Equilibrium

- Equilibrium represents the state of a process in which the properties like temp., pressure, conc. of the system do not show any change with the passage of time

- The reaction mixture contains reactants as well as products whose conc. remains constant so long as the conditions of temp, pressure etc. are kept constant. The reaction is then said to be in equilibrium.

- Equilibrium is always dynamic in nature

- Equilibrium is a general term which applies not only to chemical reactions but applies to physical change as well.

  Eg:- Ice and water are in equilibrium at 0°C & atmospheric pressure.

- In Equilibrium macroscopic property like colour, temp, conc. pressure remain constant but microscopic property continues.

- We can achieve equilibrium in any direction

  Eg:- $N_2 + 3H_2 \rightleftharpoons 2NH_3$

  $2NH_3 \rightleftharpoons N_2 + 3H_2$

- Equilibrium always happens in a closed system.
- At the time of equilibrium, ratio of product conc. and reactant conc. always remain constant which do not depend on anything except for temperature.

- Catalyst does not affect the position of Equilibrium & hence it does not have any effect on the value of equilibrium constant. Catalyst only affect the forward & reverse reaction equally.

- If the opposing process involve only physical changes, the Equilibrium is called Physical Equilibrium.

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

In general chemical equilibrium is represented as

$$aA + bB \rightleftharpoons xX + yY$$

where A & B are reactants and X & Y are products.

* Law of Mass Action

The rate at which a substance reacts is proportional to its active mass and hence the rate of a chemical reaction is proportional to the product of the active masses of the reactants.

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

$$R_f \propto [A]^a \times [B]^b$$

(Rate of foward reaction)

$$R_f = k_f [A]^a \times [B]^b$$

(Velocity constant for forward reaction)

$$R_b \propto [C]^c \times [D]^d$$

(Rate of backward reaction)

$$R_b = K_b [C]^c \times [D]^d$$

(Velocity constant for backward reaction)

Acc. to the situation Rate of forward reaction is equal to the Rate of backward reaction as reaction is in equilibrium.

$$\boxed{R_f = R_b}$$

$$K_f [A]^a \times [B]^b = K_b [C]^c \times [D]^d$$

* Relation b/w K_f & K_b

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

where K is equilibrium constant and c is concentration.

Equilibrium Constant- The product of the molar conc. of the products, each raised to the power equal to its stoichiometric coefficient divided by the product of the molar conc. of the reactants, each raised to the power equal to its stoichiometric coefficient is constant at constant temp. & is called Equilibrium Constant.

⇒ Its the ratio of velocity constant of forward reaction by the velocity constant of backward reaction.

* For Gas-phase Reaction - (i.e when the reactants & the products are gaseous) the equilibrium constant can be expressed either in terms of the conc. in moles per litre or in terms of the partial pressures of the reactants & the products. If expressed in terms of partial pressure, it is denoted by K_p.

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

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

* Relation b/w K_p & K_c

$$P_c V = nRT \qquad (PV = nRT)$$

$\frac{n_i}{V} = C \rightarrow$ (molar conc.)

(no. of moles / litre)

Similarly = $P_A = C_A RT$, $P_B = C_B RT$

$P_C = C_C PT$ $P_D = C_D RT$

$$K_p = \frac{(C_C RT)^c \times (C_D RT)^d}{(C_A RT)^a \times (C_B RT)^b}$$

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

$K_p = K_C RT^{\Delta ng}$ (where Δng = no. of moles of products − no. of moles of reactants $= (c+d) - (a+b)$)

Pg 203 (N.C.E.R.T)

Ques

$2NOCl_{(g)} \rightleftharpoons 2NO(g) + Cl_2(g)$, $K_C = 3.75 \times 10^{-6}$

$K_p = ?$ $T = 1069\ K$

$K_p = K_C (RT)^{\Delta ng}$ ($\Delta ng = (2+1) - 2 = 1$)

