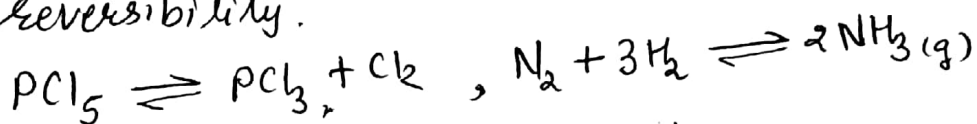


UNIT - 7 CHEMICAL EQUILIBRIUM

• Equilibrium is the state which the concentration of reactants and products do not change with time.

• The important aspect of equilibrium system is the reversibility.



• Equilibrium can attain in closed container when all the reactants and products are gases.

• At equilibrium the concentration of reactants and products becomes constant and do not change with time. This state of system is called dynamic equilibrium.

Rate of forward reaction = Rate of backward reaction

★ EQUILIBRIUM IN PHYSICAL PROCESS :->

1) Solid-liquid Equilibrium:



Rate of melting of ice = Rate of freezing of water.

The temp. at which the solid and liquid of a pure substance are equilibrium at 1 atm. pressure is called the melting point of the solid or freezing point of the liquid.

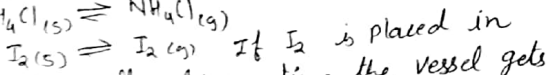
2) Liquid-vapour equilibrium:



In the beginning more and more water molecules converted into vapours. The process is called evaporation. The water vapour exerts pressure on the mercury and Hg-level in the right limb of U-tube increases. Some of the water molecules in vapour phase come back in liquid phase. This process is

called condensation. After some time rate of evaporation and rate of condensation becomes equal and called equilibrium state. So, the pressure of vapour in equilibrium with the liquid at constant temp. in a closed vessel is called vapour pressure and the temp. at which V.P. of a liquid is equal to one atm. pressure (1.013 bar) called boiling point of the liquid.

3) Solid-vapour equilibrium: \rightarrow Camphor_(s) \rightleftharpoons Camphor_(g)



If I_2 is placed in closed vessel then after some time, the vessel gets filled with violet vapour and the intensity of colour increases with time. After certain time, the

intensity of colour becomes constant and at this stage equilibrium is attained.

4) Equilibrium involving dissolution of solids: \rightarrow
eg Sugar (solution) \rightleftharpoons Sugar (solid)

Let us take some water in a beaker and add some sugar slowly to it. At first, sugar keeps on dissolving in water to form the solution. Ultimately, a stage is reached when no more sugar dissolves and some of the sugar settles down, such solution is called saturated solution. In a saturated solution, a dynamic equilibrium exists b/w the solute molecules in the solid state and solvent molecules in solution at equilibrium.

Rate of dissolution of water = Rate of crystallisation of sugar.

* The maximum amount of the solute in gram which dissolves in 100 g of the solvent at const. temp. to form the standard solution is called solubility.

5) Gas-solution equilibrium: \rightarrow (gases in liquid)
 $O_2(g) \rightleftharpoons O_2(\text{in solution})$

The amount of a gas dissolved in a liquid at const. temp. is governed by Henry's law.

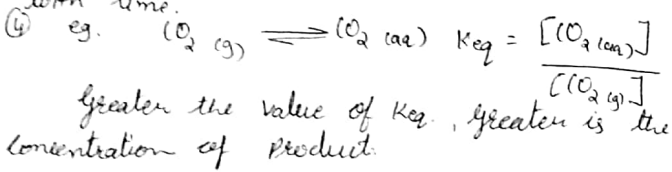
HENRY'S LAW: The mass of a gas (m) dissolved in a given mass of solvent at any temp. is proportional to the pressure of the gas above the solvent. i.e. $m \propto P$ $m = kP$

where k is called the Henry's const. and its depend upon ① nature of the gas ② nature of the solvent

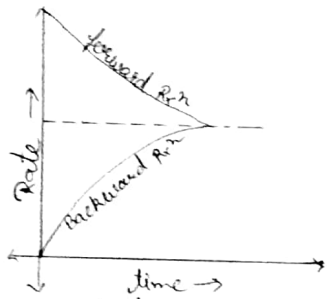
③ Temperature

★ General characteristics of equilibria involving physical processes: →

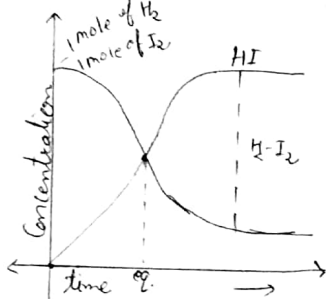
- ① Equilibrium involving gases is possible in closed vessel.
- ② At equilibrium, the two opposite processes occur at same rate. so equilibrium is dynamic not static.
- ③ At equilibrium, the conc. of reactants and products become constant and do not change with time.



