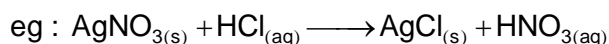


CHEMICAL & IONIC EQUILIBRIUM

In a chemical reaction, the reacting species combine with each other to form the products. When the reaction is complete, all the reacting species changes to the products. If such a reaction is carried out in a closed container, in many cases we may find that it is not completed, and after sometime the reaction mixture contains a constant concentration of reactants and products at constant temperature and pressure. Under these conditions the reaction is said to be in equilibrium.

IRREVERSIBLE REACTIONS :

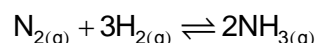
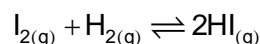
Reactions in which entire amount of reactant is converted in to product. It proceeds only in one direction. So it reaches completion.



REVERSIBLE REACTIONS

Reactions in which entire amount of reactant is not converted to products. They proceed in opposite direction under certain conditions. So they don't reach completion.

eg :



Change of reactant to product → Forward reaction

Change of product to reactant → Backward reaction

RATE OF REACTION

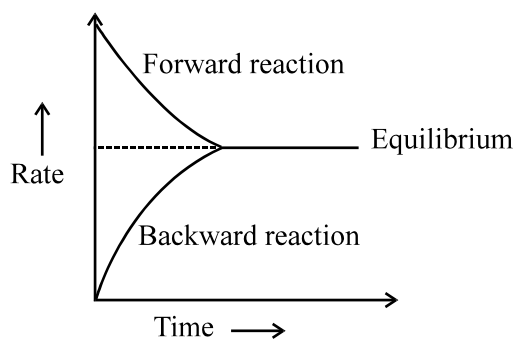
Rate of a reaction is the change in concentration of reactant/product in unit time.

EQUILIBRIUM

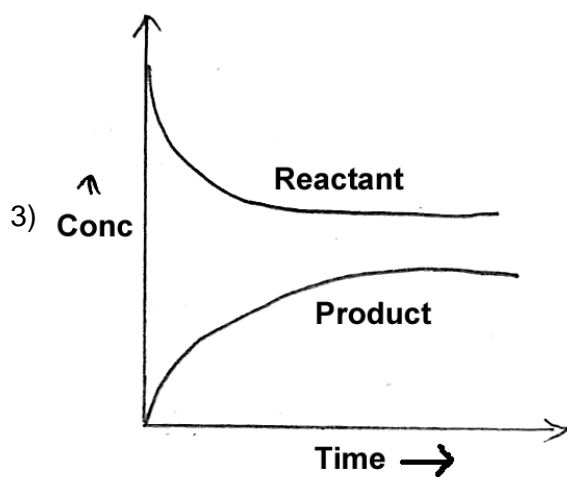
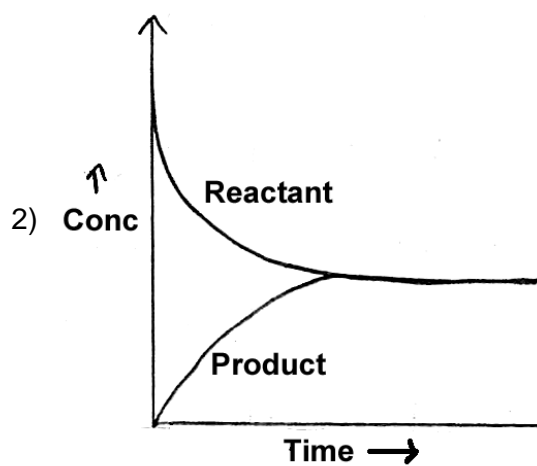
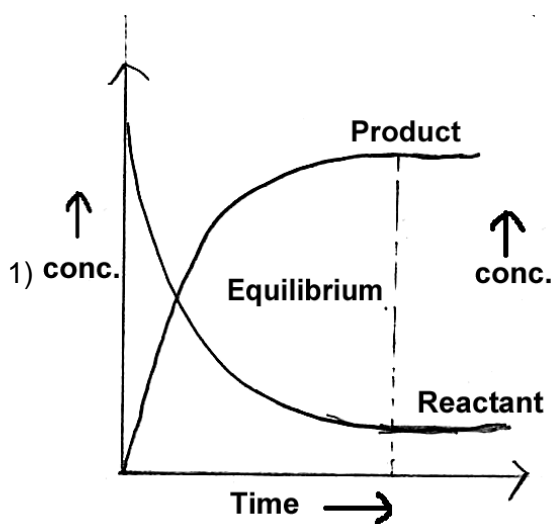
An equilibrium represents a state in a process (reversible reaction) where the observable properties such as colour, temperature, pressure, concentration etc. donot show any change.

ie, rate of forward reaction = rate of backward reaction.

At equilibrium rate of driving force and opposing force becomes equal.



- ◆ When system attains equilibrium, then the concentrations of reactant and product becomes constant.



PHYSICAL EQUILIBRIUM

Equilibrium associated with physical processes

1) solid \rightleftharpoons liquid

When a solid is heated, it starts melting at certain fixed temperature (melting point). At this stage even when heating is continued, temperature doesnot change until whole of solid is converted into liquid. The state when solid and liquid phase of substance coexists is called solid-liquid equilibrium.

Eg : ice \rightleftharpoons H₂O_(l)

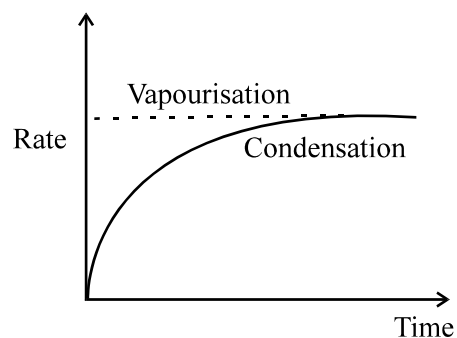
Here,

At equilibrium, rate of melting of ice=rate of freezing of water

2) Liquid \rightleftharpoons Vapour (gas)

Rate of evaporation = Rate of condensation

eg : H₂O(l) \rightleftharpoons H₂O(g)



Vapourisation equilibrium of water is an example whose consequences appear in everyday life. Fogging of bathroom mirrors, car windows & glasses occurs when water vapour in warm air come in contact with cooler surface of mirror causing vapour to condense.

Conditions necessary for liquid vapour equilibrium :

- ◆ System must be a closed system ie amount of matter in system must remain constant.
- ◆ System must be at constant temperature

Vapour pressure

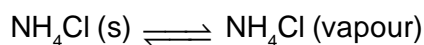
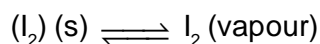
Pressure exerted by the vapour when it is in equilibrium with liquid phase and is a constant at given temperature.

3) Solid \rightleftharpoons Vapour (gas)

Obtained only in those substances which undergoes sublimation

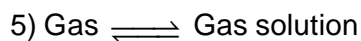
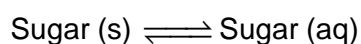
Eg :

Camphor (s) \rightleftharpoons Camphor (vapour)



When a saturated solution is in contact with solid solute, there exists a dynamic equilibrium between the solid & solution phases.

Eg : Sugar and sugar solution. At equilibrium state number of sugar molecules going into solution from solid sugar is equal to no. of molecules precipitating out from the solution.



Gases dissolve in liquids. The solubility of a gas in any liquid depends upon :

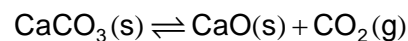
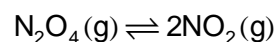
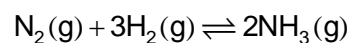
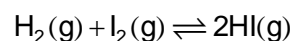
- i) Nature of the gas and that of the liquid
- ii) Temperature of the liquid
- iii) Pressure of the gas over the surface of the solution

According to Henry's law, the mass of a gas (dissolves in a definite volume of a liquid solubility of gas) is proportional to the pressure of the gas in equilibrium with the solution.

CHEMICAL EQUILIBRIUM

Equilibrium associated with chemical process

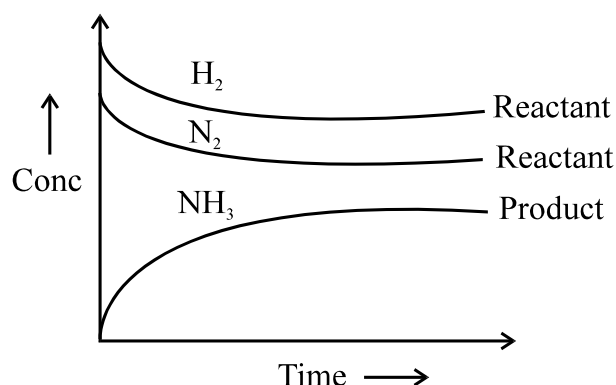
Eg :



Characteristics

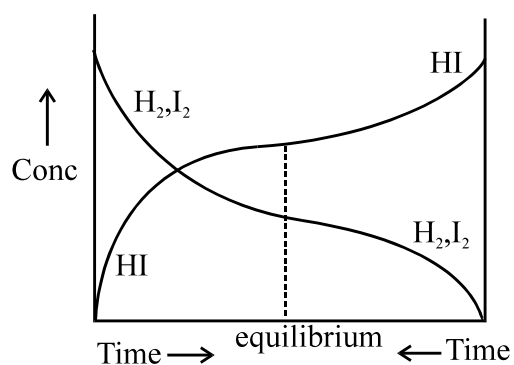
- ♦ Can be achieved only on closed containers
- ♦ Dynamic in nature i.e., forward and backward reactions still taking place even after equilibrium is attained
- ♦ Once chemical equilibrium is achieved composition of system doesn't change.

eg : Consider the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$



- ◆ Chemical equilibrium can be attained from either side. ie, equilibrium can be achieved in a reversible reaction whether we start from reactants or products.

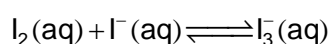
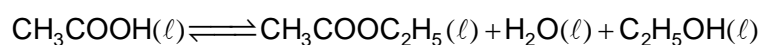
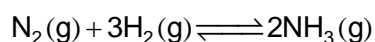
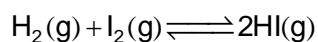
eg : $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}$



- ◆ Equilibrium is affected by change in volume, pressure, temperature etc.
- ◆ A catalyst has no effect on equilibrium
- ◆ At equilibrium, change in Gibbs free energy $\Delta G = 0$

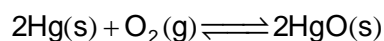
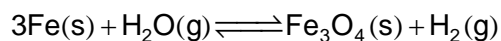
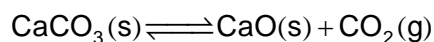
HOMOGENOUS EQUILIBRIUM

Equilibrium in which reactants & products are in same physical state.



HETEROGENOUS EQUILIBRIUM

Equilibrium in which reactants & products are in different physical state

**LAW OF MASS ACTION - Guldberg and Waage**

It states that rate of reaction is directly proportional to the product of the active mass of reactants, each raised to power equal to its corresponding stoichiometric coefficient that appears in the balanced chemical equation.

Active mass is the molar concentration i.e., no. of moles per L. It is expressed in [].

Consider the reaction $\text{A} + \text{B} \longrightarrow \text{Product}$

According to law of mass action

$$\text{rate} \propto [\text{A}] [\text{B}]$$

$$\text{rate} = k[\text{A}] [\text{B}] \quad k = \text{rate/velocity constant}$$

$$\text{When } [\text{A}] = [\text{B}] = 1$$

$$\text{then rate} = k \quad \text{ie, rate} \propto k$$

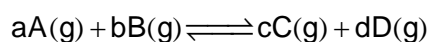
Different reaction have different rate constants.

For the reaction $a\text{A} + b\text{B} \longrightarrow \text{Product}$

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

EQUILIBRIUM CONSTANT

Consider the reaction



$$\text{Rate of forward reaction} = r_f = k_f [\text{A}]^a [\text{B}]^b$$

$$\text{Rate of backward reaction} = r_b = k_b [\text{C}]^c [\text{D}]^d$$

At equilibrium, $r_f = r_b$

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

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

Equilibrium constant in terms concentrations $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

k_f and k_b represent rate constant of backward & forward reaction

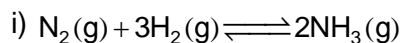
Equilibrium constant is the ratio of product of molar concentration of product to that of product of molar concentration of reactant in which each concentration term is raised to a power equal to its stoichiometric co-efficients in a balanced chemical equation.