$= 3.75 \times 10^{-6} (R \times 1069)^1$

$K_p = 3.75 \times 10^{-6} (0.0831 \times 1069)^1$ ($R = 0.0831$ L bar K^{-1} mol^{-1})

$$\boxed{K_p = 3.33 \times 10^{-2}}$$

NOTE.
- * K_C is ratio of relative conc. of product and reactant.
- * K_p & K_C are dimensionless
- * K_p is ratio of relative pressure and if pressure is expressed in bars $R = 0.0831$ L bar K^{-1} mol^{-1}

* Characteristics of Equilibrium Constant (K_c)

i) If the reaction is reversed, the value of equilibrium constant is inversed

Eg:- $A \rightleftharpoons B$

$$K_c = \frac{[B]}{[A]}$$

Reversed reaction $B \rightleftharpoons A$

$$K_c' = \frac{[A]}{[B]}$$

$$= \frac{1}{K_c}$$

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

Eg:- $2A \rightleftharpoons 2B$

$$K_c^2 = \frac{[B]^2}{[A]^2}$$

iii) If the reaction is multiplied by 3, K_c for new equation is cube of Equilibrium constant (i.e K_c^3)

Eg:- $3A \rightleftharpoons 3B$ $\quad K_c^3 = \frac{[B]^3}{[A]^3}$

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

Eg 1:- $\frac{A}{2} \rightleftharpoons \frac{B}{2}$

$K_c = \sqrt{K_c}$

v) If the equation (having equilibrium constant K_c) is divided by 3, K_c for the new equation is cube root of K_c (i.e $\sqrt[3]{K_c}$)

Eg:- $\frac{A}{3} \rightleftharpoons \frac{B}{3}$

$K_c = \sqrt[3]{K_c}$

vi) If the equation is written in 2 or more steps (having K_c, K_{c_1} & K_{c_2} respectively) then $K_c = K_{c_1} \times K_{c_2}$

Eg:- $A \rightleftharpoons D$ $\quad K_c = \frac{[D]}{[A]}$

1st Step $A \rightleftharpoons B$ $\quad K_{c_1} = \frac{[B]}{[A]}$

2nd Step $B \rightleftharpoons C$ $\quad K_{c_2} = \frac{[C]}{[B]}$

3rd Step $C \rightleftharpoons D$ $\quad K_{c_3} = \frac{[D]}{[C]}$

$$K_c = K_{c_1} \times K_{c_2} \times K_{c_3}$$

$$= \frac{[B]}{[A]} \times \frac{[C]}{[B]} \times \frac{[D]}{[C]} = \frac{[D]}{[A]}$$

* Application of K_c

i] We can predict the extent of a reaction with the help of the value of K_c

a) If $K_c > 10^3$

→ Shows forward reaction is favoured i.e conc. of product is much larger than reactant at equilibrium

Eg:- $A \rightleftharpoons B$ $K_c = 1.2 \times 10^6$

b) If $K_c = (10^{-3} \text{ to } 10^3)$

→ shows that conc. of reactant & product is comparable

Eg:- $A \rightleftharpoons B$ $K_c = 5 \times 10^{-2}$

c) If $K_c < 10^{-3}$

→ Shows that backward reaction is favourd i.e conc. of reactant is much larger than product at equilibrium

Eg:- $A \rightleftharpoons B$ $K_c = 4.8 \times 10^{-31}$

ii] We can predict the directions of reaction with the help of the value of K_c

Q_c (Reaction quotient) = Conc. ratio of product and reactant of a reaction

a) $Q_c = K_c$ (reaction is in equilibrium)

b) $Q_c > K_c$ (Q_c will decrease to become equal to K_c)

⇒ Reaction will proceed in backward direction.

c) $Q_c < K_c$ (Q_c will increase)

⇒ Reaction will proceed in forward direction.

iii) Equilibrium concentrations of all reactants & products can calculated if the initial conc. of reactant is known through following steps :-

Step 1 - Write balanced equation for the reaction
Step 2 - Assume x as the amount of reactant reacted or a product formed.
Step 3 - Calculate Equilibrium conc. of each reactant & product from the stoichiometry of the equation
Step 4 - Write expression for K_c.
Step 5 - Substitute Equilibrium conc. & calculate x
Step 6 - Check the result by substituting calculated values of equilibrium conc. to get the value of K_c

Eg 1 - Initial $2A + B \longrightarrow C + 2D$

a mol L^{-1} b mol L^{-1}

at eqm $(a-x)$ $(b-\frac{x}{2})$ $\frac{x}{2}$ x

$$K_c = \frac{[C][D]^2}{[A]^2[B]} = \frac{(x/2)(x)^2}{(a-x)^2(b-x/2)}$$

Now calculate x.

