IONIC EQUILIBRIA

Ionic Solutions:- Molecules of many substances (salts, acids & bases) on dissolution in a solvent (generally water) or on melting dissociate into ions i.e. cations & anions. Such substances are known as electrolytes. A solution of electrolyte ~~or~~ is called ionic solution.

Molecules of substance such as sugar, urea etc on dissolution in solvents (generally water) or on melting do not yield ions. Such substances are called non-electrolytes. A solution of non-electrolyte is known as non-ionic solution.

Strong & Weak Electrolytes:- Strong electrolytes are those which dissociates into ions almost completely whereas those which show poor dissociation into ions on dissolution are called weak electrolytes

~~Strong~~ Salts with few exceptions, e.g. $HgCl_2$, $CdBr_2$ etc. are generally strong electrolytes. Some mineral acids & hydroxides of alkali & alkaline earth metal are also strong electrolyte

In a solution obtained on dissolving a number of strong electrolytes the total conc. of particular ion is sum of the contribution of all the electrolytes present in solution containing that ion.

For example, If a litre of solution is obtained by dissolving 0.1 Mole of NaCl Soln., 0.1 Mole of Na_2SO_4 & 0.2 mole of HCl.

Conc. of Na^+ ions = 0.1 (from NaCl) + 0.1×2 (from Na_2SO_4) + ~~0.2~~ = 0.3 mole of Na^+ ions

Conc. of Cl^- ions = 0.1 (from NaCl) + 0.2 (from HCl)
= 0.3 mole

Conc. of SO_4^{2-} ions = 0.1 mole (from Na_2SO_4)

Conc. of H^+ ion = 0.2 mole (from HCl)

Although when an electrolyte is dissolved in water, it dissocia into ions, the solution on whole is electroneutral i.e. charge on +ve ions must be equal to that of negative ions. i.e.

$$\sum Z_i^+ [M_i^{+Z_i}] = \sum Z_i^- [A_i^{-Z_i}]$$

where $[M_i^{+Z_i}]$ is conc. of cation with $+Z_i$ charge & $[A_i^{-Z_i}]$ is conc. of anion with $-Z_i$ charge.

In the solution under study the +ve ions are Na^+ & H^+ & negative ions are Cl^- & SO_4^{2-}

$$1[Na^+] + 1[H^+] = 1[Cl^-] + 2[SO_4^{2-}]$$
$$1\times(0.3) + 1(0.2) = 1(0.3) + 2(0.1)$$
$$0.5 = 0.5$$

This is called principle of electroneutrality.

In general,

Most of the acids & bases are weak electrolytes except some mineral acids & hydroxides of alkali & alkaline earth metals. For a weak & electrolyte in a solution, there exists ionic equilibrium b/w the ions & undissociated electrolyte as, for example

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

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

no. of molecules dissociated / total no. of molecules

These are known as ionic equilibria

In case of weak electrolytes, the degree of dissociation i.e. fraction of total amount which dissociate is quite appreciable at moderate conc. & increases with dilution till at infinite dilution, there is ~~or~~ nearly complete dissociation.

In case of strong electrolytes, there is no such ionic eqbm. they are almost completely dissociated at all dilutions. The dissociation of strong electrolytes may thus be represented as

$$NaCl \longrightarrow Na^+ + Cl^-$$

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

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

Dissociation of an acid in water:— Consider a general monobasic acid HA, It may either be a neutral molecule (as acetic acid CH_3COOH) or an ion (ammonium ion, NH_4^+ hydrogen sulphate ion HSO_4^-)

A typical acid HA reacts as follows when dissolved in water.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad \text{---------- (1)}$$

Applying the law of chemical equilibria, the equilibrium constant

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad \text{---------- (2)}$$

In dilute solution the concentration of water will effectively be a constant equal to number of moles in one litre.

H_3O^+ indicates that the hydrogen ion in hydrated form & thus may be put simply as hydrogen ion H^+, as exact hydration num is not known.

We may write eq (2) as:

$$K = \frac{[H^+][A^-]}{[HA][\text{Constant}]} \quad \text{or} \quad K \times [\text{Constant}] = \frac{[H^+][A^-]}{[HA]}$$

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

where K_a = Ionisation constant or dissociation constant of acid

It is clear that from above expression that the product of concentrations of hydrogen ion & the anion ~~with~~ either contributed by the acid itself or by any other compound divided by concentration of unionized acid in solution gives a constant K_a known as dissociation constant of acid

Degree of Ionisation :- If we represent ionisation of acid HA in terms of Arrhenius concept as

$$HA \rightleftharpoons H^+ + A^-$$

If C moles of the acid HA is added per litre of the solution & α be the degree of dissociation of acid then,

	HA	$\rightleftharpoons$	H^+	$+$	A^-
Initial conc.	C		0		0
Eqbm. conc.	$C(1-\alpha)$		$C\alpha$		$C\alpha$

Now $K_a = \dfrac{[H^+][A^-]}{[HA]}$

Substituting eqbm. conc. in the above eqn.

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

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

or $$C\alpha^2 + \alpha K_a - K_a = 0$$

$$\therefore \boxed{\alpha = \frac{-K_a \pm \sqrt{K_a^2 + 4K_aC}}{2C}}$$

For weak electrolytes the degree of dissociation α is very small & hence $(1-\alpha)$ may be equal to one as $(1-\alpha \simeq 1)$

$$\therefore K_a = C\alpha^2$$

$$\text{or } \boxed{\alpha = \sqrt{\frac{K_a}{C}}}$$

$$\therefore [H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{CK_a} \Rightarrow -\log[H^+] = \frac{1}{2}[-\log K_a - \log C]$$

$$\Rightarrow pH = \frac{1}{2}[pK_a - \log C]$$

at eqbm

Hence with the help of above eqn. we can calculate hydrogen ion conc. of aqueous soln. of acids, whose dissociation constant are known.