★ EQUILIBRIUM IN CHEMICAL PROCESS: →



Rate of forward reaction and backward reaction at equilibrium state

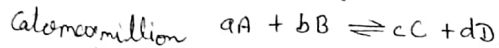


Conc. of reactants and products becomes const. at eq.

A catalyst does not change the state of equilibrium but the presence of catalyst equilibrium is attained quickly but the value of equilibrium constant remains same.

★ LAW OF MASS ACTION / THE EQUILIBRIUM EQUATION

Given by guldberg and peter waage



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

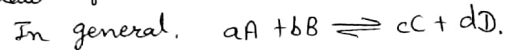
Rate of backward reaction $\propto [C]^c [D]^d$

"The rate of a chemical reaction at any particular temp. is proportional to the product of the molar concentrations of reactants with each concentration term raised to the equal to the number of molecules of the respective reactants taking part in the reaction."

Active mass = Concentration = Molarity = $[C] = \frac{\text{No. of moles dissolved per litre volume of the solution.}}{\text{Volume}}$

★ LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT: →

The law of mass action may be applied to a reversible reaction to derive a mathematical expression for equilibrium constant known as law of chemical equilibrium.



where a, b, c, d are stoichiometric co-efficient

Rate of forward reaction $\propto [A]^a [B]^b$
 $= K_f [A]^a [B]^b$ --- (i)

Rate of backward reaction $\propto [C]^c [D]^d$
 $= K_b [C]^c [D]^d$ --- (ii)

K_f = Velocity cont. or rate of conc. for forward Reaⁿ.

K_b = Velocity cont. or rate of conc. for backward Reaⁿ.

At Equilibrium:

Rate of forward Reac^n = Rate of backward Reac^n

$$k_f [A]^a [B]^b = k_b [C]^c [D]^d$$

$$K_c = \frac{k_f}{k_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad K_c = \text{eq. Constant}$$

or
The combined constant, K_c , which is equal to k_f/k_b is called equilibrium constant and has a constant value for a reaction at a given temperature. The above equation is known as law of chemical equilibrium.

* The concentration ratio i.e., ratio of the product of concentrations of products to that of reactants is also known as concentration quotient and is denoted by Q_c .

$$\text{Concentration quotient } Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

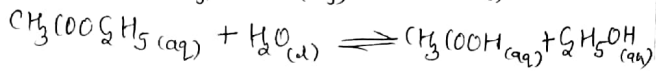
It may be noted that Q_c becomes equal to equilibrium constant (K_c) when the reaction is at equilibrium state.

Thus at equilibrium, $Q_c = K_c$.

Types of Chemical Equilibrium:

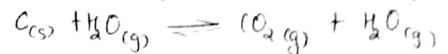
① Homogeneous chemical equilibrium Reac^n :

In homogeneous system all the reactants and products are from one phase only. The reactant and products are miscible in each other. eg. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$



② HETEROGENEOUS CHEMICAL EQUILIBRIUM $\text{Reac}^n \rightarrow$

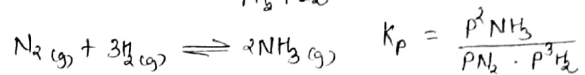
In this system, the reactants and products from more than one phase. They are not miscible in each other. eg. $\text{Ca}(\text{OH})_2(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{g})$



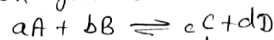
* EQUILIBRIUM CONSTANT K_p - PRESSURE IN GASEOUS SYSTEM: \rightarrow

In gaseous system, the equilibrium constant is usually expressed in terms of their partial pressure eg. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

$$K_p = \frac{P^2_{\text{HI}}}{P_{\text{H}_2} P_{\text{I}_2}}$$

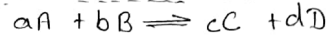


So, in general we can say



$$K_p = \frac{P_c^c \cdot P_d^d}{P_a^a \cdot P_b^b} \quad \left(\begin{array}{l} \text{The pressure of the gas is} \\ \text{taken in atm, bars or Pascals} \end{array} \right)$$