Le Chatelier's Principle

If a system in equilibrium is subjected to a change of conc., temp. or pressure, the equilibrium shifts in a direction that tends to undo the effect of the change imposed.

→ Effect of various factors

1) Effect of change of Concentration

→ If in an equilibrium reaction, the conc. of any reactant is increased, the equilibrium shifts in the forward direction.

→ If the conc. of any product is increased, the equilibrium shifts in the backward direction. The reverse happens if the conc. are decreased.

Eg:- $N_2 + 3H_2 \rightleftharpoons 2NH_3 + \Delta$

$N_2 \uparrow \longrightarrow$ shift forward
$H_2 \uparrow \longrightarrow$ shift forward
$NH_3 \uparrow \longleftarrow$ shift Backward.

2) Effect of change of Temperature

→ the increase of temp. will favour forward reaction (endothermic reaction).

→ the decrease of temp. will favour backward reaction (Exothermic reaction).

Eg:- $N_2 + 3H_2 \rightleftharpoons 2NH_3 + \Delta$

$\Delta \uparrow \longleftarrow$ Backward
$\Delta \downarrow \longrightarrow$ forward.

3) Effect of Change of Pressure

→ Low pressure favours those reactions which are accompanied by increase in total no. of moles

→ high pressure favours those reactions which takes place with decrease in total no. of moles.

NOTE :- Pressure has no effect on an equilibrium reaction which proceeds with no change in total no. of moles

$PV = nRT$ (where V, R & T are constant)

$P \propto n$

Eg :- $N_2 + 3H_2 \rightleftharpoons 2NH_3 + \Delta$

i) If Pressure ↑es, $4 \longrightarrow 2$ Forward (forward reaction increases)

$4 \longleftarrow 2$ Backward

Haber's Process (Formation of Ammonia)

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

Favourable condition to increase the production of Ammonia are :-

i) High Pressure
ii) Low Temperature

Contact Process (Formation of Sulphur Trioxide)

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

(King of chemical)

Favourable condition to increase the production of SO_3 are

i) High Pressure
ii) Low Temperature.

4) Adding Inert Gas
→ At Constant Pressure (adding Inert gas increases volume)
→ At Constant Volume (adding Inert gas increases pressure)

* At constant Pressure, Equilibrium shift to the side of reaction with greater no. of moles of gas.

* At constant volume, there will be no effect on the equilibrium condition.

NOTE:- ① Pure solid / Pure liquid have constant conc.

Eg:- ① Conc = $\frac{n}{V}$

$$= \frac{w \text{(given mass)}}{mV}$$

$$= \frac{d}{M}$$

$$= \frac{1}{18} \text{ (of } H_2O)$$

② $\underset{(g)}{CaCO_3} \rightleftharpoons \underset{(g)}{CaO} + \underset{(s)}{CO_2}$

$$\frac{K_c \times [CaCO_3]}{[CaO]} = [CO_2]$$

$K_c' = [CO_2] \Rightarrow$ (apparent Rate Constant)

$$\boxed{K_a = K_c * [H_2O]}$$

ii) Degree of dissociation $= (\alpha)$ = $\frac{\text{No. of moles dissociated}}{\text{Total no. of moles taken}}$

(how many moles broke from 1 mole)

Eg:- $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$\begin{array}{ccc} 1 & 0 & 0 \\ c(1-\alpha) & c\alpha & c\alpha \end{array}$$

$$K_a = \frac{\cancel{c}\alpha \times c\alpha}{\cancel{c}(1-\alpha)}$$

$$= \frac{c\alpha^2}{1-\alpha}$$

$$= c\alpha^2 \text{ (if } \alpha <<< 5\%)$$

~~8~~ Types of Substance

Electrolyte

(Substance that breat down when dissolved in water)

Eg:- NaCl, HCl, H_2SO_4, CH_3COOH etc.