NOTE :- 1) The dissociation constant of an acid is constant at constant temperature & varies with temperature

2) The units of dissociation constant is $mol\,L^{-1}$

3) The degree of dissociation of weak electrolytes is increased by dilution

The degree of dissociation of an acid is defined as the fraction of total no. of moles of an acid dissociated at eqbm. It is a unitless quantity.

Strength of an acid :- The magnitude of Ionisation constant is a qualitative measure of acid strength. The larger the value of K_a, the stronger is acid. Thus acetic acid ($K_a = 1.75 \times 10^{-5}$) is stronger than hydrocyanic acid ($K_a = 7.2 \times 10^{-10}$)

The strength of an acid depends on its capacity to furnish hydrogen ions which is determined in terms of its degree of dissociation. For quantitative comparison of strengths of two acids in the conc. of H^+ ions are calculated for both acids in their equinormal (or equimolar) solutions (i.e. solutions of equal normality (or molarity)). Thus, the ratio of strengths of two acids HA_1 & HA_2 at the same conc. C is equal to the conc. of hydrogen ion in each acid.

$$\frac{\text{Strength of acid } HA_1}{\text{Strength of acid } HA_2} = \frac{H^+ \text{ ion conc. in acid } HA_1}{H^+ \text{ ion conc. in acid } HA_2}$$

$$= \frac{C\alpha_1}{C\alpha_2} = \frac{\alpha_1}{\alpha_2}$$

But $K_a = C\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{C}}$

$$\therefore \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

$$\therefore \frac{\text{Strength of acid } HA_1}{\text{Strength of acid } HA_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Dissociation constant of Polybasic Acids :- Polybasic acid contains two or more hydrogens which can dissociated. They always dissociates in stages. Phosphoric acid is a tribasic acid. It dissocids in three stages as shown below :

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \qquad K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.52 \times 10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} \qquad K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.23 \times 10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-} \qquad K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.80 \times 10^{-13}$$

The reason for decrease in dissociation constant of successive stages is that in the first stage the +ively charged proton comes from neutral molecule while in IInd stage, the proton is detached from negatively charged molecule & third proton detached from a doubly negatively charged molecule

---

sociation of Base :- A base, like an acid may be neutral molecule or an ion, we shall assume that the base is a neutral molecule & represented by BOH. The dissociation of base is represented by:

$$BOH \rightleftharpoons B^+ + OH^-$$

$$\therefore \boxed{K_b = \frac{[B^+][OH^-]}{[BOH]}}$$

where K_b is dissociation or Ionisation constant of base

If C be the number of moles of base BOH added per litre of solution & α be the degree of dissociation of base then

	BOH	$\rightleftharpoons$	B^+	$+$	OH^-
Initial Conc.	C		0		0
Conc at eqbm	$C(1-\alpha)$		$C\alpha$		$C\alpha$

$$\therefore K_b = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$$\therefore \boxed{K_b = \frac{C\alpha^2}{1-\alpha}}$$

$$\therefore \alpha = \frac{-K_b \pm \sqrt{K_b^2 + 4K_bC}}{2C}$$

In case of weak base, the degree of dissociation α is very small & hence $1-\alpha \simeq 1$

$$\therefore K_b = C\alpha^2$$

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

$$\therefore [OH^-] = C\alpha = C\sqrt{\frac{K_b}{C}} = \sqrt{CK_b}$$

Many of the weak bases that we study do not have free hydroxyl ion e.g. ethyl amine & pyridine. The dissociation of such bases is represented by:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

where B represents the ~~base~~ base

$$\therefore K_b = \frac{[BH^+][OH^-]}{[B]}$$

ngth of base:- Greater the value of K_b stronger will be the base. for comparison of ~~two~~ strength of two bases we can follow the same method as that for acid.

$$\therefore \frac{\text{strength of Soln } B_1OH}{\text{strength of Soln } B_2OH} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

Num:- A monobasic acid is 3.5% dissociated in N/20 solution at 20°C. What is dissociation constant of this acid at this temp?

Sol:- given $\alpha = 3.5\% = \frac{3.5}{100} = 0.035$

$$C = N/10 = 0.05\ N$$

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

$$= \frac{0.05 \times 0.035 \times 0.035}{(1 - 0.035)}$$

$$= \frac{0.05 \times 0.035 \times 0.035}{0.965} = 6 \times 10^{-5}$$

Num:- Calculate H^+ ion conc of a 0.1N solution of an acid which has dissociation constant equal to 4.0×10^{-10}

Sol:- ~~Here~~ Since $K_a = \frac{C\alpha^2}{1-\alpha}$

Here $C = 0.1N$, $K_a = 4.0 \times 10^{-10}$

$$\therefore 4.0 \times 10^{-10} = \frac{0.1\alpha^2}{1-\alpha}$$

Since α is very small $\therefore 1 - \alpha \simeq 1$

$$\therefore 0.1\alpha^2 = 4.0 \times 10^{-10}$$

$$\alpha^2 = 40 \times 10^{-10}$$

$$\alpha = 6.32 \times 10^{-5}$$

Since $[H^+] = C\alpha = 6.32 \times 10^{-5} \times 0.1$

$$[H^+] = 6.32 \times 10^{-6}\ N$$

$$\sqrt{K_a C} = \sqrt{4.0 \times 10^{-10} \times 0.1}$$

$$= \sqrt{0.4 \times 10^{-10}} = 6.32 \times 10^{-5}$$