For gaseous reaction, equilibrium constant in terms of pressure

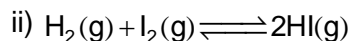
$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

P_A, P_B, P_C, P_D are partial pressure of A, B, C, D

♦ Write the representation of K_c and K_p of following reactions :



$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$$



$$K_c = \frac{[HI]^2}{[H_2][I_2]} \quad K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})}$$

Relation between K_c and K_p

Consider the reaction $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

According to ideal gas equation $PV = nRT$ $P = \frac{n}{V}RT$

ie, $P = \text{conc.} \cdot RT$

$$\therefore P_A = [A]RT \quad P_B = [B]RT \quad P_C = [C]RT \quad P_D = [D]RT$$

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

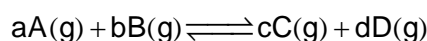
$$\text{ie, } K_p = K_c \cdot (RT)^{(c+d)-(a+b)}$$

$$\boxed{K_p = K_c \cdot (RT)^{\Delta n}} \quad \Delta n = (c + d) - (a + b)$$

Δn = no. of moles of gaseous products – no. of moles of gaseous reactants

- ◆ When $\Delta n = 0$ then $K_p = K_c$ eg: $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$
- ◆ $\Delta n = +ve$ then $K_p > K_c$ eg: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, $\Delta n = 2 - 1 = 1$
- ◆ $\Delta n = -ve$ then $K_p < K_c$ eg: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, $\Delta n = 2 - 4 = -2$

Equilibrium constant in terms of mole fraction (K_x)



$$\boxed{K_x = \frac{(x_C)^c (x_D)^d}{(x_A)^a (x_B)^b}}$$

x_A, x_B, x_C and x_D mole fractions of A, B, C and D respectively.

Relation between K_p , K_c and K_x

$$\text{For the above reaction } K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Partial pressure = $P_{\text{Total}} \times \text{mole fraction}$

$$\therefore P_A = P \cdot x_A, P_B = P \cdot x_B, P_C = P \cdot x_C, P_D = P \cdot x_D$$

$$\therefore K_p = \frac{(P \cdot x_C)^c (P \cdot x_D)^d}{(P \cdot x_A)^a (P \cdot x_B)^b} \quad \text{ie, } K_p = \frac{(x_C)^c (x_D)^d}{(x_A)^a (x_B)^b} P^{(c+d)-(a+b)}$$

$$\text{ie, } K_p = K_x \cdot P^{\Delta n}$$

$$\text{Also, } K_p = K_c \cdot (RT)^{\Delta n} = K_x \cdot P^{\Delta n}$$

$$\therefore \boxed{K_x = K_c \cdot \left(\frac{RT}{P}\right)^{\Delta n}} \quad \text{ie, } \boxed{K_x = K_c \cdot V^{\Delta n}}$$

V = Total volume of the system in litre

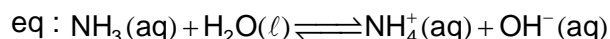
Degree of dissociation (α)

It is the fraction of total no. of moles dissociated per mole.

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{Total no. of moles}}$$

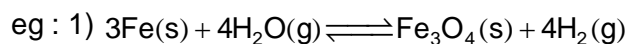
Rules for writing equilibrium constant expression

- i) It is the ratio of molar concentration of products to reactants each raised to a power equal to stoichiometric coefficient
- ii) The concentration term of solvent which is present in large excess is not included in the equilibrium constant expression.

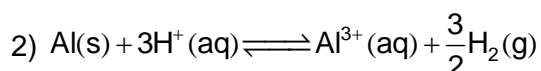


$$K_C = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

- iii) For heterogenous reactions the concentration terms for pure solid and pure liquid are not included in the expression for equilibrium constant.



$$K_C = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4} \quad K_P = \frac{(P_{\text{H}_2})^4}{(P_{\text{H}_2\text{O}})^4}$$



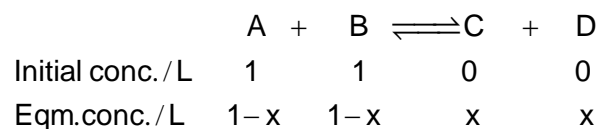
$$K_C = \frac{[\text{Al}^{3+}][\text{H}_2]^{3/2}}{[\text{H}^+]^3} \quad K_P = (P_{\text{H}_2})^{3/2}$$

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

- i) K is affected only on the equilibrium concentration and not on the initial concentration.

Let initial concentration of reactants A and B are 1 mol/L and x as the degree of dissociation.

Consider the reaction



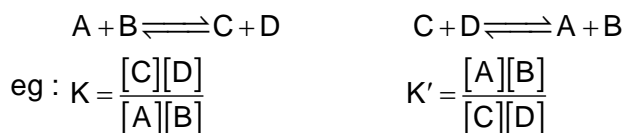
$$K_C = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} = \frac{x \cdot x}{(1-x)(1-x)} = \frac{x^2}{(1-x)^2}$$

- ii) Unit of K depends on stoichiometry of components
- iii) Value of K is not affected by change in concentration, pressure, volume, addition of catalyst, and addition of inert gas at constant pressure and volume.

iv) Factors which influence the equilibrium constant

a) Mode of representation of chemical reaction

If K is the equilibrium constant of forward reaction then equilibrium constant of backward reaction is $\frac{1}{K}$



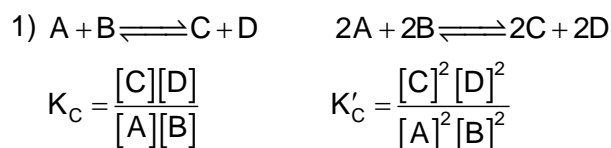
$$K' = \frac{1}{K}$$

b) Stoichiometry of reaction

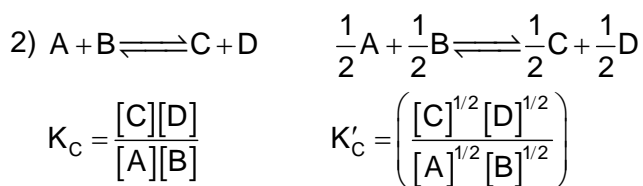
Eqn $\times n$ then $K \rightarrow K^n$

Eqn $\div n$ then $K \rightarrow K^{1/n}$

eg :



Here $K'_C = (K_C)^2$



Here, $K'_C = (K_C)^{1/2}$

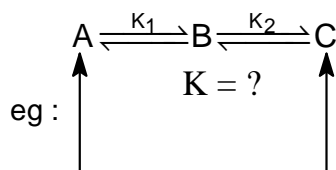
c) Temperature

Increase of temperature favours the endothermic reaction and decrease in temperature favours the exothermic reaction.

If the process is exothermic then increase in temperature decreases k_f which decreases K_C .

If the process is endothermic then increase in temperature increases k_f which increases K_C .

v) If a reaction complete in more than one step, then the overall equilibrium constant is the product of individual equilibrium constants.



$$K_1 = \frac{[\text{B}]}{[\text{A}]} \quad K_2 = \frac{[\text{C}]}{[\text{B}]} \quad K = \frac{[\text{C}]}{[\text{A}]} = K_1 \cdot K_2$$

THERMODYNAMICS OF EQUILIBRIUM - Van't Hoff equation

$$\Delta G = \Delta G^0 + RT \ln K$$

\ln - natural logarithm ($\ln = 2.303 \log$)

ΔG^0 -Gibb's free energy change at standard condition ie at 1 atm and 273 K

$$\Delta G = \Delta G^0 + 2.303RT \log K$$

At equilibrium $\Delta G = 0$

$$\therefore \boxed{\Delta G^0 = -2.303 RT \log K} \quad \dots(1)$$

where $K = K_c, K_p$ or K_{sp}

$$\text{Also } \Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \dots(2)$$

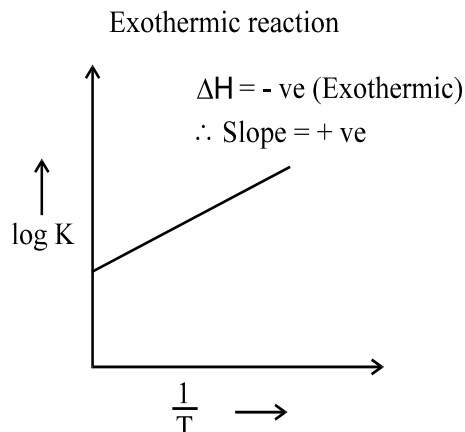
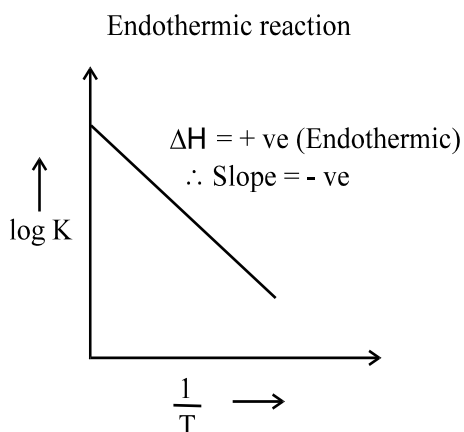
ΔH^0 - standard enthalpy change

ΔS^0 - standard entropy change

$$(1) \text{ and } (2) \Rightarrow -2.303RT \log K = \Delta H^0 - T\Delta S^0$$

$$\log K = \frac{-\Delta H^0}{2.303} \times \frac{1}{RT} + \frac{\Delta S^0}{2.303R}$$

If $\log K$ vs $\frac{1}{T}$ is plotted it is a straight line with slope = $\frac{-\Delta H^0}{2.303R}$ and intercept = $\frac{\Delta S^0}{2.303R}$



Let K_1 and K_2 are the equilibrium constants at temperature T_1 and T_2 ($T_2 > T_1$)

$$\log K_1 = \frac{-\Delta H^0}{2.303 R} \cdot \frac{1}{T_1} + \frac{\Delta S^0}{2.303 R} \quad \dots(3)$$

$$\log K_2 = \frac{-\Delta H^0}{2.303 R} \cdot \frac{1}{T_2} + \frac{\Delta S^0}{2.303 R} \quad \dots(4)$$

$$(4) - (3) \Rightarrow \log K_2 - \log K_1 = \left[\frac{-\Delta H^0}{2.303 R} \cdot \frac{1}{T_2} + \frac{\Delta S^0}{2.303 R} \right] - \left[\frac{-\Delta H^0}{2.303 R} \cdot \frac{1}{T_1} + \frac{\Delta S^0}{2.303 R} \right]$$

$$\text{ie, } \boxed{\log \frac{K_2}{K_1} = \frac{\Delta H^0}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]} \Rightarrow \text{van't Hoff equation}$$

If $\Delta H = +ve$ then $\log \frac{K_2}{K_1} = +ve$

ie, $\log K_2 - \log K_1 = +ve$

$\therefore K_2 > K_1$

If $\Delta H = -ve$, then $\log \frac{K_2}{K_1} = -ve$

ie, $\log K_2 - \log K_1 = -ve$

$\therefore K_2 < K_1$

★ REACTION QUOTIENT (Q_c)

Ratio of product concentration to reactant concentration at any stage of reaction

$$\boxed{Q_c = \frac{[P]}{[R]}}$$

$Q_c = 0$: reaction not started

$Q_c = K_c$: reaction at equilibrium

$Q_c > K_c$: favours backward reaction

$Q_c < K_c$: favours forward reaction

◆ APPLICATION OF K

★ used to predict extent of reaction

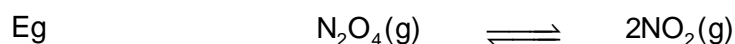
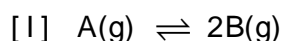
If $K_c > 10^3$: product predominates over reactants

If $K_c < 10^{-3}$: reactant predominates over product

If K_c is $10^3 - 10^{-3}$: appreciable concentration of both reactant and product are present

★ It can be used to predict direction of reaction i.e Q_c and K_c

♦ K_p and K_c of some Reactions



Initial conc : 1 Mol/L 0 mol/L

Equilibrium conc : $1 - x$ $2x$

Total no. of moles : $1 - x + 2x = 1 + x$

at equilibrium

active mass

$$= \frac{\text{Eqm conc.}}{\text{Vol. of container}} = \frac{1-x}{v} \quad \frac{2x}{v}$$

