')

$$S' = \frac{K_{sp}}{C^2}$$

Ex. (iii) Find out the solubility of NaCl in the presence of C CaCl_2 solution ?



Let solubility of NaCl in the presence of CaCl_2 solution is S' mol L^{-1} .



According to L.M.A.

$$K_{sp} = [\text{Na}^+][\text{Cl}^-]$$

$$K_{sp} = S' (S' + 2C) = S'^2 + 2S'C$$

(Neglecting the higher power terms of S')

$$S' = \frac{K_{sp}}{2C}$$

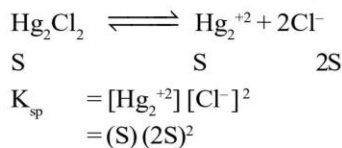
Group precipitation :

- (i) $K_{sp} > [] [] \Rightarrow$ Unsaturated } No precipitation
- (ii) $K_{sp} = [] [] \Rightarrow$ Saturated } No precipitation
- (iii) $K_{sp} < [] [] \Rightarrow$ Super saturated \Rightarrow precipitation

Group	Radicals	Condition for precipitation (Group reagent)	Forms of precipitation
Zero	$\text{NH}_4^+, \text{K}^+, \text{Na}^+$	1-2 drops of CH_3COOH	—
First	$\text{Ag}^+, \text{Hg}_2^{+2}, (\text{Hg}_2^{+2}), \text{Pb}^{+2}$	By mixing of dilute HCl	Chloride $\text{AgCl}, \text{Hg}_2\text{Cl}_2, \text{PbCl}_2$
Second	$\text{Pb}^{+2}, \text{Hg}^{+2}, \text{Cu}^{+2}, \text{Cd}^{+2}$ $\text{Sn}^{+2}, \text{Sn}^{+4}, \text{As}^{+3}, \text{Sb}^{+3}, \text{Bi}^{+3}$	H_2S gas passed in the presence of acidic medium	Sulphide $\text{PbS}, \text{HgS}, \text{CuS}, \text{CdS}, \text{SnS}, \text{SnS}_2, \text{As}_2\text{S}_3, \text{Sb}_2\text{S}_3, \text{Bi}_2\text{S}_3$
Third	$\text{Al}^{+3}, \text{Fe}^{+3}, \text{Cr}^{+3}$	NH_4OH mixed in the presence of NH_4Cl	Hydroxide $\text{Al}(\text{OH})_3, \text{Fe}(\text{OH})_3, \text{Cr}(\text{OH})_3$
Fourth	$\text{Mn}^{+2}, \text{Co}^{+2}, \text{Ni}^{+2}$ Zn^{+2}	H_2S gas passed in presence of basic medium	Sulphide $\text{MnS}, \text{CoS}, \text{NiS}, \text{ZnS}$
Fifth	$\text{Ba}^{+2}, \text{Sr}^{+2}, \text{Ca}^{+2}$	$(\text{NH}_4)_2\text{CO}_3$ mixed in the presence of NH_4Cl and NH_4OH	Carbonate $\text{BaCO}_3, \text{SrCO}_3, \text{CaCO}_3$
Sixth	Mg^{+2}	By mixing of Na_2HPO_4	Hydrogen phosphate (MgHPO_4)

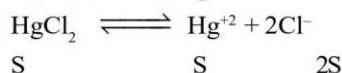
(iv) **Important points :**

(a). $\text{Hg}^{+1}(\text{us}) \rightarrow$ Unstable in aqueous solution. [Stable in dimer form (Hg_2^{+2}) \Rightarrow Hg_2Cl_2]



$$K_{sp} = 4\text{S}^3$$

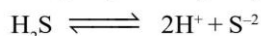
(b). $\text{Hg}^{+2}(\text{ic}) \rightarrow \text{HgCl}_2 \rightarrow$ stable in aqueous solution



$$K_{sp} = 4\text{S}^3$$

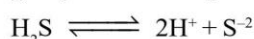
(c). For precipitation of II group, H_2S gas is passed in acidic medium to decrease S^{-2} concentration by common ion effect. So that ionic product of cations of group II and S^{-2} ions exceed the solubility product of their corresponding metal sulphides. Therefore only the cations of group II gets precipitated. But the sulphides of the cation of the other groups (III, IV & V) are not precipitated under these conditions because their solubility products are quite high.

