# IONIC EQUILIBRIUM

➢ ***ACCORDING TO STRENGTH IONIC CONDUCTORS ARE OF 2 TYPES :***

1. ***Strong electrolyte :*** Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolyte.

   ***Ex.*** $Na^+Cl^-$, $K^+Cl^-$, etc.

   (a) Strong acid → $H_2SO_4$, HCl, $HNO_3$ $HClO_4$, $H_2SO_5$, HBr, HI

   (b) Strong base → KOH, NaOH, $Ba(OH)_2$ CsOH, RbOH

   (c) All Salts → NaCl, KCl, $CuSO_4$.....

2. ***Weak electrolytes :*** Those electrolytes which are partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of $\alpha$ is less than one.

   ***Ex.***

   (a) Weak acid → HCN, $CH_3COOH$, HCOOH, $H_2CO_3$, $H_3PO_3$, $H_3PO_2$, $B(OH)_3$

   (b) Weak base → $NH_4OH$, $Cu(OH)_2$, $Zn(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$

➢ ***ACIDS BASES AND SALTS :***

***Arrhenius concept :***

***Arrhenius Acid :*** Substance which gives $H^+$ ion on dissolving in water ($H^+$ donor)

***Ex.*** $HNO_3$, $HClO_4$, HCl, HI, HBr, $H_2SO_4$, $H_3PO_4$ etc.

◆ $H_3BO_3$ is not Arrhenius acid.

➢ ***Arrhenius base :*** Any substance which releases $OH^-$ (hydroxyl) ion in water ($OH^-$ ion donor).

◆ First group elements (except Li.) form strong bases

➢ ***Bronsted - Lowery concept : (Conjugate acid - base concept) (Protonic concept)***

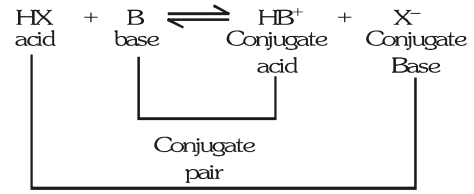
***Acid :*** substances which donate $H^+$ are Bronsted Lowery acids ($H^+$ donor)

***Base :*** substances which accept $H^+$ are Bronsted Lowery bases ($H^+$ acceptor)

➢ ***Conjugate acid - base pairs :***

In a typical acid base reaction

$$HX + B \rightleftharpoons X^- + HB^+$$




***Ex :***

| *Acid* | *Conjugate base* | *Base* | *Conjugate acid* |
|---|---|---|---|
| HCl | $Cl^-$ | $NH_3$ | $NH_4^+$ |
| $H_2SO_4$ | $HSO_4^-$ | $H_2O$ | $H_3O^+$ |
| $HSO_4^-$ | $SO_4^{2-}$ | $RNH_2$ | $RNH_3^+$ |
| $H_2O$ | $OH^-$ | | |

➢ ***LEWIS CONCEPT (electronic concept) :***

An acid is a molecule/ion which can accept an electron pair with the formation of a coordinate bond.

Acid $\rightarrow$ $e^-$ pair acceptor

***Ex.*** Electron deficient molecules : $BF_3$, $AlCl_3$

Cations : $H^+$, $Fe^{2+}$, $Na^+$

Molecules with vacant orbitals : $SF_4$, $PF_3$

A base is any molecule/ion which has a lone pair of electrons which can be donated.

Base $\rightarrow$ (One electron pair donor)

***Ex.*** Molecules with lone pairs : $NH_3$, $PH_3$, $H_2O$, $CH_3OH$

Anions : $^-OH$, $H^-$, $^-NH_2$

➢ ***IONIC PRODUCT OF WATER :***

According to arrhenius concept

$H_2O \rightleftharpoons H^+ + OH^-$ so, ionic product of water, $K_w = [H^+][OH^-] = 10^{-14}$ at 25 (exp.)

Dissociation of water is endothermic, so on increasing temperature $K_w$ increases.

$K_w$ increases with increase in temperature.

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

$pH = 7 = pOH \Rightarrow$ neutral

$pH < 7$ or $pOH > 7 \Rightarrow$ acidic } at 25 C

$pH > 7$ or $pOH < 7 \Rightarrow$ Basic

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

➢ ***Degree of dissociation of water :***

$$H_2O \rightleftharpoons H^+ + OH^- \Rightarrow \alpha = \frac{\text{no. of moles dissociated}}{\text{Total no. of moles initially taken}}$$

$$= \frac{10^{-7}}{55.55} = 18 \quad 10^{-10} \text{ or } 1.8 \quad 10^{-7}\ \% \qquad [\text{at } 25\ C]$$

➢ ***Absolute dissociation constant of water :***

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_a = K_b = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \quad 10^{-16}$$

So, $pK_a = pK_b = -\log(1.8 \quad 10^{-16}) = 16 - \log 1.8 = 15.74$

❑ ***ACIDITY AND pH SCALE :***

Acidic strength means the tendency of an acid to give $H_3O^+$ or $H^+$ ions in water.