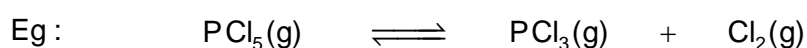
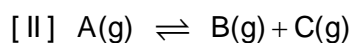
$$\text{mole fraction : } \frac{1-x}{1+x} \quad \frac{2x}{1+x}$$

Partial pressure

$$= P \text{ total mole fraction } P \left(\frac{1-x}{1+x} \right) \quad P \left(\frac{2x}{1+x} \right)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{2x}{v} \right)^2}{\left(\frac{1-x}{v} \right)} = \boxed{\frac{4x^2}{v(1-x)}}$$

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{\left(P \frac{2x}{1+x} \right)^2}{P \left(\frac{1-x}{1+x} \right)} = \boxed{\frac{P \cdot 4x^2}{1-x^2}}$$



Initial con : 1 mol/L 0 0

Equilibrium conc : $1 - x$ x x

Total no. of moles : $1 - x + x + x = 1 + x$

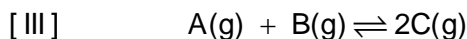
at equilibrium

active mass :	$\frac{1-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$
mole fraction :	$\frac{1-x}{1+x}$	$\frac{x}{1+x}$	$\frac{x}{1+x}$
partial pressure :	$P \frac{(1-x)}{1+x}$	$P \frac{(x)}{1+x}$	$P \frac{(x)}{1+x}$

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{v} \cdot \frac{x}{v}}{\frac{1-x}{v}} = \boxed{\frac{x^2}{(1-x)v}}$$

$$K_P = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = \frac{P \left(\frac{x}{1+x} \right) \cdot P \left(\frac{x}{1+x} \right)}{P \left(\frac{1-x}{1+x} \right)}$$

$$\text{ie } \boxed{K_P = \frac{Px^2}{1-x^2}}$$



Eg :	$H_2(g)$	+	$I_2(g)$	\rightleftharpoons	$2HI(g)$
Initial conc -	a		b		0
Eqm conc-	a - x		b - x		2x
Total no. of moles = a - x + b - x + 2x = a + b					
active mass -	$\frac{a-x}{v}$		$\frac{b-x}{v}$		$\frac{2x}{v}$
Mole fraction -	$\frac{a-x}{a+b}$		$\frac{b-x}{a+b}$		$\frac{2x}{a+b}$
Partial pressure -	$P \frac{(a-x)}{a+b}$		$P \frac{(b-x)}{a+b}$		$P \frac{(2x)}{a+b}$

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x/v)^2}{(a-x/v)(b-x/v)} = \boxed{\frac{4x^2}{(a-x)(b-x)}}$$

$$K_P = \frac{(P(HI))^2}{(P_{H_2})(P_{I_2})} = \frac{\left(P \frac{2x}{a+b} \right)^2}{\left(P \frac{(a-x)}{a+b} \right) \left(P \frac{(b-x)}{a+b} \right)} = \boxed{\frac{4x^2}{(a-x)(b-x)}}$$

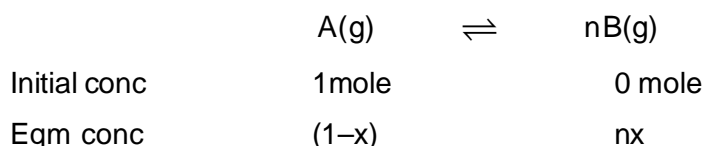
DEGREE OF DISSOCIATION & VAPOUR DENSITY

Vapour density of gas with respect to Hydrogen

$$VD = \frac{\text{molecular mass of A}}{\text{molecular mass of H}_2} = \frac{M_A}{2}$$

∴ VD is mass of 11.2 L gas at STP

Consider the reaction



$$\text{total no. of moles at equilibrium } 1 - x + nx = 1 + x(n-1)$$

$$\text{Let } v \text{ be volume of 1 mole } \therefore v \text{ of } 1 + x(n-1) \text{ moles} = v[1 + x(n-1)]$$

$$\text{Vapour density before dissociation} \rightarrow D = \frac{M}{v} \quad (\text{theoretical})$$

$$\text{Vapour density after dissociation} \rightarrow d = \frac{m}{(1 + x[n-1])v} \quad (\text{observed})$$

$$\frac{D}{d} = 1 + x(n-1)$$

$$\frac{D}{d} - 1 = x(n-1) \quad \left[D = \frac{M}{2} \right]$$

$$x = \frac{D-d}{(n-1)d} \quad x - \text{degree of dissociation}$$

D - V. D before dissociation

d - V.D after dissociation

n : no. of moles of particles obtained from one mole of reactant

◆ LE CHATELIER'S PRINCIPLE

It states that "If a system at equilibrium is disturbed by a change in temperature, pressure or concentration of components, then equilibrium will shift its equilibrium position so as to minimize the effect of that change."

(1) Effect of change in reactant /product concentration

Addition of reactant or removal of product shift equilibrium to right

Removal of reactant or addition of product shift equilibrium to left.

Addition or removal of pure solid /pure liquid not disturb equilibrium because the concentration of

pure solid or pure liquid, remain constant. But concentration of pure gas is not a constant because it change with pressure of gas

(2) Effect of change in pressure or volume

Increase of pressure or decrease of v shift equilibrium to the side which has lesser no. of gaseous moles [decrease of pressure or increase of volume shift equilibrium to side which has more no. of gaseous moles]

Types of reaction	Effect of 'P' or 'V'
(i) $\Delta n = 0$ $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	No effect
(ii) $\Delta n = +\text{ve}$ $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	$\uparrow P$ or $\downarrow V$ shift equilibrium to left (favours backward reaction)
(iii) $\Delta n = -\text{ve}$ $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3$	$\uparrow P$ or $\downarrow V$ shift equilibrium to right (favours forward reaction)

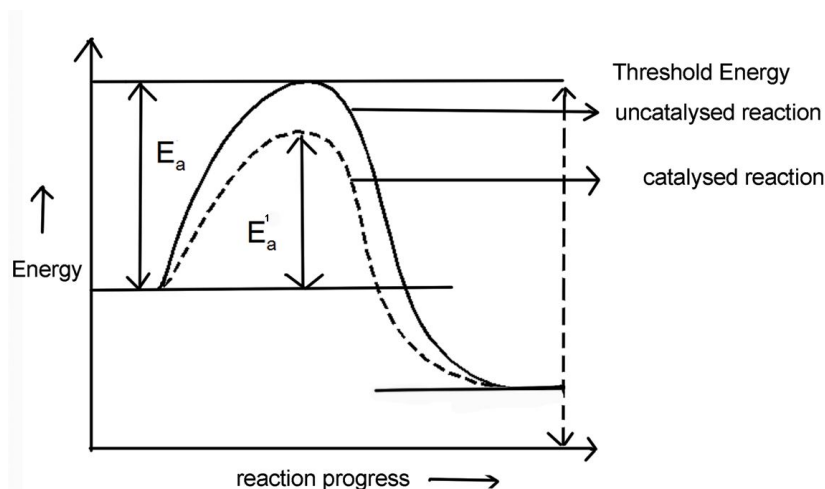
(3) Effect of change of temperature

Increase in temperature shift equilibrium in the direction of endothermic reaction and decreases in temperature shift equilibrium in the direction of exothermic reaction

(4) Effect of Addition of catalyst

The minimum energy required by reactants to undergo a chemical reaction is called threshold energy. The additional energy required by reactant to attain threshold energy is called activation energy. [E_a]

i.e. activation energy $E_a = \text{Threshold energy} - \text{energy of reactants}$. The addition of positive catalyst make available a new lower energy path of conversion of reactants to products. Because the forward & backward reactions pass through same transition state, a catalyst lowers the activation energy for forward & backward reaction by exactly the same amount. As a result the rate of forward & backward reaction increases by same factor. i.e. presence of catalyst fastens the attainment of equilibrium but not affect the forward or backward reaction independently



E_a – Activation energy without catalyst

E_a^1 – Activation energy with catalyst

(5) **Addition of inert gas**

(i) At const. volume

The total pressure of the system is increased but the partial pressure and molar concentration of reactant & product remain unchanged. So equilibrium is not affected if $\Delta n = 0$, +ve or –ve

(ii) At const. pressure

The total volume of equilibrium mixture will increase but the no. of moles per unit volume of reactant & product will decrease. i.e. concentration decreases so equilibrium will shift to side where more no. of moles of gaseous components are present.

Types of reaction	Effect of Addition of inert (g)
(i) $\Delta n = 0$ $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	at const. V } at const. P } no effect
(ii) $\Delta n = +ve$ $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	at const. V – no shift at const. P – equilibrium shift Right
(iii) $\Delta n = -ve$ $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	at const V – no shift at const P – Equilibrium shift Left

Applications

→ In chemical equilibrium with the help of Le Chatelier's principle (LCP), we can predict favourable conditions of concentration temperature & pressure to get better yield of product in some industrial chemical reaction

Reaction	Favourable Condition
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) + 27.8 \text{ kCal}$	Low temperature, high pressure, more NO & O_2 , removal of NO_2
contact process $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 45 \text{ kCal}$	low temperature $\approx 500^\circ\text{C}$, high Pressure more SO_2 & O_2 , removal of SO_3
Habers process $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 23 \text{ kCal}$	low temperature (500°C), high pressure (200 atm), more N_2 & $3H_2$, isolation of NH_3
Birkeland Eyde process $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43 \text{ kCal}$	High temp, pressure low, more N_2 , O_2 , removal of NO
Bosch process $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) + x \text{ kCal}$	low temperature, pressure has no role, more CO & H_2O , removal of CO_2 & H_2
$N_2O_4(g) \rightleftharpoons 2NO_2(g) - 14 \text{ kCal}$	High temp., low pressure, more N_2O_4 , removal of NO_2

- In physical equilibrium

→ melting of ice ($\text{ice(s)} \rightleftharpoons \text{H}_2\text{O(l)}$)

at 0° C ice and water are present and are in a state of equilibrium. Melting of ice is an endothermic process so it favours high temperature. When pressure increase, volume should decrease according to LCP. ∴ equilibrium will shift to R. in this case because v of fixed mass of water is less than that of ice [Hence ice is less denser than water]

∴ favourable condition; temperature increase & pressure increase

→ Evaporation of water ($\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)} - 40.6\text{kJ}$)

Evaporation of water is endothermic. So favours increase of temperature ; the liquid state have less pressure compared to molecules of vapour state. ∴ increase of pressure favours evaporation.

→ Dissolution of solid in H_2O

Solids and liquids are highly incompressible so pressure has no role in solubility of solid in liquid.

★ If dissolution is exothermic, then it favours increase of temperature

Eg : NaCl, KCl, NH_4Cl , KI, AgNO_3 etc

★ If dissolution is endothermic, then it favours decrease of temperature

Eg: NaOH, Na_2CO_3 , Li_2CO_3 , Li_2SO_4 etc.

→ Dissolution of gas in water

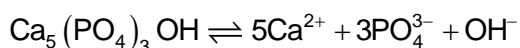
Dissolution of gas in liquid is an exothermic process so it favours decrease of temperature according to Henry's law solubility of gas in liquid is 'α' to pressure of gas

- Day to day application

→ Clothes dry quicker in windy day - when wet clothes are spread on stand water evaporates & surrounding air gets saturated and this delay the process of drying. On windy day when breeze blows nearby wet air is replaced by dry air which helps the process of evaporation to fasten.

→ We sweat more on humid day - on humid day air is already saturated with water vapour. ∴ sweat from body does not evaporate resulting in greater sweating.

→ Decaying of teeth by sweets - our teeth are coated with insoluble enamel $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Sugar present in sweets slowly get fermented to produce H^+ ions which combines with OH^- ions to form H_2O . ∴ equilibrium get shifted to right which means enamel from teeth will slowly get removed. As a result decaying occurs.



♦ IONIC EQUILIBRIUM

Electrolytes

The substance which conduct electricity in molten state or aqueous solution

Strong electrolytes

Which undergoes complete ionisation

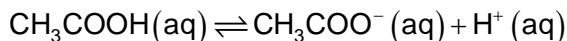
Eg : HCl, HNO_3 , H_2SO_4 , KOH, NaOH, KCl, NaCl

Weak electrolytes

Which undergoes partial ionisation

Eg: HCOOH (formic acid), H₂CO₃ (carbonic acid), CH₃COOH (acetic acid), ammonium hydroxide, aluminium hydroxide.