When H_2S gas is directly passed through solution then IV^{th} group is also precipitated with II^{nd} group.



$$K_{sp_{II}} < K_{sp_{IV}} < [\text{radicals of II}^{\text{nd}} \text{ and IV group}] [\text{S}^{-2}]$$

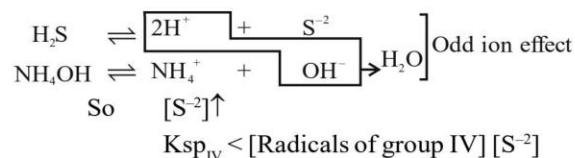
When H_2S gas pass in acidic medium $[\text{H}^+]$ then only II^{nd} group radicals are precipitated.



$$K_{sp_{II}} < [\text{radicals of II}^{\text{nd}} \text{ and IV group}] [\text{S}^{-2}] < K_{sp_{IV}}$$

(d). For precipitation of group III, NH_4OH is added in the presence of NH_4Cl to decrease the concentration of OH^- by common ion effect so ionic product of cations of group III and hydroxides ions exceed the solubility product of their corresponding metal hydroxides and only group III cations will precipitated. On the other hand cations of group IV, V and VI, which require large concentration of OH^- due to their high solubility product, will not be precipitated.

(e). In IV group, H_2S gas is passed in basic medium to increase S^{-2} ion concentration by odd ion effect, so that the ionic product of cations of group IV and S^{-2} ions exceed the solubility product of their corresponding metal sulphide and hence gets precipitated.



(f) In V group, order of K_{sp} and precipitation is –
 $\text{BaCO}_3 < \text{SrCO}_3 < \text{CaCO}_3$

• **Precipitation of soap and salt (NaCl)**

(i) **Precipitation of NaCl (common salt) :**

For the precipitation of NaCl, HCl gas passed in saturated solution of NaCl to increase the concentration of Cl^- ion by common ion, so ionic product of concentration of Na^+ and Cl^- ion is more than K_{sp} of NaCl and NaCl easily precipitated.

Saturated solution of NaCl $K_{sp} = [\text{Na}^+][\text{Cl}^-]$

By passing of HCl gas $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$
 due to common ion $K_{sp} < [\text{Na}^+][\text{Cl}^-] \uparrow$

(ii) **Precipitation of soap :**

For precipitation of soap, NaCl mixed in saturated solution of soap to increase the concentration of Na^+ ion by common ion. So ionic product of concentration of Na^+ and stearate ions is more than K_{sp} of soap and soap is easily precipitated.

Ex. $\text{C}_{17}\text{H}_{35}\text{COONa}$ (Sodium stearate)

Saturated solution of $\text{C}_{17}\text{H}_{35}\text{COONa}$ $K_{sp} = [\text{C}_{17}\text{H}_{35}\text{COO}^-][\text{Na}^+]$

By mixing of NaCl solution $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$

due to common ion $K_{sp} < [\text{C}_{17}\text{H}_{35}\text{COO}^-][\text{Na}^+] \uparrow$

Example-68

Solubility products of $\text{M}(\text{OH})_3$ and $\text{M}(\text{OH})_2$ are 10^{-23} and 10^{-14} respectively. Which will be precipitated first on adding NH_4OH , if M^{+2} and M^{+3} both the ions are in solution ?

- (1) M^{+2}
- (2) M^{+3}
- (3) Both M^{+2} and M^{+3} together
- (4) Precipitation will not take place.