* Relation between K_p and K_c :



$$K_p = \frac{P_c^c \cdot P_d^d}{P_a^a \cdot P_b^b} \quad \text{--- (i)} \quad \text{and} \quad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{--- (ii)}$$

Ideal gas equation, $PV = nRT$

$$\therefore P = \frac{n}{V} \cdot RT \quad \therefore P = C \cdot RT \quad \left(\because \frac{n}{V} = C \text{ in mol/m}^3 \right)$$

From ideal gas equation $P = CRT$ or $P = [C]RT$

Partial pressure of gas = Molar concentration RT

$$P_A = [A] \cdot RT, P_B = [B] \cdot RT, P_C = [C] \cdot RT, P_D = [D] \cdot RT$$

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

④

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

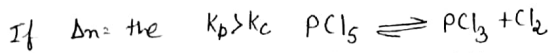
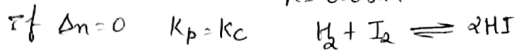
$\therefore K_p = K_c \cdot RT^{\Delta n}$ where $\Delta n = (c+d) - (a+b) = n_p - n_R$

$1 \text{ Pa} = 1 \text{ Nm}^{-2}$

$1 \text{ bar} = 10^5 \text{ Pa}$

$R = 0.0831$ (when $P = 1 \text{ bar}$)

$R = 0.0821$ (when $P = 1 \text{ atm}$)



★ APPLICATION OF Equilibrium constant: \rightarrow

① It does not depend the initial concentration of reactants and products.

② It is const at given temp.

③ Equilibrium const for forward $Rx^n = \frac{1}{\text{const for reverse } Rx^n}$

④ It depends on stoichiometric co-efficient of the reactants and products in the reversible chemical reaction.

⑤ It does not depend on pressure, volume, catalyst.

⑥ It is used to predict

(i) the extent of reaction on basis of its magnitude.

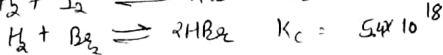
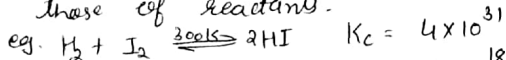
(ii) the direction of reaction.

(iii) Calculate the equilibrium concentration of reactants and products.

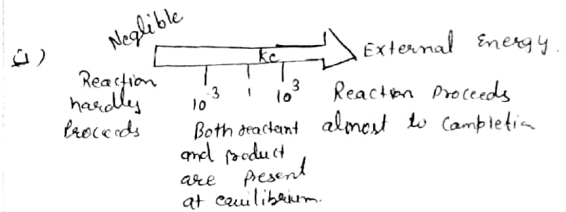
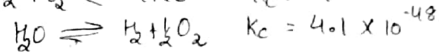
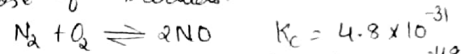
⑦ Predicting the extent of a reaction

(i) if $K_c > 10^3$ forward reaction

i.e concentration of products are much larger than those of reactants.



(ii) if $K_c < 10^{-3}$ backward reaction is favoured. i.e concentration of reactants are much larger than those of products



(iii) if K_c has intermediate value between 10^{-3} to 10^3 this shows that appreciable concentration of both reactants and products are present at equilibrium. eg. $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ $K_c = 4.64 \times 10^{-3}$

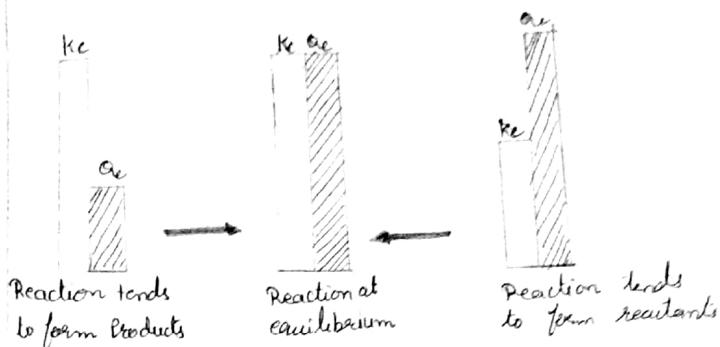
(b) Predicting the direction of the reaction Q_c (Reaction quotient) is calculated when equilibrium has not been attained e.g. before equilibrium. $Q_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$ (Before equilibrium)

(i) if $Q_c > K_c$ the reaction proceed in backward direction so that Q_c becomes equal to K_c

(ii) if $Q_c < K_c$ the reaction proceed in forward direction so that Q_c becomes equal to K_c

(iii) if $Q_c = K_c$ no net reaction occurs.