The equilibrium involving ions of weak electrolytes in aq. solution is called ionic equilibrium

**ACID BASE CONCEPT**

Mainly there are 3 acid base concepts

- i) Arrhenius concept
- ii) Lowry Bronsted concept
- iii) Lewis concept

(1) Arrhenius concept

- ★ Acids are H containing compounds which on hydrolysis gives free H⁺ ions

Eg : HCl, HNO₃, H₂SO₄, CH₃COOH, HCOOH, H₂CO₃, H₃PO₄, HClO₄

- ★ Bases are OH containing compound which gives free OH⁻ ions on dissolving in water.

Eg: NaOH, KOH, Ca(OH)₂, Mg(OH)₂, Al(OH)₃, NH₄OH

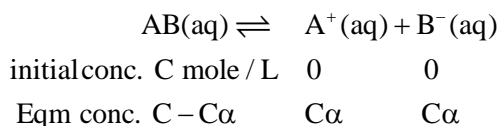
Limitations

- Applicable only in aqueous medium
- Not explained the acidic character of CO₂, SO₂, SO₃ etc and basic character of NH₃
- Nature of H⁺ ions :

According to this concept an acid gives H⁺ ions in water but due to its small size & strong +ve charge it does not exist independently. It combine with a molecule of H₂O to form H₃O⁺

OSTWALD'S DILUTION LAW FOR WEAK ELECTROLYTES

Consider dissociation of weak electrolyte AB. Let C mol/L be the initial molar concentration and let α be degree of dissociation 1 mole.



$$K = \frac{C\alpha \cdot C\alpha}{C - C\alpha} = \frac{C^2\alpha^2}{C - C\alpha}$$

for weak electrolytes α is very very low

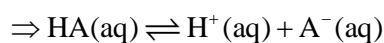
$$K = \frac{C^2\alpha^2}{C - 0} = \frac{C^2\alpha^2}{C} = C\alpha^2$$

$$\alpha = \sqrt{\frac{K}{C}}$$

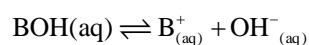
$$\text{for an acid} \quad \alpha = \sqrt{\frac{K_a}{C}}$$

dissociation constants of acid and base respectively which represent their strength

$$\text{for a base} \quad \alpha = \sqrt{\frac{K_b}{C}}$$



$$\alpha = \sqrt{\frac{K_a}{C}}$$



$$\alpha = \sqrt{\frac{K_b}{C}}$$

$$\text{p}K_a = -\log K_a; \text{p}K_b = -\log K_b$$

As K_a and K_b increases strength of acids base also increases but as $\text{p}K_a$ & $\text{p}K_b$ increases strength decreases

◆ COMPARISON OF STRENGTH OF ACID AND BASES

Degree of dissociation of an acid (α) is its proton releasing tendency. So it represents strength of an acid.

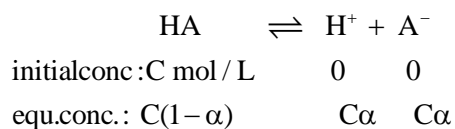
$$\alpha = \sqrt{\frac{K_a}{C}}$$

For 2 acids having same concentration.

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} = \frac{\text{strength of acid 1}}{\text{strength of acid 2}}$$

$$\text{like that } \frac{\text{strength of base 1}}{\text{strength of base 2}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

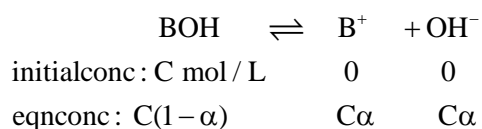
- H⁺ ion concentration of weak acid**



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

$$[\text{H}^+] = C\sqrt{\frac{K_a}{C}} \quad \boxed{[\text{H}^+] = \sqrt{K_a \cdot C}}$$

- OH⁻ ion Concentration of weak base**



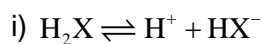
$$[\text{OH}^-] = C\alpha \quad \alpha = \sqrt{\frac{K_b}{C}}$$

$$[\text{OH}^-] = C\sqrt{\frac{K_b}{C}} \quad \boxed{[\text{OH}^-] = \sqrt{K_b \cdot C}}$$

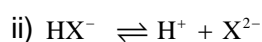
- ◆ DISSOCIATION OF POLYACIDIC BASE & POLYBASIC ACID**

Polybasic acid and poly acidic base dissociates in more than 1 steps

Eg: A dibasic acid $\text{H}_2\text{X}(\text{H}_2\text{S})$ dissociates as



$$K_{a_1} = \frac{[\text{H}^+][\text{HX}^-]}{[\text{H}_2\text{X}]}$$

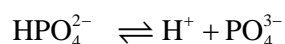
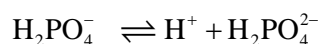
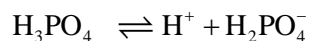


$$K_{a_2} = \frac{[\text{H}^+][\text{X}^{2-}]}{[\text{HX}^-]}$$

Releasing an H^+ ion from an anion is difficult compared to neutral molecule. \therefore 2nd step always occur to a lower extent than 1st step.

\therefore For dibasic / diprotic acid $K_{a_1} > K_{a_2}$

Similarly for triprotic acid like H_3PO_4 $K_{a_1} > K_{a_2} > K_{a_3}$

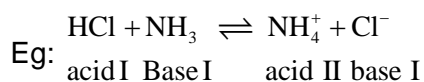


Similarly for diacidic bases $K_{b_1} > K_{b_2}$ and for triacidic bases $K_{b_1} > K_{b_2} > K_{b_3}$

2) Lowry Bronsted Concept

Acid : Substance which have tendency to donate proton.

Base: Substance which have tendency to accept proton.



Advantages

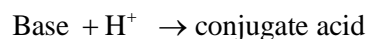
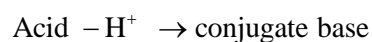
- A substance can act as an acid and as a base even in the absence of water.
- Not limited to molecules, even ions can act as a base and acid
- Explained basic character of Ammonia.

Limitations

- Failed to explain acidic characters of SO_2 , SO_3 , CO_2 , BF_3 , $AlCl_3$ etc.
- Didnot explained reaction between an acid and a base where no proton exchange takesplace.

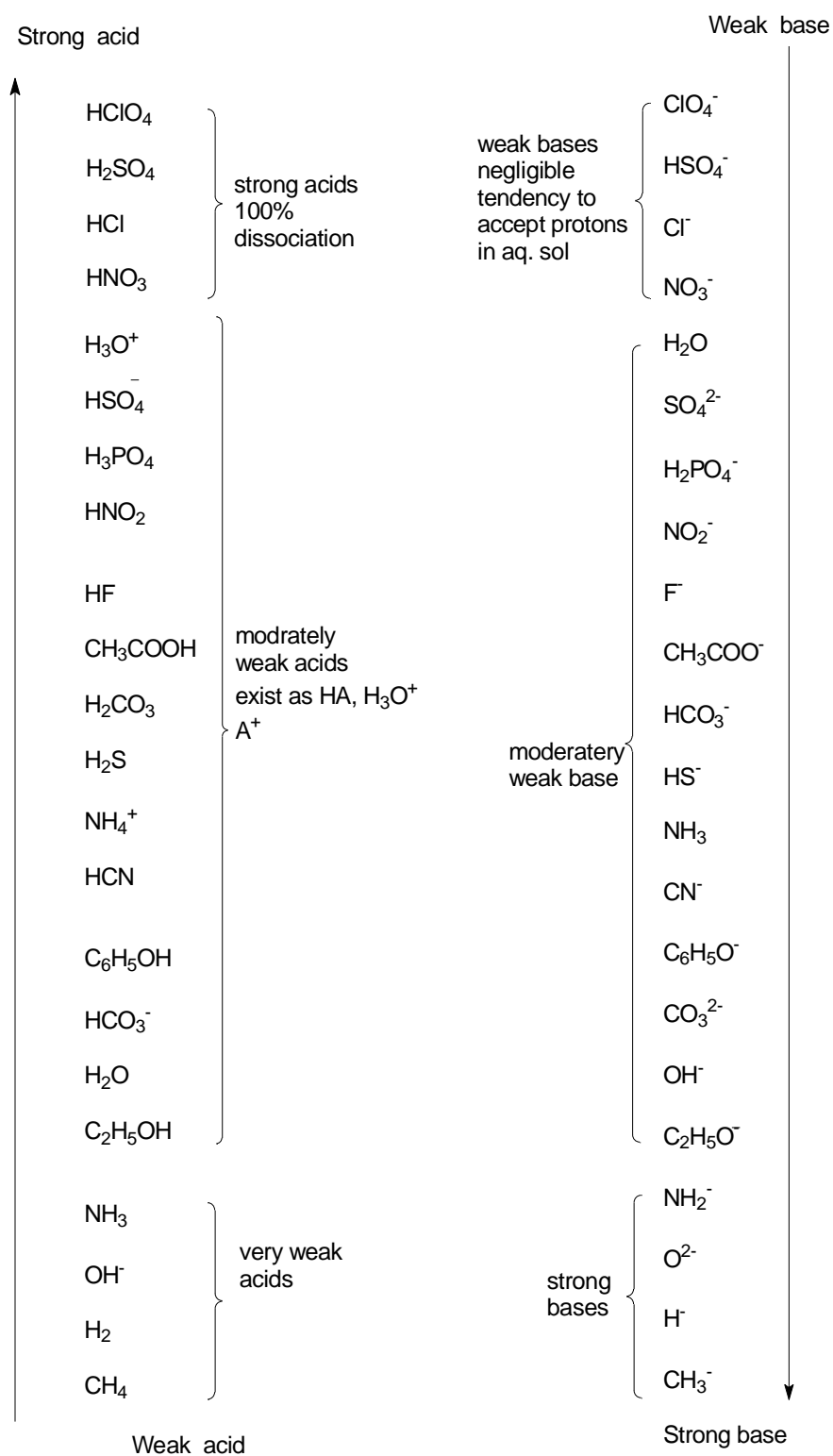
Conjugate Acids and Bases

For every acid there a corresponding base known as conjugate base and for every base there is a corresponding acid known as conjugate acid. They always occurs as conjugated pairs.



Strong acids conjugate base is weaker and weak acids conjugate base is stronger. It is same in case of base also.

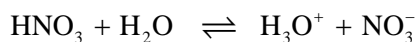
◆ **Relative Strength of Conjugate acid base pair**



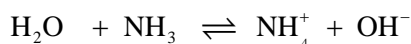
- Amphoteric species**

According to Lowry bronsted concept, species which can act as acid as well as base is called amphoteric species.

Eg: H_2O



acid base



acid base

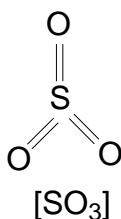
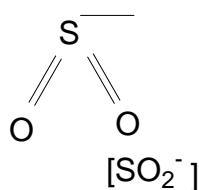
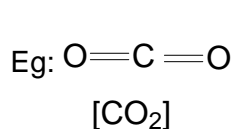
- Some substances can act as conjugate acid and conjugate base**

Conjugate Base	Species	Conjugate acid
OH^-	H_2O	H_3O^+
NH_2^-	$\xrightleftharpoons[+\text{H}^+]{-\text{H}^+} \text{NH}_3 \xrightleftharpoons[-\text{H}^+]{+\text{H}^+} \text{NH}_4^+$	NH_4^+
CO_3^{2-}	HCO_3^-	H_2CO_3
SO_4^{2-}	HSO_4^-	H_2SO_4

3) Lewis Concept

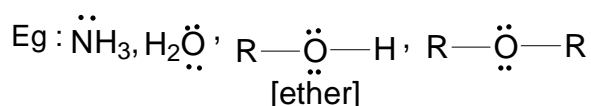
Acid is a substance (molecule / ion) which can accept a pair of electrons, While base is a molecule / ion which can donate a pair of electron during covalent bonding. Types of Lewis Acids:

- Molecules in which central atom has incomplete octet. Eg: BF_3 , AlCl_3 etc.
- Simple cations. Eg: H^+ , Ag^+ (Small) – Strong acid. Na^+ , Ca^{2+} (Big) - Weak acid
- Molecules in which central atom has vacant orbitals. Eg: SiCl_4 , SnCl_4 , SnCl_2 , SF_4 , PF_4 , CCl_4 is not a lewis acid due to absence of vacant d orbitals.
- Molecules in which atoms of different electro negativity are linked by multiple bonds.