Ans. (2)

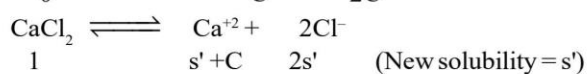
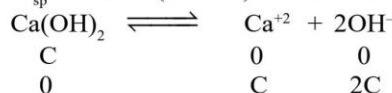
Example-69

Solubility of CaCl_2 is 4×10^{-8} , then find out its K_{sp} and its new solubility in the presence of $10^{-2} \text{ M Ca}(\text{OH})_2$.

Sol. $\text{CaCl}_2 \rightleftharpoons \text{Ca}^{+2} + 2\text{Cl}^-$

$$\begin{array}{ccc} 1 & s & 2s \end{array} \quad (\text{Initial solubility} = s)$$

$$K_{sp} = 4s^3 = 4(4 \times 10^{-8})^3 = 256 \times 10^{-24} \quad \dots\dots(i)$$



$$K_{sp} = [\text{Ca}^{+2}][\text{Cl}^-]^2 = [s'+C][2s']^2 = 4s'^3 + 4s'^2C \quad (s'^3 = \text{negligible})$$

$$K_{sp} = 4s'^2C \quad \dots\dots(ii)$$

$$\text{From equation (i) and (ii) } s'^2 = \frac{K_{sp}}{4C} = \frac{256 \times 10^{-24}}{4 \times 10^{-2}}$$

$$= 64 \times 10^{-22}$$

$$s' = 8 \times 10^{-11} \text{ mol L}^{-1}$$

Example-70

Assertion : In acidic medium, Zn^{2+} is not precipitated

by S^{2-} ions.

Reason: Common ion effect reduced the concentration of S^{2-} ions to the minimum value.

Ans. (A)

SOLVED EXAMPLE

Example-71

If equal concentrations are mixed (of products & reactants) then which of the reaction will proceed to the right and which will proceed to the left.



Sol. (A) Right; (B) Left

Example-72

- (a) Write conjugate acids of SO_4^{2-} , RNH_2 , NH_2^- , $C_2H_5O^-$, C_2H_5 , F^-
 (b) Write conjugate base of HNO_2 , OH^- , H_2CO_3 , $HClO_4$.
 (c) Write conjugate acids and conjugate base of amphoteric species.

Sol. (a) HSO_4^- , RNH_3^+ , NH_3 , $(C_2H_5)_2OH^+$, HF
 (b) NO_2^- , O^{2-} , HCO_3^- , ClO_4^-
 (c) Conjugate acids: H_2S , NH_4^+ , $C_2H_5OH_2^+$, H_3O^+
 Conjugate base: S^{2-} , NH_2^- , $C_2H_5O^-$, OH^-

Example-73

Which of the following is the strongest base-

- (A) $C_2H_5^-$ (B) $C_2H_5COO^-$
 (C) $C_2H_5O^-$ (D) OH^-

Ans. (A)

Sol. Acidic strength, $C_2H_6 < C_2H_5OH < H_2O < C_2H_5COOH$.

Example-74

Calculate the pH of solution obtained by mixing 10 mL of 0.1 M HCl and 40 mL of 0.2 M H_2SO_4 .

Sol. Milli equivalent of H^+ from HCl = $10 \times 0.1 = 1$
 Milli equivalent of H^+ from $H_2SO_4 = 40 \times 0.2 \times 2 = 16$
 \therefore Total Meq. of H^+ in solution = $1 + 16 = 17$

$$\therefore [H^+] = \frac{17}{50} = 3.4 \times 10^{-1} \quad \left(\because [H^+] = \frac{\text{Meq.}}{V_{\text{in mL}}} \right)$$

$$\therefore \text{pH} = -\log [H^+] = -\log 0.34$$

$$\text{pH} = 0.47$$

Example-75

Calculate pH of a KOH solution having :

- (a) 5.6 g of KOH mixed in 50 water
 (b) if it is further diluted to make 100 ml.