Relation between ΔG and K .
 $\Delta G^\ominus = -2.303 RT \log K_c$



*** FACTORS AFFECTING EQUILIBRIA :-**

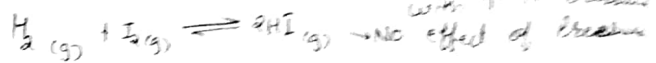
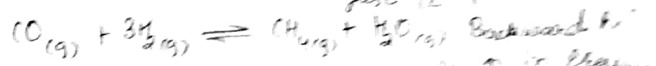
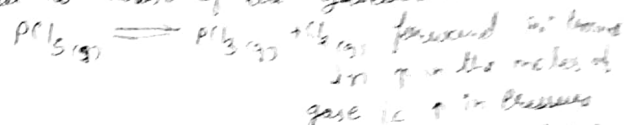
When a system at equilibrium is subjected to a change in concentration, pressure, temp etc then the system does not remain at equilibrium and the reaction proceed in such direction until the equilibrium is again attained. The system adjust itself in such a way so as to neutralize the effect of change.

Le-Chatelier's Principle :- It states that if any a system at equilibrium is subjected to a change in concentration, pressure or temp then the equilibrium shifts itself in such a way so as to undo or minimise the effect of change.

1) Effect of Concentration: on addition of more reactants, reaction proceed in forward direction and on adding of products, reaction proceed in

backward direction.

2) Effect of Pressure :- Low pressure favours that direction in which no. of moles of gases are more. High pressure favours that direction in which no. of moles of gases are less. Pressure has no effect on chemical equilibrium reaction in which the total no. of gaseous reactant is equal to those of the gaseous products.



3) Effect of change of Temperature

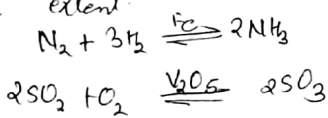
- If reaction is exothermic ($\Delta H = -ve$) low temp is favourable for forward reaction
- If ΔH is endothermic ($\Delta H = +ve$) high temp is favourable for forward reaction

4) Effect of Volume change :- we know that \uparrow in pressure means decrease in volume so that the effect of change of volume will be exactly reverse to that of pressure. Thus, decreasing the volume of a mixture of gases at equilibrium shifts the equilibrium in the direction of lesser number of gaseous molecules while \uparrow the volume shifts the equilibrium in the direction of large number of gaseous molecules.

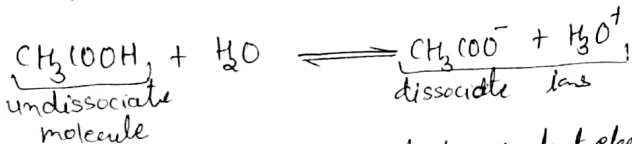
5 Effect of inert gas addition →

- (i) At const. Volume - There will be no effect
- (ii) At const. Pressure Reaction Process towards that direction which contains more no. of moles of gas

6 Effect of catalyst: A catalyst does not change equilibrium state, moreover a catalyst does not change in composition of the reaction mixture at equilibrium. In the presence of catalyst equilibrium attained quickly but the value of equilibrium const. remains same. It is because the catalyst increases the rate of forward reacⁿ as well backward reacⁿ to the same extent.



IONIC EQUILIBRIUM IN SOLUTION



Electrolytes: These sub. which conduct electricity in molten state and in aq. solution are called electrolytes and free ions are responsible for the flow of current.
Ex. Acid, Base, salt, metal oxide etc.

Non-electrolytes: These sub. which do not conduct electricity in molten state and in aqueous solution are called non-electrolyte eg. sugar, glucose, urea, alcohol etc.

degree of dissociation (α) = $\frac{\text{no. of moles dissociated}}{\text{Total no. of moles taken}}$
→ depending upon the degree of dissociation in aq. solⁿ electrolytes classified in to two categories.