- **TYPES OF LEWIS BASE:**

- i) Negatively charged ions.
Eg: F^- , Cl^- , OH^- , CN^- etc.
- ii) Neutral molecules with atleast one ℓ_p pair of electrons which they can donate easily.



- iii) Multiple bonded compounds which can donate the lp of electrons
eg: CO, NO etc

Limitaions

- failed to explain acidic character of common acids like HCl , HNO_3 , H_2SO_4 etc.
- When Lewis acid and Lewis base react, coordinate bond is formed. Coordinate bonds are formed slowly but acid base reactions are quite fast.

lewis acids \rightarrow electrophiles

lewis bases \rightarrow Neutrophiles

“Bronsted Acids are Arrhenius acids

Bronsted bases are lewis bases"

- **Factors affecting strength of Lewis acids**

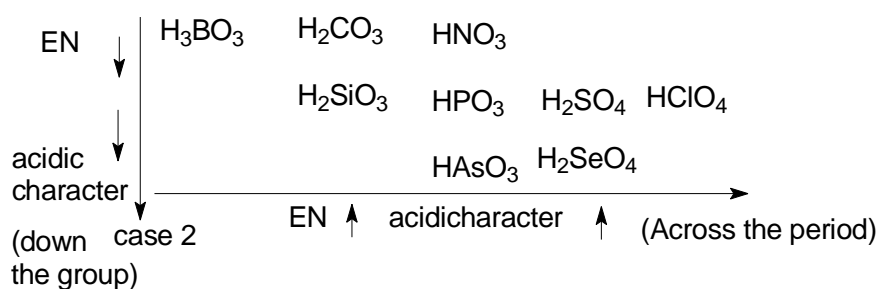
- Nuclear charge on central atom. Greater the charge increase acidic strength.
- No. of E.N atom attached to central atom. eg: SO_3 stronger than SO_2
- No. of +ve charges on central atom of Sn^{4+} stronger than Sn^{2+} .
- When charge same acidic strength depends on lower atomic raddi. eg: $\text{Li}^+ > \text{Ne}^+ > \text{Cl}^-$

- **Strength of Acid**

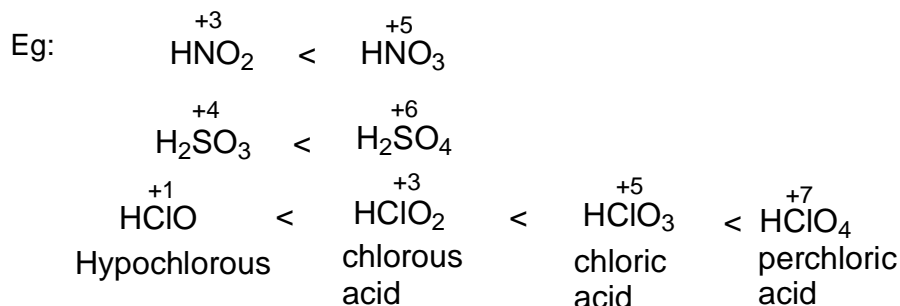
- i) **OXOACIDS** are compound in which central atom has at least one double bond with oxygen and one bond with OH group.

Case 1

When non metals are different, acidic character directly proportional to EN of non metals.



- When non metals are similar acidic character is directly proportional to oxidation No.



ii) HYDRIDES

Size ↑	B ₂ H ₆	CH ₄	NH ₃	H ₂ O	HF
		SiH ₄	PH ₃	H ₂ S	HCl
acidic character ↑		GeH ₄	AsH ₃	H ₂ Se	HBr
		SnH ₄	SbH ₃	H ₂ Te	HI
(Down the group) ↓		PbH ₄	BH ₃		
	EN ↑	Acidic character ↑			(Across the period)

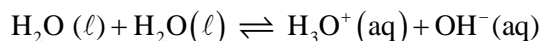
STRENGTH OF BASE

In case of Hydroxides

			1	
Basic character		\propto	$\frac{1}{\text{electronegativity of metal}}$	
Down the group ↓	LiOH	Be (OH) ₂	B(OH) ₃	
EN ↓	NaOH	Mg(OH) ₂	Al(OH) ₃	
	KOH	Ca(OH) ₂	Ga(OH) ₃	
basic character ↑	RbOH	Sr (OH) ₂	In (OH) ₃	
	CsOH	Ba (OH) ₂	Tl (OH) ₃	
	EN ↑	basic character ↓		(Across the period)

• IONIC PRODUCT OF WATER

Pure water is a weak electrolyte and it undergoes self ionisation to small extent



$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]} \quad K[\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-]$$

= K_w ; ionic product of H_2O

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

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

K_w varies with temperature . At 25°C or 298 K ; For acidic, basic and neutral solutions.

$$K_w = 1 \times 10^{-14} \text{ mol}^2\text{L}^{-2}$$

@ all temp for neutral sol, $[\text{H}^+] = [\text{OH}^-]$

$$\text{ie } [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol}^1\text{L}^{-1}$$

$$\text{for acid solution } [\text{H}^+] > [\text{OH}^-]$$

$$\text{for basic solution } [\text{H}^+] < [\text{OH}^-]$$

• Effect of Temp on K_w

Value of K_w increase with increase in temperature because ionisation of water increase with rise in temperature.

$$\text{p}K_w = -\log K_w$$

As temperature increase K_w increases but $\text{p}K_w$ decreases

Eg: 25°C or 298 K ,

$$K_w = 1 \times 10^{-14} \text{ mol}^2\text{L}^{-2}$$

$$\text{p}K_w = -\log K_w = -\log 10^{-14} = -(-14 \log 10) = 14$$

At 90°C ; $K_w = 1 \times 10^{-12} \text{ mol}^2\text{L}^{-2}$

$$\text{p}K_w = -\log K_w = -\log 10^{-12} = -(-12 \log 10) = 12$$

• pH SCALE

Introduced by German chemist Sorensen

Used to find out where their given substance is acid base or neutral.

pH stand for 'potenz de Hydrogen' i.e. potential of H.

@ 298 K scale varies from 0 – 14

0-7 : acid 7 : Neutral 7 - 14 : base

pH of solution is defined as negative logarithm of H_3O^+ concentration.

$$\text{ie } \text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{ie } \text{pH} = -\log[\text{H}^+]$$

$$\text{Also } \text{pOH} = -\log[\text{OH}^-]$$

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

taking log on both sides

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

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

$$\text{Multiply with } -1, -\log[\text{H}^+] + -\log[\text{OH}^-] = -\log K_w$$

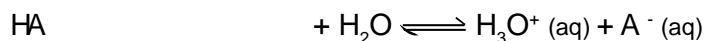
$$\boxed{\text{pH} + \text{pOH} = \text{p}K_w}$$

TEMPERATURE & pH

As temperature increases H^+ ion concentration increases, pH decrease but water never becomes acidic / basic with variation of temperature because in case of neutral solution @ all temperature $[\text{H}^+] = [\text{OH}^-]$

RELATION BETWEEN K_a & K_b FOR AN ACID & ITS CONJUGATE. BASE

A weak acid HA ionises in aq. solution as



weak acid

conjugate base

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad (1)$$



$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \quad (2)$$

$$(1) \times (2) \quad K_a \times K_b = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

Taking - log on both sides

$$-\log K_a + -\log K_b = -\log K_w$$

$$\boxed{\text{p}K_a + \text{p}K_b = \text{p}K_w}$$

pH CALCULATION OF MIXTURE OF SOLUTION

→ According to volumetry

$$M_1 V_1 + M_2 V_2 = M_3 V_3$$

$$N_1 V_1 + N_2 V_2 = N_3 V_3$$

$$N_3 = \frac{N_1 V_1 + N_2 V_2}{V_3}$$

→ This is the base equation for calculation of pH of mixture of strong acid and strong base

If the given concentration is molarity then convert to normality. For monobasic acid and monoacidic base normality = molarity

for poly basic acids & poly acidic base

normality = molarity \times n factor (n acidity / Basicity)

(i) Mixture of 2 strong acids $[H^+]_f = \frac{[H^+]V_1 + [H^+]V_2}{V_1 + V_2}$

(ii) Mixture of 2 strong bases

$$[OH^-]_f = \frac{[OH^-]V_1 + [OH^-]V_2}{V_1 + V_2}$$

$$\left[[H^+]_f = \frac{K_w}{[OH^-]_f} \right]$$

(iii) Mixture of strong acids & strong bases

Case I : If $[H^+]_A V_A > [OH^-]_B V_B$

$$[H^+]_f = \frac{[H^+]_A V_A - [OH^-]_B V_B}{V_A + V_B}$$

Case II : $[H^+]_A V_A < [OH^-]_B V_B$

$$[OH^-]_f = \frac{[OH^-]_B V_B - [H^+]_A V_A}{V_A + V_B}$$

(iv) mixture of 2 weak acid $= \sqrt{K_{a1}C_1 + K_{a2}C_2}$

(v) mixture of Strong acid & weak acid

$$[H^+] = \frac{C_2 + \sqrt{C_2^2 + 4KaC_1}}{2}$$

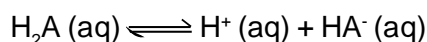
C_1 : Concentration of weak acid

C_2 : Concentration of strong acid

Ka : dissociation concentration of weak acid

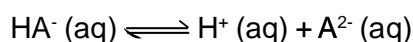
pH OF AMPHOTERIC SPECIES

Consider dissociation of H_2A



HA^- is amphoteric

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} \text{----- (1)}$$



$$K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]} \text{----- (2)}$$

$$\Rightarrow [HA^-] = \frac{[H^+][A^{2-}]}{K_{a2}} \text{----- (2)}$$

Substituting (3) in (1),

$$K_{a1} = \frac{[H^+]^2[A^{2-}]}{K_{a2}[H_2A]}$$

$$K_{a1} \cdot K_{a2} = \frac{[H^+][A^{2-}]}{[H_2A]}$$

on complete dissociation if $[H_2A] = [A^{2-}]$

$$K_{a1} \cdot K_{a2} = [H^+]^2$$

$$[H^+] = (K_{a1} \cdot K_{a2})^{1/2}$$

$$pH = -\log [H^+] = -\log (K_{a1} \cdot K_{a2})^{1/2}$$

$$pH = \frac{1}{2} [-\log K_{a1} + -\log K_{a2}]$$

$$pH = \frac{1}{2} [pK_{a1} + pK_{a2}]$$

ISOHYDRIC SOLUTIONS

If concentration of common ions in the solution of 2 electrolytes is same [eg : $[OH^-]$ in $Ca(OH)_2$ & $Ba(OH)_2$ solution. Then on mixing them there is no change in degree of dissociation of either of electrolytes. Such solution are called Isohydric solutions.

Levelling effect of water

HCl , HNO_3 , H_2SO_4 , $HClO_4$ etc when dissolved in water, they dissociate almost completely and they behave as equally strong in water. ie in aq solution all acids stronger than H_3O^+ appear equally strong.

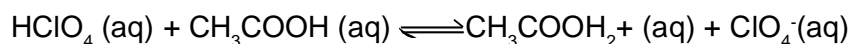
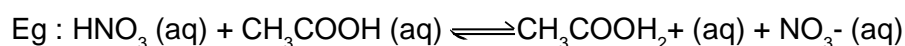
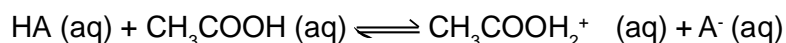
Similarly a number of strong bases behave as equally strong in water.

This is called “Levelling effect of water” because solvent water levels them to the same strength.

∴ to compare relative strength of strong acid or strong base, solvent selected should be such that it ionises acids & bases to different extents. Such a solvent is called “differentiating solvent”.

Eg : acetic acid

Its a poor proton acceptor so it accepts protons to different extents and an equilibrium exist as



Their equilibrium constants can be determined, hence relative strength can be found.

Classification of solvents

- i) PROTOPHILIC : tendency to accept protons Eg : H_2O , NH_3 (l), CH_3OH
 - ii) PROTOGENIC : tendency to give protons Eg : H_2O , NH_3 (l), CH_3COOH , HCl
 - iii) AMPHIPROTIC : act as protophilic & protogenic Eg : H_2O , NH_3
 - iv) APROTIC : Neither donate or accept protons Eg : Benzene
1. What is the pH of aq sol of 10^{-8} M HCl @ 298K ?