Ans. (a) 14.3 (b) 14

Sol. (a) Mole of KOH = $\frac{5.6}{56} = 0.1$
 $[OH^-] = 2 \text{ M}$
 $\text{pOH} = -0.3 \Rightarrow \text{pH} = 14.3$
 (b) $[OH^-] = 1 \text{ M}$
 $\text{pOH} = 0 \Rightarrow \text{pH} = 14$

Example-76

Calculate the pH of a solution which contains 100 mL of 0.1 M HCl and 9.9 mL of 1.0 M NaOH.

Sol. $HCl + NaOH \rightarrow NaCl + H_2O$

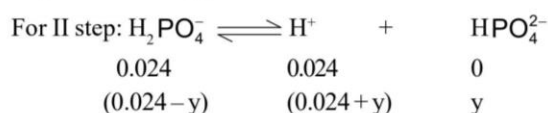
Meq. before reaction	$100 \times 0.1 = 10$	$9.9 \times 1 = 9.9$	0	0
Meq. after reaction	0.1	0	9.9	9.9

$$\therefore [H^+] \text{ left from HCl} = \frac{0.1}{109.9} = 9.099 \times 10^{-4} \text{ M}$$

$$\therefore \text{pH} = -\log H^+ = -\log 9.099 \times 10^{-4}$$

$$\text{pH} = 3.04$$

The value of K_1 is much larger than K_2 and K_3 . Also dissociation of II and III steps occurs in presence of H^+ furnished in I step and thus, dissociation of II and III steps is further suppressed due to common ion effect.



The dissociation of $H_2PO_4^-$ occurs in presence of $[H^+]$ furnished in

Step I.

Thus, $K_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$

or $6.2 \times 10^{-8} = \frac{(0.024 + y)y}{(0.024 - y)}$

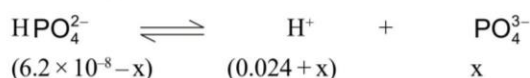
\therefore y is small $\therefore 0.024 - y \approx 0.024$ and neglecting y^2 .

$$\therefore 6.2 \times 10^{-8} = \frac{0.024y}{0.024}$$

$$\therefore y = 6.2 \times 10^{-8} \text{ M}$$

or $[HPO_4^{2-}] = K_2 = 6.2 \times 10^{-8} \text{ M}$ (Insignificant)

For III step:



$$\therefore K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{(0.024 + x)x}{(6.2 \times 10^{-8} - x)}$$

Again neglecting x^2 and assuming,

$$6.2 \times 10^{-8} - x = 6.2 \times 10^{-8}$$

$$\therefore 3.6 \times 10^{-13} = \frac{0.024x}{6.2 \times 10^{-8}}$$

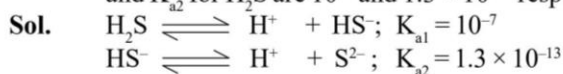
$$\therefore x = \frac{3.6 \times 10^{-13} \times 6.2 \times 10^{-8}}{0.024}$$

$$= 9.3 \times 10^{-19} \text{ M (Insignificant)}$$

NOTE: For weak polyprotic acid having no other electrolyte, the anion concentration produced in II step of dissociation is always equal to K_2 if concentration is reasonable.

Example-76

A solution contains 0.1 M H_2S and 0.3 M HCl . Calculate the conc. of S^{2-} and HS^- ions in solution. Given K_{a1} and K_{a2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.