- (i) Strong $\alpha > 90\%$
- (ii) weak $\alpha = 30-40\%$

→ There are no. eq. b/w the strong electrolyte and the ions in aq. solⁿ of NaCl contains only Na^+ & Cl^- only.

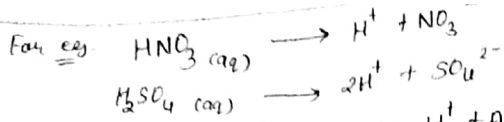
→ under ordinary conditions, there is an eq. between the unionised molecule of the weak electrolytes and the ions in aq. solⁿ.

* Equilibrium involving ions and unionised molecules in weak electrolytes is called ionic equilibrium.

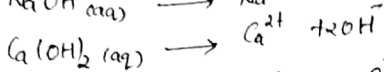
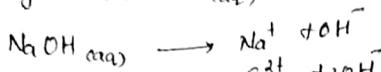
★ ACID - BASE CONCEPTS.

There are three main concepts of acids and bases. These are:

- ① Arrhenius Concepts of acids and bases: "An acid is a substance which dissociates in aq. solⁿ to give $H^+(aq)$, and base is a sub. which dissociates in aq. solⁿ to give $OH^-(aq)$ "



So in general, $\text{HA}(\text{aq}) \rightarrow \text{H}^+ + \text{A}^-$



So, in general, $\text{B}(\text{OH}) \rightarrow \text{B}^+ + \text{OH}^-$

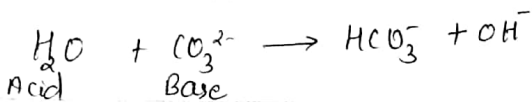
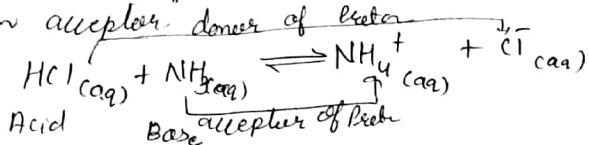
Limitations: (i) It is applicable to aq. soln only. It does not explain the acidic and basic behaviour of the substance in solution like alcohols and liquid NH_3

(ii) It is unable to explain the acidic and basic behaviour of $\text{CO}_2, \text{SO}_2, \text{SO}_3, \text{NH}_3$ etc.

(2) Bronsted-Lowery Concept:

According to him "An acid is a substance which can donate proton (H^+) while base is a substance which can accept a proton (H^+)"

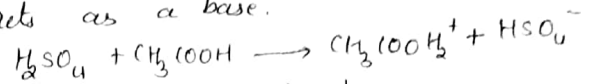
"Acid is a proton donor and base is a proton acceptor"



$\text{SH}^-, \text{HCO}_3^-, \text{HSO}_4^-$ acts as acid as well as base are called amphoteric



→ when two acids are mixed together, the strong acid acts as an acid and weak acid acts as a base.

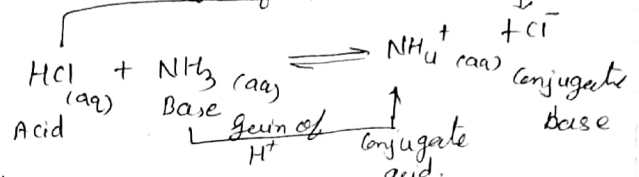


Acid - H^+ → conjugate base

Base + H^+ → conjugate acid

* If acid is strong conjugate base will be weak

* If base is strong conjugate acid will be weak



Advantages over Arrhenius concept:

(i) It can explain the basic character of sub. like $\text{Na}_2\text{CO}_3 \cdot \text{NH}_3$ etc

(ii) It is not limited to molecules only but also covers even in ionic species to act as acids or bases

(iii) It can explain the reaction in non-aqueous medium also.

* Limitations: (i) It fails to explain the behaviour of $\text{CO}_2, \text{SO}_2, \text{SO}_3$ etc (ii) sub. like $\text{BF}_3, \text{AlCl}_3$ etc are behaves as acid but they do not donate proton

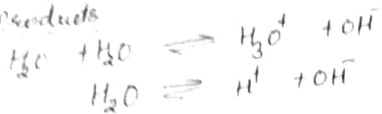
For a weak electrolyte at const temp the α is directly proportional to the square root of the volume containing one mole of electrolyte or inversely proportional to the square root of the molar concentration and it is the Ostwald's Dilution Law.