A) 8

B) 7.1

C) 6.9

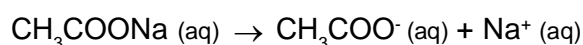
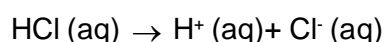
D) 7

If $[\text{H}^+]$ of strong acid is greater than 10^{-6} neglect $[\text{H}^+]$ of water but if $[\text{H}^+]$ from strong acid $< 10^{-6}$ then consider $[\text{H}^+]$ from water also

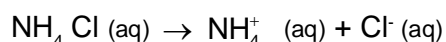
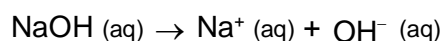
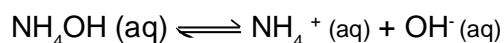
COMMON ION EFFECT

It is suppression of dissociation weak electrolyte by the addition of strong electrolyte having common ion with it

Eg : dissociation of acetic acid can be suppressed by the addition of HCl or sodium acetate



Eg : dissociation of ammonium hydroxide can be suppressed by the addition of NaOH or NH_4Cl



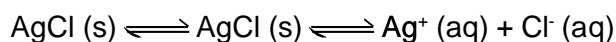
SOLUBILITY

- Amount of substance that can be dissolved in a specified amount of solvent @ particular temperature or it is the no. of moles of solute that can be saturate one litre of solution.
- Substance with solubility less than 1g but more than 0.001 g / 100 ml solution is called sparingly soluble substances.

→ **Solubility product (K_{sp})**

The product of ionic concentration of a saturated solution of sparingly soluble salt is a constant at a particular temperature. This is called solubility product. It varies with temperature.

consider solubility of AgCl in water



undissolved dissolved

$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]} \quad K [\text{AgCl}] = K_{sp}$$

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

K_{sp} is applicable only to saturated solution whereas ionic product is applicable to saturated / unsaturated / supersaturated solution.

Ionic product < K_{sp} : Unsaturated solution

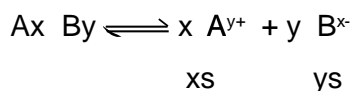
Ionic product = K_{sp} : Saturated solution

Ionic product > K_{sp} : Supersaturated solution

At a particular temperature K_{sp} of solid is constant in different solvent / solution but individual solubility varies.

GENERAL EQUATION FOR K_{sp}

Consider the dissociation of electrolyte 'Ax By' and let 's' be the solubility.

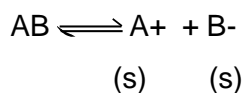


$$K_{sp} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$$

$$= [x s]^x [y s]^y = x^x y^y s^{x+y}$$

$$s = \left(\frac{K_{sp}}{x^x y^y} \right)^{\frac{1}{x+y}}$$

K_{sp} of Binary Electrolyte (AB) [AgCl, PbSO₄, CaCO₃, BaSO₄]



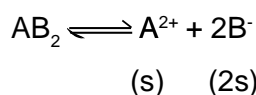
$$K_{sp} = [\text{A}^+][\text{B}^-] = s^2$$

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

$$s = \sqrt{K_{sp}}$$

$$s = (K_{sp})^{1/2}$$

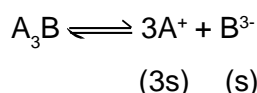
K_{sp} of Tertiary electrolyte (Ag₂SO₄, PbI₂ etc)



$$K_{sp} = [A^{2+}] [B^-]^2 = s \times (2s)^2 = 4s^3$$

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

K_{sp} of quarternary electrolyte (AB₃/A₃B) [FeCl₃, Na₃PO₄]



$$K_{sp} = (3s)^3 \times s = 27 s^4$$

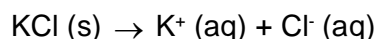
$$s = \left(\frac{K_{sp}}{27} \right)^{1/4}$$

Common Ion effect in solubility

The common ion present in the solution decrease solubility of given compound.

Eg : Consider saturated solution of AgCl

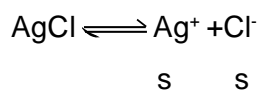
If a salt having either of the common ion [Ag⁺ /Cl⁻] say KCl then,



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

[Cl⁻] in solution increase due to presence of KCl and thus to keep K_{sp} as a constant [Ag⁺] will decrease i.e AgCl will precipitate out from solution i.e solubility of AgCl will decrease with increase in concentration of KCl in solution.

Q : let solubility of AgCl in water is 2×10^{-5} mol/L. What is solubility of it in 0.1M KCl ?

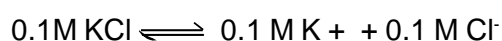


$$K_{sp} = [Ag^+][Cl^-] = s^2$$

$$\text{Here } s = (K_{sp})^{1/2}$$

$$\text{Given } s = 2 \times 10^{-5}$$

$$\therefore K_{sp} = (2 \times 10^{-5})^2 = 4 \times 10^{-10}$$



$$\text{new concentration of } Cl^- = \frac{2 \times 10^{-5} + 0.1}{(\text{negligible})} \approx 0.1$$

\therefore T is constant K_{sp} is constant

After addition $\Rightarrow K_{sp} = [Ag^+][Cl^-]$

$$4 \times 10^{-10} = [Ag^+][Cl^-]$$

$$= [Ag^+] 0.1$$

new

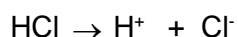
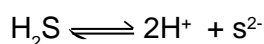
$$[Ag^+] = 4 \times 10^{-9}$$

i.e. s decrease

APPLICATIONS OF COMMON ION EFFECT AND SOLUBILITY PRODUCT

- i) Application in qualitative analysis
- a) Addition of HCl in group 2 analysis of cations

(depends on the reaction with group reagents the cations are classified into different groups)
The group 2 cations are Hg^{2+} , Pb^{2+} , Br^{3+} , Cu^{2+} , Sn^{2+} , As^{3+} , Cd^{2+} . These are precipitated as their coloured sulphides by passing H_2S gas in aqueous mixture solution. But before passing the gas, the solution must be acidified with dilute HCl



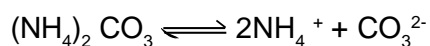
Strong acid HCl suppresses the ionisation of weak acid H_2S and keeps sulphide ion concentration at lower level. This is to prevent precipitation of group 4 cation (Mn^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+}) as their sulphides. Thus only the ionic product of group 2 radicals exceeds their solubility product and get precipitated.

- b) Addition of NH_4Cl in group 3 analysis of cations

$[Fe^{3+}, Al^{3+}, Cr^{3+}]$ group reagents are NH_4Cl and NH_4OH . The cations are precipitated as their hydroxides. Strong electrolyte NH_4Cl suppresses the ionisation of weak electrolyte NH_4OH and keeps concentration of OH^- ion at lower level. Thus ionic product of hydroxides of group 3 radicals exceeds corresponding solubility product and get precipitated, while hydroxides of group 4 cations will remain in solution if present. Since their K_{sp} values are higher and ionic product is less than their K_{sp} value.

- c. Addition of NH_4Cl in group 5 analysis

$[Ba^{2+}, Ca^{+2}, Sr^{+2}]$ cations of group 5 are precipitated as their carbonates by addition of saturated solution of $(NH_4)_2CO_3$. This is done in presence of NH_4Cl which suppresses or decreases the concentration of CO_3^{2-} ion and prevents precipitation of group 6 cations (Mg^{2+})



NOTE

Group 0 cations - NH_4^+ , K^+ , Na^+

Group 1 cations - Ag^+ , Hg_2^{2+}

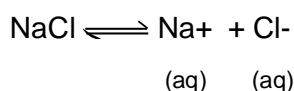
[dissolved in dilute HCl and precipitated as chlorides]

ii) Preparation of NaHCO_3 by solway process

Precipitation of NaHCO_3 from its saturated solution is done by the addition of NH_4HCO_3 [HCO_3^- are common ion]

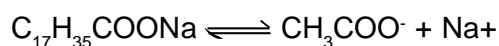
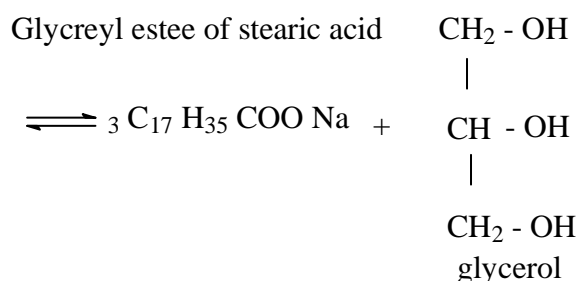
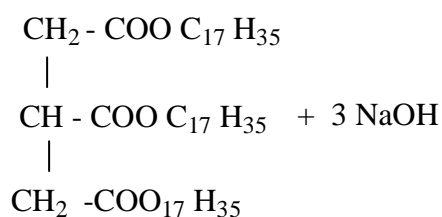
iii) In Purification of common salt

In a saturated solution of NaCl & impurities, by passing HCl gas through it increase $[\text{Cl}^-]$ concentration which shift equilibrium to left and causes precipitation of NaCl



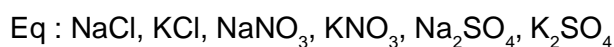
iv) Salting out of soap

Glycerol ester of higher fatty acids like stearic acid, palmitic acid, oleic acid etc on alkaline hydrolysis gives soap and glycerol [saponification]. Soap and glycerol are in colloidal form. From this soap can be precipitated by addition of calculated amount of NaCl to saturated solution. This process is called salting out of soap.

**SALT**

A substance which ionises in water to produce ions other than H^+ and OH^- is called a salt. Salts are produced by neutralisation reaction. There are 4 types of salt:

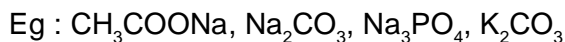
i) Salt of strong acid & strong base



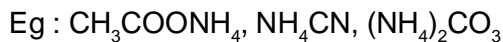
ii) Salt of Strong acid and weak base



iii) Salt of weak acid and strong base



iv) Salt of weak acid and weak base



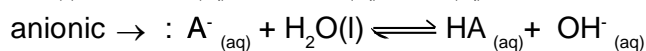
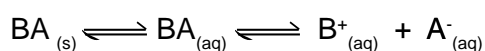
If the acids and bases are mixed in equal amounts it will lead to salt hydrolysis. If acids and bases are mixed in different equivalence or amounts it will lead to formation of buffer solution.

SALT HYDROLYSIS

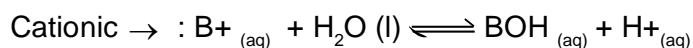
Reverse of neutralisation



The salt can be acidic /basic / neutral \rightarrow if salt is BA then



hydrolysis

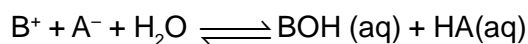


hydrolysis

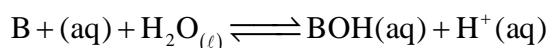
Salt of strong acid and strong base donot undergo hydrolysis because possible product of hydrolysis are strong electrolytes and themselves get fully ionised and pH of solution is 7.

Hydrolysis of salt of SA and WB

The salt is acidic in nature due to more H^+ ion. Let BA is the salt, HA strong acid and BOH, weak base.