Due to common ion effect the dissociation of H_2S is suppressed and the $[H^+]$ in solution is due to HCl .

$$\therefore K_{a1} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$\Rightarrow 10^{-7} = \frac{[0.3][HS^-]}{[0.1]} \quad [\because [H^+] \text{ from } HCl = 0.3]$$

$$\therefore [HS^-] = \frac{10^{-7} \times 0.1}{0.3} = 3.3 \times 10^{-8} \text{ M}$$

Further $K_{a2} = \frac{[H^+][S^{2-}]}{[HS^-]}$

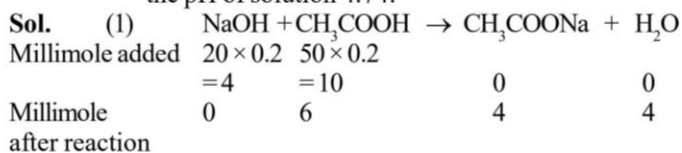
$$\Rightarrow 1.3 \times 10^{-13} = \frac{[0.3][S^{2-}]}{3.3 \times 10^{-8}}$$

$$\therefore [S^{2-}] = \frac{1.3 \times 10^{-13} \times 3.3 \times 10^{-8}}{0.03} = 1.43 \times 10^{-19} \text{ M}$$

Example-77

20 mL of 0.2 M $NaOH$ are added to 50 mL of 0.2 M acetic acid ($K_a = 1.8 \times 10^{-5}$).

- What is pH of solution ?
- Calculate volume of 0.2 M $NaOH$ required to make the pH of solution 4.74.

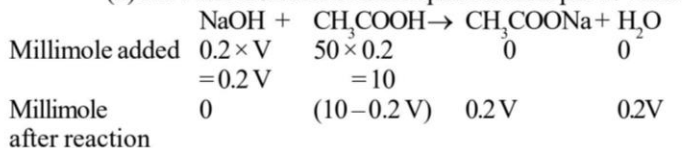


$$\therefore [\text{Molarity}] = \frac{\text{millimole}}{\text{Total volume}}$$

$$\therefore [CH_3COOH] = \frac{6}{70} \quad [CH_3COONa] = \frac{4}{70}$$

$$\therefore pH = -\log 1.8 \times 10^{-5} + \log \frac{4/70}{6/70} = 4.57$$

(2) Let V mL of 0.2 M $NaOH$ is required to make pH 4.74 then



$$\therefore [\text{Acid}] = \frac{10 - 0.2V}{50 + V}; [\text{Salt}] = \frac{0.2V}{50 + V}$$

$$\therefore 4.74 = -\log 1.8 \times 10^{-5} = \log \frac{(0.2V)/(50 + V)}{(10 - 0.2V)/(50 + V)}$$

$$\therefore V = 25 \text{ mL}$$

Example-78

Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre and of other solution containing 1 mole CH_3COONa + 1 mole of acetic acid per litre.

Sol. Case I: pH when 1 mole CH_3COONa and 1 mole HCl are present.



$$\therefore [CH_3COOH] = 1 \text{ M}$$

$$\therefore [H^+] = C \cdot \alpha = C \sqrt{\frac{K_a}{C}} = \sqrt{K_a \cdot C} = \sqrt{K_a}$$

$$\therefore C = 1$$

$$\therefore pH_1 = -\frac{1}{2} \log K_a$$

Case II: pH when 1 mole CH_3COONa and 1 mole of CH_3COOH ; a buffer **Solution**.

$$\therefore pH_2 = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore [\text{Salt}] = 1 \text{ M}$$

$$pH_2 = -\log K_a$$

$$\therefore [\text{Acid}] = 1 \text{ M}$$

$$\therefore \frac{pH_1}{pH_2} = \frac{1}{2}$$

Example-79

Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer **Solution** of pH 9. when total concentration of buffering reagents is 0.6 mol litre⁻¹. pK_b of $NH_3 = 4.7$, $\log 2 = 0.30$

Sol. $pOH = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$

$$5 = 4.7 + \log \frac{a}{b}$$

$$\frac{a}{b} = 2$$

$$\therefore a = 2b$$

Given $a + b = 0.6$

$$2b + b = 0.6$$

$$\therefore 3b = 0.6$$

or $b = 0.2 \text{ mole}$ and $a = 0.4 \text{ mole}$

Thus, $[\text{Salt}] = 0.4 \text{ M}$ and $[\text{Base}] = 0.2 \text{ M}$