\rightarrow greater is the value of α or H^+ or OH^- at a given temp greater is the acidic or basic strength.

Relative strength of acids or bases

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}} = \sqrt{\frac{K_{b1}}{K_{b2}}}$$

* Ionisation constant of water and its ionic products



$$K = \frac{[H^+][OH^-]}{[H_2O]} \text{ at } 25^\circ C \text{ in pure water}$$

$$K[H_2O] = [H^+][OH^-]$$

$$\therefore K_w = K[H_2O] = [H^+][OH^-] = 1 \times 10^{-14} \text{ mol/L}$$

K - ionisation const of water
 K_w - ionic product of water

So, $K_w = 1 \times 10^{-7} \times 10^{-7}$

$$\therefore K_w = 1 \times 10^{-14}$$

$$K = \frac{K_w}{[H_2O]}$$

$$K = \frac{10^{-14}}{[H_2O]_{55.5}} = 1.8 \times 10^{-16}$$

Less value of K for water shows that water is ionised to a very small extent. On \uparrow the temp, more H_2O molecules come to give H^+ and OH^- , so value of K_w increases with \uparrow in temp but at all temp (at $25^\circ C$)

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

If $[H^+] > [OH^-]$ acidic solution

$[H^+] = [OH^-]$ Neutral solution

$[H^+] < [OH^-]$ basic solution

* The pH scale:

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as pH scale. It is the logarithm of $[H^+]$ one.

$$pH = -\log [H^+] \quad pOH = -\log [OH^-]$$

To calculate pH, we will consider normality

$N = M \times \text{acidity or basicity}$

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

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

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

$$pK_w = pH + pOH$$

$$pH + pOH = 14 \text{ at } 25^\circ C$$

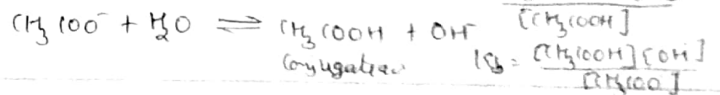
$$\therefore pK_w = 14$$

* Relation between K_a and K_b of the conjugate base or pK_a and pK_b the conjugate acid.



conjugate base

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$



conjugate acid

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

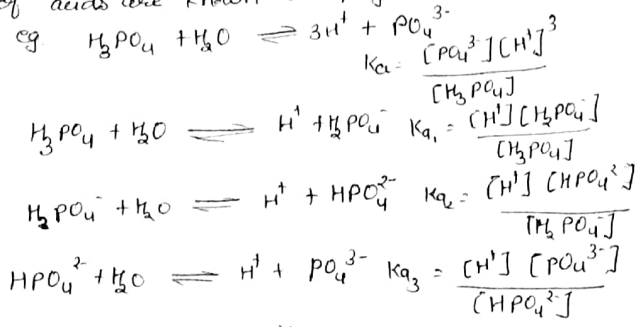
$$K_a \cdot K_b = [H^+][OH^-]$$

$$K_a \times K_b = 10^{-14} \quad K_a \cdot K_b = K_w$$

$$pK_a + pK_b = pK_w \quad [pK_a + pK_b = 14]$$

* Di and polybasic acids and di and polyacidic base:

Some of the acids like oxalic acid, Sulphuric acid, phosphoric acid have more than one ionisable proton per molecule. Such type of acids are known as polybasic or polyprotic acids.



$$K_a = K_{a1} \times K_{a2} \times K_{a3}$$

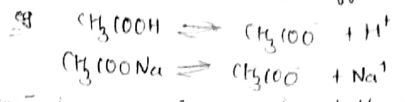
$$= \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \times \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \times \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$K_a = \frac{[H^+]^3 [PO_4^{3-}]}{[H_3PO_4]}$$

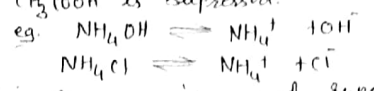
Same for base $K_b = K_{b1} \times K_{b2} \times K_{b3}$

* Common Ion Effect: →
Shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium. This phenomenon is called common ion effect.
Dissociation of weak electrolyte is suppressed by the addition of a strong electrolyte having a common

ion is called common ion effect



CH_3COO^- ion is common in both according to Le Chatelier's Principle, on ↑ the conc of CH_3COO^- , the equilibrium shifts in backward i.e. the dissociation of CH_3COOH is suppressed.