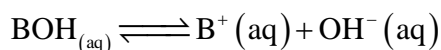


Only B^+ ion is hydrolysed so it is known as cationic hydrolysis



Hydrolysis const. $K_h = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+]}$ (1)

Weak base BOH undergoes further dissociation



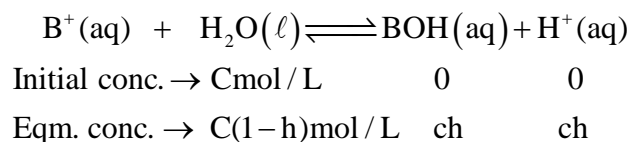
Dissociation constant. $K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]}$ (2)

Ionic product of H_2O , $K_w = [\text{H}^+][\text{OH}^-]$ (3)

$(1) \times (2) \div (3) = \frac{K_h \times K_b}{K_w} = 1$

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

Let h be the degree of dissociation



$$K_h = \frac{[BOH][H^+]}{[B^+]} = \frac{ch \cdot ch}{c(1-h)} = \frac{c^2 h^2}{c(1-h)} \quad (1-h \approx 1)$$

$$K_h = ch^2 \quad h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_b \cdot c}} \text{ from eq.(4)}$$

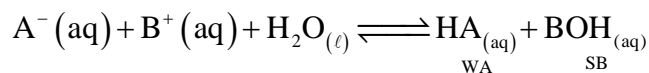
$$[H^+] = ch = c \cdot \sqrt{\frac{K_w}{K_b \cdot c}} = \sqrt{\frac{K_w \cdot c}{K_b}} = \left(\frac{K_w \cdot c}{K_b} \right)^{1/2}$$

$$\begin{aligned} pH &= -\log [H^+] = -\log \left(\frac{K_w \cdot c}{K_b} \right)^{1/2} \\ &= \frac{1}{2} \times -[\log K_w + \log C - \log K_b] \\ &= \frac{1}{2} \times [-\log K_w - \log C - (-\log K_b)] \end{aligned}$$

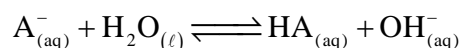
$$\boxed{pH = \frac{1}{2} [pK_w - \log c - pK_b]}$$

Hydrolysis of salt of SB and WA

Let BA be the salt. HA is WA and BOH is SB

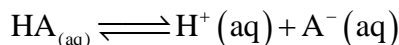


After hydrolysis BOH will again get hydrolysed with B⁺ and OH⁻ ion thus only A⁻ ions are hydrolysed to give weak acid HA and OH⁻ ions. This is known as anionic hydrolysis.



$$K_h = \frac{[HA][OH^-]}{[A^-]} \dots\dots\dots(1)$$

Weak acid HA dissociates as

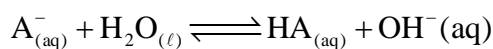


$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \dots\dots\dots(2)$$

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

$$(1) \times (2) / 3 = \frac{K_h \cdot K_a}{K_w} = 1$$

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



Initial	c	1	0	0
---------	---	---	---	---

Eqm	c(1-h)	1	ch	ch
-----	--------	---	----	----

$$K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{c^2 h^2}{c(1-h)} = \frac{ch^2}{1-h}$$

$$K_h = ch^2 \quad (\because 1-h=1)$$

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_a c}} \quad \text{from 4}$$

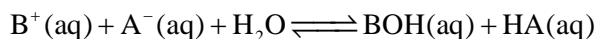
$$\text{pH} = -\log[\text{H}^+] = -\log\left[\frac{K_w K_a}{c}\right]^{1/2}$$

$$\begin{aligned} \text{pH} &= \frac{1}{2} \times -[\log K_w + \log K_a - \log C] \\ &= \frac{1}{2} [-\log K_w + (-\log K_a) + \log C] \end{aligned}$$

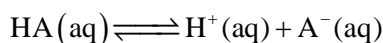
$$\boxed{\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]}$$

Hydrolysis of WA and WB

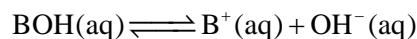
Let BA be the salt, HA be WA, BOH be WB. Both A⁻ and B⁺ ion will get hydrolysed because neither of HA and BOH are completely ionisable. ie both anionic and cationic hydrolysis occurs. Nature of salt will be acidic /basic/neutral depending on H⁺ and OH⁻



$$K_h = \frac{[\text{BOH}][\text{HA}]}{[\text{B}^+][\text{A}^-]} \dots\dots\dots(1)$$



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \dots\dots\dots(2)$$

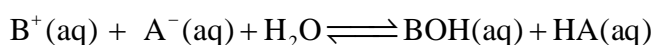


$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} \dots\dots\dots(3)$$

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

$$\frac{(1)(2)(3)}{(4)} = \frac{K_h \times K_a \times K_b}{K_w} = 1$$

$$K_h = \frac{K_w}{K_a K_b}$$



Initial	c	1	0	0
Eqm	c(1-h)	c(1-h)	ch	ch

$$K_h = \frac{[\text{BOH}][\text{HA}]}{[\text{B}^+][\text{A}^-]} = \frac{ch \cdot ch}{c(1-h)c(1-h)}$$

$$K_h = h^2 (\because 1-h=1)$$

$$h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a K_b}} \dots\dots\dots(6)$$

$$\text{From (2), } [\text{H}^+] = \frac{K_a [\text{HA}]}{[\text{A}^-]} = \frac{K_a \cdot ch}{c(1-h)} (\because 1-h=1)$$

$$\text{From (6), } [\text{H}^+] = K_a \sqrt{\frac{K_w}{K_a \cdot K_b}}$$

$$[\text{H}^+] = \left(\frac{K_w \cdot K_a}{K_b} \right)^{1/2}$$

$$\text{pH} = -\log \text{H}^+ = -\log \left(\frac{K_w K_a}{K_b} \right)^{1/2} = \frac{1}{2} [-\log K_w + (-\log K_a) - (-\log K_b)]$$

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

Type of salt	Nature of solutions	Example	Type of Hydrolysis	K_h	h	$[H^+]$	pH
SA + SB	Neutral	NaCl, KCl, NaNO ₃ , KNO ₃ , Na ₂ SO ₄ , K ₂ SO ₄	No hydrolysis	—	—	$[H^+] = 10^{-7}$ at 298 K	pH = 7 @ 298 K
SA + WB	Acidic due to more $[H^+]$	NH ₄ Cl, (NH ₄) ₂ SO ₄ , NH ₄ NO ₃	Cationic hydrolysis	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_h}{c}}$ $= \sqrt{\frac{K_w}{K_b \cdot c}}$	$[H^+] = ch$ $= \sqrt{\frac{K_w \cdot c}{K_b}}$	$pH = \frac{1}{2}$ $[pK_w - pK_b - \log C]$
WB + SB	Basic due to more $[OH^-]$	CH ₃ COONa, Na ₂ CO ₃ , K ₂ CO ₃	Anionic hydrolysis	$K_h = \frac{K_w}{K_a \cdot K_f}$	$h = \sqrt{\frac{K_h}{c}}$ $= \sqrt{\frac{K_w}{K_a \cdot c}}$	$[H^+] = \sqrt{\frac{K_w K_a}{c}}$ $[OH^-] = ch$	$pH = \frac{1}{2}$ $[pK_w + pK_a + \log C]$
WA + WB	Acidic/Basic/Neutral depending on $[H^+]$ and $[OH^-]$	CH ₃ COONH ₄ , NH ₄ CN, (NH ₄) ₂ CO ₃	Both Anionic and cationic hydrolysis	$K_h = \frac{K_w}{K_a \cdot K_b}$	$h = \sqrt{K_h}$ $= \sqrt{\frac{K_w}{K_a K_b}}$	$[H^+] = K_a h$ $= \sqrt{\frac{K_a K_w}{K_b}}$	$pH = \frac{1}{2}$ $[pK_w + pK_a - pK_b]$

BUFFER SOLUTIONS

The solutions whose pH not alters by the addition of little bit of acid or base. There are 2 types of buffer solutions.

i. Simple buffer

Solution of salt of WA and WB

Eg : CH₃COONH₄, NH₄CN

ii. Mixed buffer

There are further 2 types

Acidic buffer - Mixture of WA and its salt with a strong base.

Eg : CH₃COOH + CH₃COONa

HCOOH + HCOOK

H₂CO₃ + NaHCO₃

H₃PO₄ + NaH₂PO₄

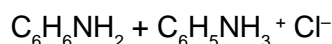
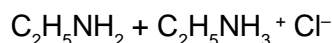
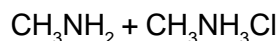
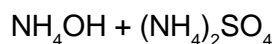
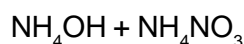
HCN + NaCN

C₆H₅COOH + C₆H₅COONa

HCN + KCN

Basic buffer - Mixture of WB and a salt with SA and contains excess weak base

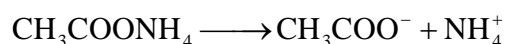
Eg: $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$



The property of buffer solution to resist any change in pH even when small amount of acid or base are added to it is called buffer action. A mixed buffer can control pH of solution better compared to simple buffer.

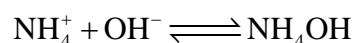
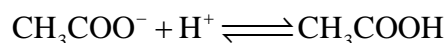
BUFFER ACTION OF SIMPLE BUFFER

Eg : Buffer action of $\text{CH}_3\text{COONH}_4$. Ammonium acetate almost completely dissociate in aq. solution as



When a few drops of acid like HCl are added to the solution then H^+ ions given by the acid combine with CH_3COO^- ion to form weakly ionised molecule of acetic acid.

When a few drops of base like NaOH are added then OH^- ion given by base combine with NH_4^+ and forms weakly ionised molecule of NH_4OH

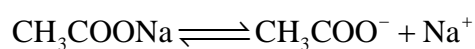
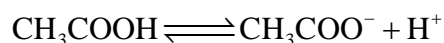
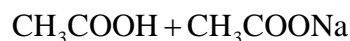


The $[\text{H}^+]$ or $[\text{OH}^-]$ of solution remains constant.

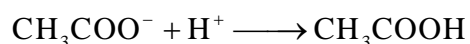
BUFFER ACTION OF ACIDIC BUFFER

Eg : Acetic acid (CH_3COOH) & sodium acetate (CH_3COONa)

CH_3COOH dissociate to a small extent whereas CH_3COONa is almost completely dissociated in the aqueous solution.



By common ion effect ionisation of CH_3COOH is further suppressed, thus in solution there are excess CH_3COO^- ion and small amount of H^+ ion. When a few drops of an acid is added to it the H^+ ion given by acid combine with acetate ion to form weakly ionised molecule of acetic acid.



Thus H^+ ion concentration and pH of solution remains almost constant.

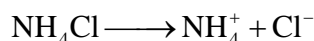
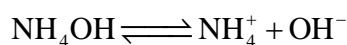
Similarly when a few drops of base is added the OH^- ion given by base combines with H^+ ion already present in it to form weakly ionised molecule of water. As the H^+ ions are consumed, equilibrium shift towards right. Thus more acetic acid dissociates to make up more of H^+ ions. So the pH of solution doesnot change.

BUFFER ACTION OF BASIC BUFFER

Eg : $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$

By common ion effect ionisation of NH_4OH is further suppressed. In solution there are excess NH_4^+ ion and small amount of OH^- ions. When few drops of base are added the OH^- ions of base, combine with NH_4^+ ions to form weakly ionised.

NH_4OH

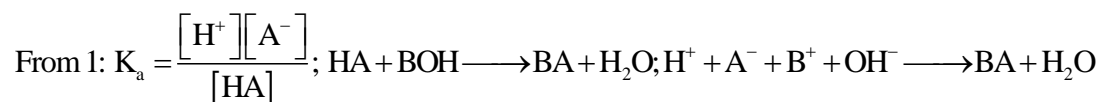
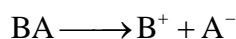
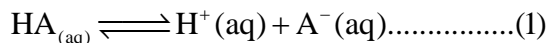


When a small amount of an acid is added the H^+ ion given by it combines with OH^- ion already produced by NH_4OH to form water. As the OH^- ions are consumed. Equilibrium shift in forward direction. So NH_4OH makes up the loss of OH^- so pH remains constant.

HENDERSON - HASSELBALCH EQUATION FOR THE BUFFER

For acid buffer

If weak acid is HA and its salt is BA then



$$[\text{H}^+] = \frac{[\text{HA}]K_a}{[\text{A}^-]}$$

But $[\text{A}^-] = [\text{BA}]$ ie salt $[\text{HA}] = [\text{acid}]$

$$[\text{H}^+] = \frac{K_a \cdot [\text{Acid}]}{[\text{Salt}]}$$

$$\text{pH} = -\log [\text{H}^+] = -\log \frac{[\text{Acid}]}{[\text{Salt}]} K_a$$

$$= -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

For basic buffer

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{pH} = 14 - \text{pOH} = 14 - \text{pK}_b - \log \frac{[\text{salt}]}{[\text{base}]}$$

BUFFER CAPACITY

Defined as no. of moles of acid/base required to be added to 1L of buffer so as to change its pH by 1 unit.

$\text{BC} = \frac{\text{no. of moles of acid / base added 1L of buffer}}{\text{change in pH}}$ $\text{BC} = \frac{n}{\Delta \text{pH}}$
--

ACID BASE TITRATION

Titration is a technique where a solution of known conc. is used to detect the concentration of an unknown solution.