Strong Electrolyte

(complete break-down of substance)

Eg:- HCl, H_2SO_4

Weak Electrolyte

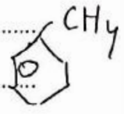
(incomplete break down of substance)

Eg:- CH_3COOH, NH_4OH

Non-Electrolyte

(Substance that do not breakdown when dissolved in water)

Eg:- C_6H_6, ~~CH_4~~, CCl_4,



- Acid $\rightarrow$ Strong Acid (HCl), (H_2SO_4)
  $\rightarrow$ Weak Acid (CH_3COOH)

- Base $\rightarrow$ strong Base (NaOH)
  $\rightarrow$ Weak Base (NH_4OH)

- Salt $\rightarrow$ Completely dissolved in water (NaCl)
  $\rightarrow$ Partially dissolved in water (AgCl)

- Ostwald's Dilution Law

$$K_a = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{C}} \quad \left(\text{we see} = \alpha \propto \sqrt{\frac{1}{C}}\right)$$

$\Rightarrow$ Acc. to thus law, if we increase dilution then the degree of dissociation will be increase.

* Arrhenius Concept of Acid and Bases

(proposed by Arrhenius in 1884)

→ An acid is defined as a substance which contains hydrogen and which when dissolved into water gives hydrogen ions (H^+).

Eg:- $HCl \xrightarrow{water} H^+ + Cl^-$

→ A base is defined as a substance which contains hydroxl groups & which when dissolved in water gives hydroxl ions (OH^-)

Eg:- $NaOH \xrightarrow{water} Na^+ + OH^-$

⇒ Limitations

1) Acids & Bases are substance which give H^+ and OH^- ions respectively in aqueous solution. But as discussed, these ions cannot exist in aqueous solution but exist as hydrated ions written as $H^+(aq)$ & $OH^-(aq)$.

2) Inability to explain acidic & basic characteristics of certain substances

* Bronsted-Lowry Concept of Acids & Bases

(proposed by Bronsted (Danish chemist) & lowry (English Chemist in 1923)

→ An acid is defined as a substance which has the tendency to give a proton (H^+) & a base is defined as substance which has a tendency to accept a proton.

In other words, an acid is a proton donor whereas a base is a proton acceptor.

Eg:- $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

⇒ Limitation

1) Substances like BF_3, $AlCl_3$ etc do not have any hydrogen and hence cannot give a proton but are known to behave as acids

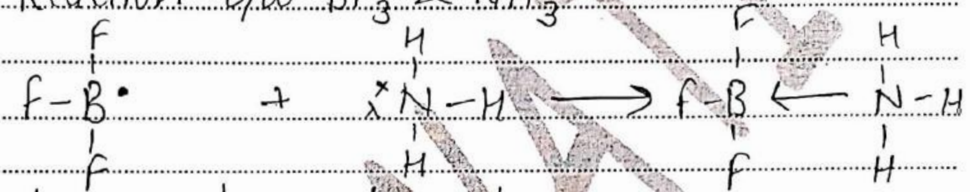
* Lewis Concept of Acids & Bases.

(Proposed by G.N Lewis in 1923)

→ An acid is defined as substance (atoms, ion or molecule) which is capable of accepting a pair of electrons & a base is defined as a substance which is capable of donating an unshared pair of electrons.

In other words, an acid is an electron pair acceptor while a base is an electron pair donor.