NH_4^+ is common ion and suppresses the dissociation of NH_4OH .

* Hydrolysis of salts and the pH of their

Solutions: when the salt is dissolved in water it is almost completely dissociated into cations and anions. The ion of the salt may react with water to reform the corresponding acids and bases. It is called salt hydrolysis.

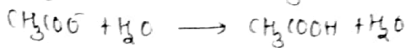
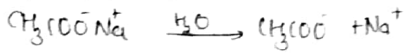
The interaction of cations / anions or both with water making the solution acidic or basic is called salt hydrolysis.

Salt hydrolysis is a reversible process. Only those ions get hydrolysed which produce weak acids or weak bases on interaction with water.

1) Salt of strong acids and strong bases:
Salts of this type are not hydrolysed.
eg. $NaCl$, Na_2SO_4 . It is because the cations on interaction with water produce strong bases.

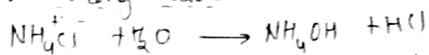
Such as NaOH which are completely dissociated in water and the anions on interaction with water produce strong acids such as HCl, which are completely ionised in aq solution & there is no salt hydrolysis

2> Salts of weak acids and strong bases:



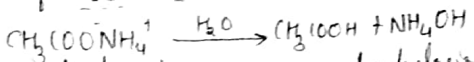
Solution is alkaline ($\text{pH} > 7$) is also called anionic hydrolysis

3> Salts of strong acids and weak bases:



Solution is acidic ($\text{pH} < 7$) is also called cationic hydrolysis

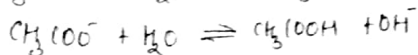
4> Salts of weak acids and weak bases:



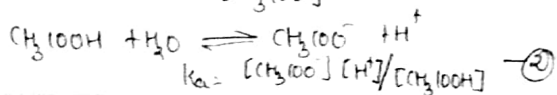
It is called cationic-anionic hydrolysis

* Hydrolysis constant (K_h), degree of hydrolysis (h) and pH of salt solution:

1) Salt of weak acid and strong bases:



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



Use know that

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

$$K_w = K_a \cdot K_h \quad \text{--- (4)}$$

$$K_h = K_w / K_a$$



$$c(1-h) \qquad \qquad \qquad ch \qquad \qquad \qquad ch$$

$$K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{1-h} \quad 1-h \approx 1$$

$$\therefore K_h = ch^2 \quad \text{--- (5)}$$

$$h = \sqrt{K_h/c} \quad \text{--- (6)}$$

$$[\text{OH}^-] = ch = c \cdot \sqrt{K_h/c} = \sqrt{K_h c} \quad \text{--- (7)}$$

$$[\text{OH}^-] = \sqrt{\frac{K_w}{K_a} \cdot c} \quad \text{(from eqn (4))}$$

$$\log [\text{OH}^-] = \frac{1}{2} \log K_w + \frac{1}{2} \log c - \frac{1}{2} \log K_a$$

$$-\log [\text{OH}^-] = -\frac{1}{2} \log K_w - \frac{1}{2} \log c + \frac{1}{2} \log K_a$$

$$\text{pOH} = 7 - \frac{1}{2} \log c + \frac{1}{2} \log K_a \quad \text{--- (8)}$$

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

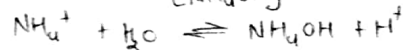
$$= 14 - [7 - \frac{1}{2} \log c + \frac{1}{2} \log K_a]$$

$$\text{pH} = 7 + \frac{1}{2} \log c - \frac{1}{2} \log K_a \quad \text{--- (9)}$$

2) Salts of strong acid and weak base:



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \text{--- (1)}$$



$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \quad \text{--- (2)} \quad K_w = [\text{H}^+][\text{OH}^-] \quad K_w = K_a \cdot K_b$$

$$K_h = \frac{K_w}{K_b} \quad (1)$$



$$K_h = \frac{c \cdot h \cdot c}{c(1-h)} = \frac{ch^2}{1-h} \quad (1-h \approx 1)$$

$$\therefore K_h = ch^2 \Rightarrow h = \sqrt{\frac{K_h}{c}} \quad (2)$$

$$h = \sqrt{\frac{K_w}{K_b \cdot c}} \quad (3)$$

$$[\text{H}^+] = c \cdot h = c \cdot \sqrt{\frac{K_w}{K_b \cdot c}} \Rightarrow [\text{H}^+] = \sqrt{\frac{K_w}{K_b}} \cdot c \quad (4)$$

$$\log [\text{H}^+] = \frac{1}{2} \log K_w + \frac{1}{2} \log c - \frac{1}{2} \log K_b$$

$$-\log [\text{H}^+] = -\frac{1}{2} \log K_w - \frac{1}{2} \log c + \frac{1}{2} \log K_b$$