End point and Equivalence point

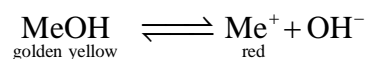
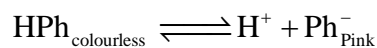
The point at which the reaction is observed to be complete is called end point. A titration is stopped at end point.

Equivalence point is the point at which acid and bases have been added in equivalent quantities.

Indicators

Acid base indicators are the substances which indicate the endpoint of titration by changing their colour. These are organic compounds of complex structures that change colour in solution as the pH changes. Acid base indicators are either weak organic acids or weak organic bases.

Examples: Phenolphthalein (HPh) can be considered as weak organic acid and methyl orange (MeOH) as weak organic base.



Every indicator shows colour change only in a narrow pH range called its pH range.

Indicator	pH range	Acidic colour	Alkaline colour
Methyl orange	3.1 - 4.5	Red	Golden yellow
Bromocresol green	3.8 - 4.6	Yellow	Blue
Methyl red	4.2 - 6.2	Red	Yellow
Litmus	5.0 - 8.0	Red	Blue
Bromothymol Blue	6 - 7.5	Orange	Blue
Phenol red	6.4 - 8.2	Yellow	Red
Phenolphthalein	8.3 - 10	Colourless	Pink
Thymol phthalein	9.3 - 10.5	Colourless	Blue

pH OF ACIDIC INDICATOR

Consider eqm between ionised and unionised form of an indicator HIn.



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

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

K_{In} : Indicator const or dissociation const. of indicator

$$\text{pH} = -\log \text{H}^+ = -\log \left(K_{\text{In}} \frac{[\text{HIn}]}{[\text{In}^-]} \right)$$

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

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

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

$$\text{pH} = \text{p}K_{\text{In}} + \log \frac{[\text{ionised form}]}{[\text{unionised form}]}$$

The exact point of colour will be at the pH when $[\text{HIn}] = [\text{In}^-]$

ie $\text{pH} = \text{p}^{K_{\text{In}}}$

Explanation of pH range of 2 units of indicators

Our eyes can detect the change in colour if conc. of coloured form is atleast 10 times greater than the conc. of other let to see acidic colour.

$$[\text{In}^-] = 1 \quad [\text{HIn}] = 10 \quad \log \frac{1}{10} = \log 10^{-1} = -1$$

$$\text{then } \text{pH} = \text{p}^{K_{\text{In}}} + \log \frac{1}{10}$$

$$\text{pH} = \text{p}^{K_{\text{In}}} - 1$$

now to see base colour

$$[\text{In}^-] = 10 \quad [\text{HIn}] = 1$$

$$\text{then } \text{pH} = \text{p}^{K_{\text{In}}} + \log 10 \quad \log 10 = 1; \text{p}K_{\text{In}} \pm 1$$

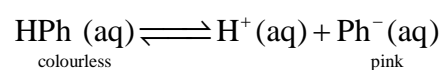
$$\text{pH} = \text{p}^{K_{\text{In}}} + 1$$

\therefore colour change of an indicator $\text{pH} = \text{p}^{K_{\text{In}}} \pm 1$

ie pH range of 2 units

ACIDIC INDICATOR ACTION

Phenolphthalein (HPh) is a colourless weak acid ($\text{C}_{20}\text{H}_{14}\text{O}_4$)

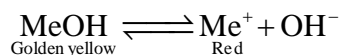


If solution is acidic then H^+ ion given by acid \uparrow so eqm will shift towards to left ie., Solution remains

colourless. By addition of an alkali OH^- of alkali combine with H^+ of phenolphthalein to form water and eqm shift towards to right i.e., solution becomes pink.

BASIC INDICATOR ACTION ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$)

When methyl orange (MeOH) is dissolved in water it undergoes dissociation to a small extent.

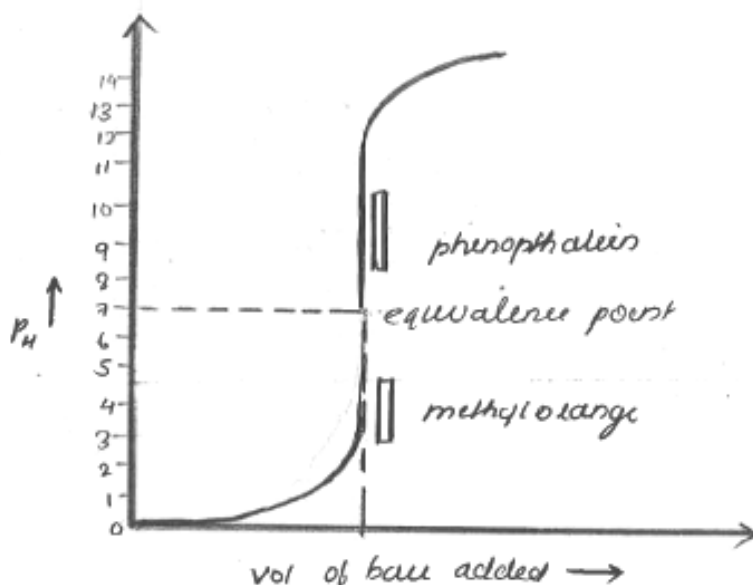


If the solution is acidic then the H^+ furnished by acid combines with OH^- ions of indicator to form water. This shift eqm towards right giving red coloured solution. In the presence of an alkali the OH^- ion \uparrow and due to common ion effect dissociation of MeOH suppresses and eqm shift left. Hence solution in alkaline medium remains golden yellow in colour.

TITRATION CURVE

1. STRONG ACID IS STRONG BASE

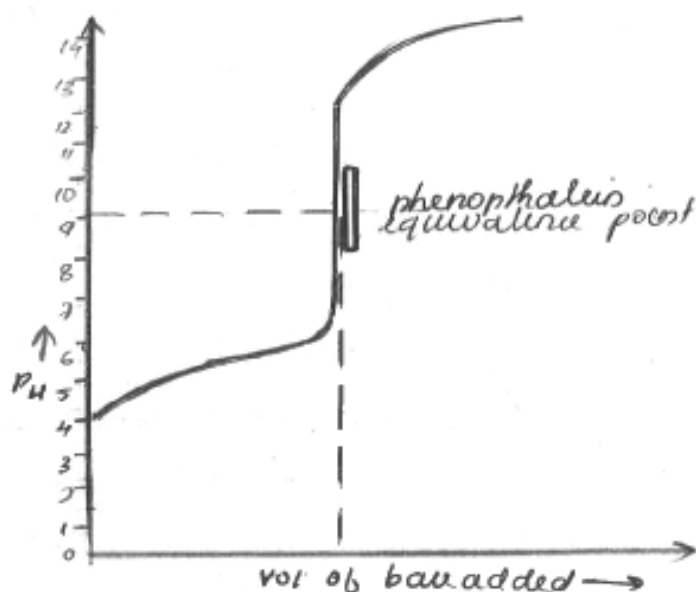
When equivalent amount of SA and SB are mixed the resulting solution has a pH near 7 and any indicator of pH range 3 – 11 can be used in such neutralisation titration i.e. methyl orange, methyl red and phenolphthalein.



2. WEAK ACID + STRONG BASE

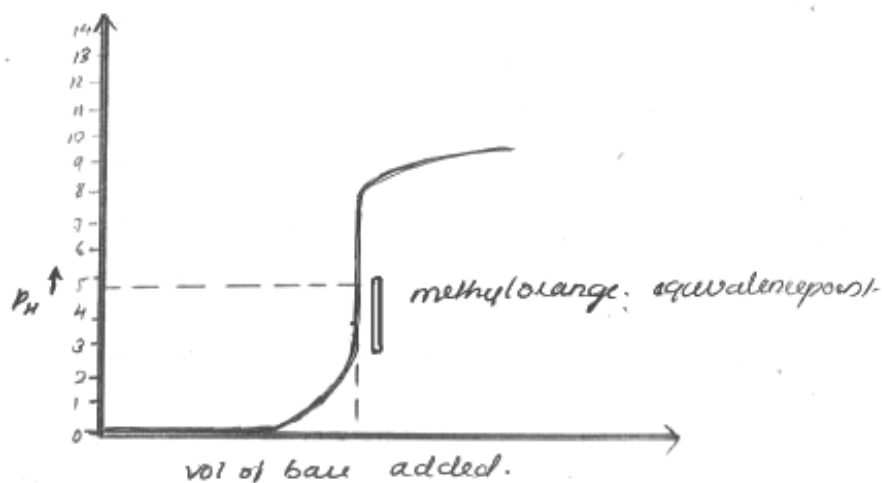
If to a weak acid solution an equivalent amount of strong base is added the resulting solution becomes alkaline. Then pH of solution at equivalence point lies on the alkaline side.

Hence in such titration, indicators whose colour changes takes place in a higher range such as phenolphthalein. \therefore Bromothymol blue etc are used.



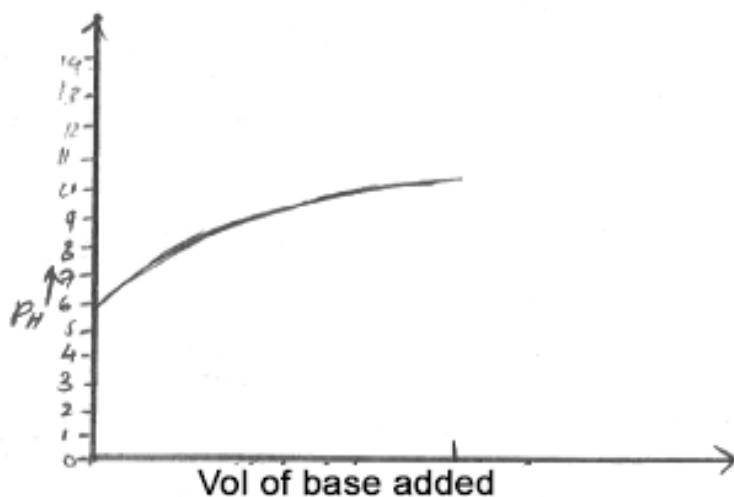
3. STRONG ACID AND WEAK BASE

To a strong acid if equivalent amount of weak base is added, resulting solution not become acidic i.e. pH of solution lies in acidic range. Hence in such titration indicators whose colour change takes place in acidic pH range such as methyl orange, methyl red etc can be used.



4. WEAK ACID AND WEAK BASE

In titration of weak acid and weak base, the steep rise of use of pH near equivalence point do not occur, that is pH changes, in this is not equal to the pH transition range of any indicator. For this reason, actually no suitable indicator can be used to detect the end point. In some cases we can use phenol red.



UNIVERSAL INDICATOR

Mixture of no. of indicators

Which shows colour changes at different pH ranges

pH	Colour
2	Red
4	Orange
6	Yellow
8	Green
10	Blue
12	Purple

Condition	Weak acid Vs Strong base	Strong base Vs weak acid	Weak base Strong acid
1) When no titrant is added	It is a weak acid $[H^+] = \sqrt{K_a \cdot c}$ $pH = \frac{1}{2}[pK_a - \log c]$	It is a strong base $pOH = -\log[OH^-]$	It is a weak base $[OH^-] = \sqrt{K_b \cdot c}$ $pOH = \frac{1}{2}[pK_b - \log c]$
2) When titration is less than 100%	Salt of WA and SB and excess WA i.e. acidic buffer $pH = pK_a + \log \frac{[salt]}{[acid]}$	Salt of weak acid and strong base and excess strong base. Medium is basic. $pOH = -\log[OH^-]$	Salt of WA + SB and excess WB is basic buffer. $pOH = pK_b + \log \frac{[salt]}{[base]}$ $pH = 14 - pOH$
3) When titration is 100%	Salt of WA + SB $pH = \frac{1}{2}[pK_w + pK_a + \log c]$	Salt of WA + SB $pH = \frac{1}{2}[pK_w + pK_a + \log c]$	Salt of WA + SB $pH = \frac{1}{2}[pK_w - pK_b + \log c]$
4) When titration is more than 100%	WA is completely neutralised and SB is in excess. $pOH = -\log[OH^-]$ \therefore medium is basic	Salt of WA and SB and excess WA. i.e. acidic buffer $pH = pK_a + \log \frac{[salt]}{[acid]}$	WB is completely neutralised and SA acid is in excess. \therefore medium is acidic $pH = -\log[H^+]$