Eg:- i) Reaction b/w BF_3 & NH_3



$$F-\overset{F}{\underset{F}{B}}\cdot \;+\; \overset{\times}{_{\times}}\overset{H}{\underset{H}{N}}-H \longrightarrow F-\overset{F}{\underset{F}{B}} \leftarrow \overset{H}{\underset{H}{N}}-H$$

lewis acid　　lewis base

Since NH_3 can donate a lone pair of electrons while BF_3 can accept a pair of electrons, NH_3 is a base & BF_3 is a acid.

* pH → defined as the negative logarithm of Hydrogen ion concentration

$$pH = -\log[H^+]$$

* pOH → defined as the negative logarithm of hydroxide ion concentration

$$pH = -\log[OH^-]$$

At 25°C, $H_2O \rightleftharpoons \underset{(10^{-7})}{H^+} + \underset{(10^{-7})}{OH^-}$ (H_2O is amphoteric in nature but behave neutral)

* amphoteric = substance that can either be acidic or basic.

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K_c \times [H_2O] = [H^+][OH^-]$$

$K_w = [H^+] \times [OH^-] \Rightarrow 10^{-7} \times 10^{-7} \Rightarrow 10^{-14}$

(Ionic product of water)

$K_w = 10^{-14}$ (constant)

* Common Ion Effect

- If to the solution of a weak electrolyte, which ionizes to a small extent, a strong electrolyte having a common ion is added which ionizes almost completely, the ionization of the weak electrolyte is further surpressed.
- Similarly, if to the solution of a sparingly soluble salt, if a soluble salt having a common ion is added, the solubility of the sparingly soluble salt further decreases.

Eg:- $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (weak acid)

$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$ (strong base added to weak acid)

Result - i) the conc. of CH_3COO^- ion increases

ii) Shift backwards i.e. dissociation of acetic acid is further surpressed.

* Relation b/w pH + pOH =

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

$pK_w = pH + pOH$

$\boxed{pH + pOH = 14}$

Eg:- $NaOH = 10^{-2} M$

$pOH = -\log[10^{-2}]$

$= 2$

$pH = 14 - 2 = 12$

Eg. 2 Given $H_2SO_4 = 10^{-2} M$

$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

$10^{-2} \quad 0 \quad 0$

$0 \quad 2\times10^{-2} \quad 10^{-2}$

$pH = -\log[H^+]$

$= -\log(2\times10^{-2})$

$= -(\log 2 + \log 10^{-2})$

$= -(.3010 - 2) \Rightarrow 1.7$

Ques ① $CH_3COOH = \cdot1 M \quad K_a = 1\cdot25\times10^{-7} \quad pH = ?$

Ans $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$\cdot1 \quad 0 \quad 0$

$\cdot1 - x \quad x \quad x$

$K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$1.75\times10^{-7} = \dfrac{x \times x}{(\cdot1 - x)}$ → neglect it.

$x^2 = 1.75\times10^{-7}$

$x = \sqrt{1.75\times10^{-7}}$

Ques ② $CH_3COOH = \cdot1 M \quad K_a = 1.75\times10^{-7} \quad pH = ?$

~~Ans~~ in the presence of $CH_3COONa = \cdot1 M$

Ans. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$1 \quad 0 \quad 0$

$1 - x \quad x \quad x$

$K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$\cdot1 \quad 0 \quad 0$

$0 \quad \cdot1 \quad \cdot1$

$(CH_3COO^-) = \cdot1 + x \approx \cdot1$

(Because of common Ion effect)

$[CH_3COOH] = \cdot 1 - x \approx \cdot 1$ (Because of Common Ion Effect)

$1.75 \times 10^{-7} = \frac{\cancel{\cdot 1} \times x}{\cancel{\cdot 1}} \Rightarrow x = 1.75 \times 10^{-7}$

$pH = -\log(1.75 \times 10^{-7})$

* **Buffer** = A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid or base
Eg:- Blood.