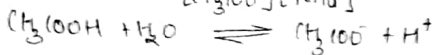
$$\text{pH} = -\frac{1}{2} \cdot 14 + \frac{1}{2} \log c - \frac{1}{2} \text{p}K_b$$

$$\therefore \text{pH} = 7 + \frac{1}{2} \log c - \frac{1}{2} \text{p}K_b \quad (5)$$

③ Salts of weak acid and weak base: →



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



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



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad (3)$$

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

$$K_h = \frac{K_w}{K_a \cdot K_b} \quad (5)$$



$$K_h = \frac{ch^2}{c(1-h)c(1-h)} = \frac{h^2}{1-h} \quad (1-h \approx 1)$$

$$K_h = h^2$$

$$h = \sqrt{K_h} \quad (6)$$

$$\text{From eq (5)} \quad [\text{H}^+] = K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{K_a \cdot ch}{c(1-h)}$$

$$[\text{H}^+] = \frac{K_a \cdot h}{1-h}$$

$$[\text{H}^+] = K_a \cdot h \quad (7)$$

$$[\text{H}^+] = K_a \sqrt{K_h} = K_a \sqrt{\frac{K_w}{K_a \cdot K_b}}$$

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

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

$$\text{pH} = 14 + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

$$\text{pH} = 14 + \frac{1}{2} (\text{p}K_a - \text{p}K_b) \quad (9)$$

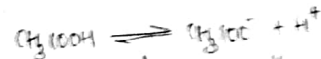
* BUFFER SOLUTIONS:

A solution which resists the change in pH when small amount of strong acid or strong base is added to it is called buffer solution.

↳ Acidic Buffer

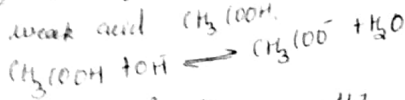
∴ contains weak acid and its salt with a

strong base



on adding an acid eg HCl, the H^+ combine with CH_3COO^- and form CH_3COOH .

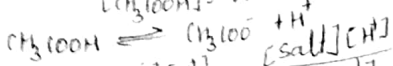
on adding base eg NaOH, the OH are neutralise by the weak acid CH₃COOH.



So, pH remains same

$$[\text{CH}_3\text{COONa}] = [\text{CH}_3\text{COO}^-] = [\text{Salt}]$$

$$[\text{CH}_3\text{COOH}] = [\text{Acid}]$$



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

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

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

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

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

It is called Henderson equation

Basic buffers:

It contains a weak base and its

Salt with strong acids.



on adding a small amount of strong acid

eg HCl, the H⁺ ions are neutralise by the weak base NH₄OH



on adding a small amount of strong base

eg NaOH, the OH combine with NH₄⁺ and form weak

base NH₄OH



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

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

$$[\text{OH}^-] = K_b \cdot \frac{[\text{Base}]}{[\text{Salt}]}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$K_w = \text{pH} - \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$-\text{pH} = -K_w + \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{pH} = 14 - \text{p}K_b - \log \frac{[\text{Salt}]}{[\text{Base}]}$$

* Solubility equilibria of sparingly soluble salts

Two important factors which determine the solubility of salt are

(i) Lattice enthalpy and (ii) solvation enthalpy of ions

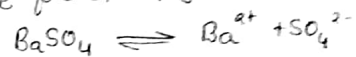
Soluble salt solubility > 0.1 M

Slightly soluble 0.01 M < Solubility < 0.1 M

Sparingly soluble solubility < 0.01 M

Solubility Product (K_{sp}):

Applicable for sparingly soluble salt



$$K_{sp} = \frac{[\text{Ba}^{2+}][\text{SO}_4^{2-}]}{[\text{BaSO}_4]}$$

at a given temp. K_{sp} is equal to the product of the molar concentration of the ions in its saturated solution each one raised to the power equal to its no of ions produced by the dissociation of one molecule of the electrolyte.