Acidic Buffer	Basic Buffer
formed by the mixture of weak acid & its salt with a strong base.	formed by the mixture of weak base and its salt with strong acid.
Eg:- $CH_3COOH + CH_3COONa$	Eg:- $NH_4OH + NH_4Cl$,
$HCN + NaCN$, Boric acid + Borax	$NH_4OH + NH_4NO_3$
	Glycine + Glycine hydrochloride

* **Buffer Actions**

a) **Acidic Buffer**

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (incomplete dissociation)
$CH_3COONa \rightarrow CH_3COO^- + Na^+$ (complete dissociation)
$H_2O \rightleftharpoons H^+ + OH^-$ (incomplete dissociation)

Action of Acid ~~=~~ when a drop of strong acid (HCl) is added in the above Buffer solution H^+ ions combine with CH_3COO^- ions to form feebly ionized CH_3COOH whose ionization is further surpressed due to common ion effect. So pH of the solution unaltered.

Action of base = when a drop of strong base (NaOH) is added to the above buffer solution it react with free acid to form undissociated water molecules. So pH of the solution unaltered.

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

b) Basic Buffer-

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ (incomplete dissociation)

$NH_4Cl \rightarrow NH_4^+ + Cl^-$ (complete dissociation)

$H_2O \rightleftharpoons H^+ + OH^-$ (incomplete dissociation)

Action of acid When a drop of HCl is added, the added H^+ ions combine with NH_4OH to form undissociated water molecules. So the pH of buffer is unaffected.

$$NH_4OH + OH^- \rightleftharpoons NH_4^+ + H_2O$$

Action of base- When a drop of NaOH is added, the added OH^- ions combine with NH_4^+ ions to form feebly ionized NH_4OH. It is further suppressed due to common ion effect. So the pH of buffer is unaffected.

→ Henderson's Equation (pH of buffer)

a) Acidic Buffer

$$pH = pka + \log \frac{[S] \rightarrow \text{Salt}}{[A] \rightarrow \text{Acid}}$$

b) Basic Buffer

$$pOH = pK_b + \log \frac{[S]}{[B] \rightarrow \text{Base}}$$

Ques $NH_3 = .1\,M$ pH = ?

$K_b = 1.75 \times 10^{-5}$

$NH_3 = .1\,M\ (50\,ml)\ /\ HCl = .1\,M\ (25\,ml)$ pH = ?

Ans. $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$.1 \quad\quad 0 \quad\quad 0$

$.1 - x \quad\quad x \quad\quad x$

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

$$1.75 \times 10^{-5} = \frac{x \times x}{.1 - x}$$

$x = [OH^-]$ $\quad pOH = -\log[OH^-]$

$14 - pOH = pH$

$\boxed{pH = 11.12}$

(Simple Method)

Now, $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$

$\cdot 1M \quad \cdot 1M$ (2.5 ml mol formed)

50 ml $\quad$ 25 ml

$$C = \frac{n}{V}$$

for $NH_4OH \Rightarrow \cdot 1 = \frac{n}{50} \Rightarrow n = 5$ ml mol (Reacted = 2.5 ml mol) left = 2.5 ml mol

$HCl = \cdot 1 = \frac{n}{25} = n = 2.5$ ml mol

$[NH_4OH] = \frac{2.5 \text{ ml mol}}{75 \text{ ml}} = \cdot 033M$

$[NH_4Cl] = \frac{2.5 \text{ ml mol}}{75 \text{ ml}} = \cdot 033M$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$\cdot 033 \quad 0 \quad 0$

$\cdot 033 - x \quad x \quad x$

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

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$\cdot 033 \quad 0 \quad 0$

$\cancel{\cdot 033} \rightarrow 0 \quad \cdot 033 \quad \cdot 033$

$[NH_4^+] = \cdot 033 + x \approx \cdot 033$ (common ion effect)

$[NH_4OH] = \cdot 033 - x \approx \cdot 033$ (common ion effect)

$$1.75 \times 10^{-5} = \frac{.033 \times x}{.033}$$

$$x = 1.75 \times 10^{-5} = [OH^-]$$

$$pOH = -\log(1.75 \times 10^{-5})$$

$$14 - pOH = pH = 9.24$$

OR

(Buffer Method)

$$pOH = pK_b + \log\frac{[S]}{[B]}$$

$$pOH = -\log(1.75 \times 10^{-5}) + \log\frac{.033}{.033}$$

$$pH = 14 - pOH = 9.24$$

+ ## Conjugate acid-base pairs

In a Bronsted-Lowry acid-base reaction, a conjugate acid is the species formed after the base accepts a proton. In contrast, a conjugate base is the species formed after an acid donates its proton.

Eg:- 1) $\underset{Acid}{HCl} + \underset{Base}{H_2O} \rightleftharpoons \underset{C\cdot Acid}{H_3O^+} + \underset{C\cdot Base}{Cl^-}$

2) $\overset{(Acid)}{H_2SO_4^-} \rightleftharpoons \underset{(Acid)}{\overset{(C\cdot Base)}{HSO_4^{2-}}} + H^+ \rightleftharpoons H^+ + \overset{(C- Base)}{SO_4^{2-}}$

~~3) H~~

3) $\underset{(Acid)}{HSO_4^-} \longrightarrow \underset{(C-Base)}{SO_4^{2-}} + H^-$

4) $\underset{(Base)}{HSO_4^-} + H^+ \longrightarrow H_2SO_4$ (C. Acid)

* pH — 1) Acid
2) Base

1) Acid

Strong acid
HCl

10^{-2} M pH = ?

$HCl \rightarrow H^+ + Cl^-$

10^{-2} 0   0

0   10^{-2} 10^{-2}

$pH = -\log[H^+]$

CH_3COOH

10^{-2} M, pH = ?

$K_a = 1.75 \times 10^{-5}$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

10^{-2} 0   0

$10^{-2} - x$ x   x

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

2) Base

$NaOH$

10^{-2} M

$NaOH \rightarrow Na^+ + OH^-$

10^{-2} 0   0

0   10^{-2} 10^{-2}

$pOH = -\log[OH^-]$

$14 - pOH = pH$

NH_4OH

10^{-2} M, $K_b = 1.75 \times 10^{-5}$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

10^{-2} 0   0

$10^{-2} - x$ x   x

$$K_b = \frac{x \times x}{10^{-2} - x}$$

Case I — $HCl + NaOH \rightarrow NaCl + H_2O$

Equal (7) | Acid ↑ (<7) | Base ↑ (>7)

Case II — $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Equal

$7 + \frac{1}{2}(Pka + \log c)$

Acid ↑

$\underline{CH_3COOH} + NaOH \rightarrow CH_3COONa + H_2O$

$Pka + \log \frac{[S]}{[A]}$

Case III $NH_4OH + HCl \rightarrow NH_4Cl + H_2O$

Equal

$7 - \frac{1}{2}(Pk_b + \log c)$

Base ↑

NH_4OH, NH_4Cl

$Pk_b + \log \frac{[S]}{[B]}$

Case IV $CH_3COOH + NH_4OH \rightarrow \underline{CH_3COONH_4} + H_2O$

$pH = 7 + \frac{1}{2}(Pka - Pkb)$ or $7 - \frac{1}{2}(Pkb - Pka)$

$= 7$

Ques Why Neutralisation reaction is called Neutralisation Reaction?

Ans. When acid & base react with each other, they form salt and water. Water & salt both are neutral which means that whenever acid & base react together, they are neutralised by each other. Therefore, it is termed as a neutralisation reaction.

$$\text{Eg:- } \underset{\text{(strong base)}}{NaOH} + \overset{\text{(strong acid)}}{HCl} \longrightarrow \underset{\text{(strong salt)}}{NaCl} + H_2O \text{ (weak)}$$

$$\begin{matrix} \cancel{Na^+} & H^+ & \longrightarrow & \cancel{Na^+} & H_2O \\ OH^- & \cancel{Cl^-} & & \cancel{Cl^-} & \end{matrix}$$

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

* Salt hydrolysis

→ The reaction of anion or cation of the salt with water to produce an acidic / basic solution.
Hydrolysis is the reverse of neutralization.

→ The equilibrium constant of such a reaction is called Hydrolysis constant.

→ The fraction of the total salt that gets hydrolyzed at equilibrium is called Degree of Hydrolysis.

⇒ Hydrolysis of Salts of

i) Weak acid & Strong Base − ($pH > 7$)

$$\text{Eg:- } CH_3COONa + H_2O \longrightarrow CH_3COOH + NaOH$$

$$\begin{matrix} CH_3COO^- & & & & \\ \cancel{Na^+} & + H_2O & \longrightarrow & CH_3COOH & + \cancel{Na^+} \\ & & & & OH^- \end{matrix}$$

$$CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$$

* Since water is reacting with anion, the hydrolysis will be anionic hydrolysis

$$pH = 7 + \frac{1}{2}(pka + \log c)$$

2) Strong acid & weak base. (pH<7)

Eg:- $NH_4Cl + H_2O \rightarrow NH_4OH + HCl$

$$\begin{array}{l} NH_4^+ + H_2O \rightarrow NH_4OH + H^+ \\ \cancel{Cl^-} \qquad\qquad\qquad\qquad \cancel{Cl^-} \end{array}$$

$$pH = 7 - \frac{1}{2}(pka + \log c)$$

3) Strong acid & Strong base

Eg:- $NaCl + H_2O \rightarrow NaOH + HCl$

$$\begin{array}{l} \cancel{Na^+} + H_2O \rightarrow \cancel{Na^+} + H^+ \\ \cancel{Cl^-} \qquad\qquad\qquad OH^- \quad \cancel{Cl^-} \end{array}$$

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

$$\boxed{pH = 7 \text{ (approx)}}$$

Salt of	Example	Hydrolysis constant	Degree of Hydrolysis	pH=
S.B + W.A	CH_3COONa	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_w}{K_a C}}$	$\frac{1}{2}[pK_w + pKa + \log c]$
S.C + W.B	NH_4Cl	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_w}{K_b C}}$	$\frac{1}{2}[pK_w - pKa - \log c]$
W.A + W.B	CH_3COONH_4	$K_h = \frac{K_w}{K_a \cdot K_b}$	$h = \sqrt{\frac{K_w}{K_b \cdot K_a}}$	$\frac{1}{2}[pK_w + pKa + pK_b]$
S.A + S.B	NaCl	do not hydrolysed		

* Solubility Product

the product of the molar conc. of its ions in a saturated solution, each conc. raised to the power equal to the number of ions produced on dissociation of one molecule of the electrolyte.

Eg:- $\underset{(Solid)}{AgCl} \rightleftharpoons \underset{(aq)}{AgCl} \rightarrow Ag^+ + Cl^-$

$$AgCl \rightarrow Ag^+ + Cl^-$$

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

$$K_c \times [AgCl] = [Ag^+][Cl^-]$$

$$\boxed{K_{sp} = S \times S}$$

Ques: $AB_2 \rightarrow A^{2+} + 2B^-$, $K_{sp} = 1.2 \times 10^{-7}$

$S \quad 0 \quad 0$

$0 \quad S \quad 2S$

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

$$\Rightarrow [4S^3]$$

$$S = \sqrt[3]{\frac{K_{sp}}{4}}$$

Log & Antilog

* Log

Eg :- 9696

$\Rightarrow 9.696 \times 10^3$

$\log [9.696 \times 10^3]$

$\log 9.696 \times \log 10^3$

$.9866 + 3$

$\Rightarrow 3.9866$

[In log table
⇒ 96 at 9 is 9863
⇒ 96 at 6 is 3
Adding both the value
9863 + 3 ⇒ 9866]

* Antilog

Eg :- 3.9866

$\rightarrow .9866 \times 10^3$

$\text{Antilog} (.9866 \times 10^3)$

$\text{Antilog} (.9866) \times 10^3$

$\Rightarrow 9.696 \times 10^3$

$\Rightarrow 9696$

[In Antilog table
→ 98 at 6 is 9683
⇒ 98 at 6 is 13
Adding both the value
9683 + 13 ⇒ 9696