So greater then tendency to give $H^+$, more will be the acidic strength of the substance.

Basic strength means the tendency of a base to give $OH^-$ ions in water.

So greater the tendency to give $OH^-$ ions, more will be basic strength of the substance.

The concentration of $H^+$ ions is written in a simplified form introduced by Sorenson known as pH scale.

pH is defined as negative logarithm of activity of $H^+$ ions.

$\therefore$ $pH = -\log a_{H^+}$ (where $a_{H^+}$ is the activity of $H^+$ ions)

Activity of $H^+$ ions is the concentration of free $H^+$ ions or $H_3O^+$ ions in a dilute solution.

The pH scale was marked from 0 to 14 with central point at 7 at 25 C taking water as solvent.

If the temperature and the solvent are changed, the pH range of the scale will also change. For example

0 - 14 at 25 C ($K_w = 10^{-14}$) Neutral point, pH = 7

0 - 13 at 80 C ($K_w = 10^{-13}$) Neutral point, pH = 6.5

pH can also be negative or > 14

➢ ***pH Calculation of different Types of solutions :***

***(a) Strong acid solution :***

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

In this case $H^+$ ions coming from water can be neglected,

so $[H^+]$ = normality of strong acid solution

(ii) If concentration is less than $10^{-6}$ M

In this case $H^+$ ions coming from water cannot be neglected.

So $[H^+]$ = normality of strong acid + $H^+$ ions coming from water in presence of this strong acid

***(b) pH of a weak acid (monoprotic) Solution :***

- Weak acid does not dissociated 100 % therefore we have to calculate the percentage dissociation using $K_a$ dissociation constant of the acid.
- We have to use Ostwald's Dilution law (as have been derived earlier)

| | HA $\rightleftharpoons$ | $H^+$ + | $A^-$ |
|---|---|---|---|
| t = 0 | C | 0 | 0 |
| $t_{eq}$ | C(1 – α) | Cα | Cα |

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

If $\alpha << 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$ (is valid if $\alpha < 0.1$ or 10%)

$[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C}$ So $pH = \frac{1}{2}(pK_a - \log C)$

on increasing the dilution $\Rightarrow C\downarrow = \alpha\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

***(c) pH of a mixture of weak acid (monoprotic) and a strong acid solution :***

- Weak acid and Strong acid both will contribute $H^+$ ion.
- For the first approximation we can neglect the $H^+$ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.
- To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.
- If the total $[H^+]$ from the acid is more than $10^{-6}$ M, then contribution from the water can be neglected, if not then we have to take $[H^+]$ from the water also.

➢ ***Relative strength of weak acids and bases :***

For two acids of equimolar concentrations.

$$\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

***(d) pH of a mixture of two weak acid (both monoprotic) solution :***

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

| | $HA_1 \rightleftharpoons H^+ + A_1^-$ | | | $HA_2 \rightleftharpoons H^+ + A_2^-$ | | |
|---|---|---|---|---|---|---|
| t = 0 | $C_1$ | 0 | 0 | $C_2$ | 0 | 0 |
| At eq. | $C_1(1-\alpha_1)$ | $C_1\alpha_1 + C_2\alpha_2$ | $C_1\alpha_1$ | $C_2(1-\alpha_2)$ | $C_2\alpha_2 + C_1\alpha_1$ | $C_2\alpha_2$ |

$$K_{a_1} = \frac{C_1\alpha_1(C_1\alpha_1 + C_2\alpha_2)}{C_1(1-\alpha_1)} \qquad K_{a_2} = \frac{(C_2\alpha_2 + C_1\alpha_1)C_2\alpha_2}{C_2(1-\alpha_2)}$$

(Since $\alpha_1$, $\alpha_2$ both are small in comparision to unity)

$$K_{a_1} = (C_1\alpha_1 + C_2\alpha_2)\alpha_1 \; ; \; K_{a_2} = (C_1\alpha_1 + C_2\alpha_2)\alpha_2 \Rightarrow \frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1}{\alpha_2}$$

$$[H^+] = C_1\alpha_1 + C_2\alpha_2 = \frac{C_1K_{a_1}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} + \frac{C_2K_{a_2}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} \Rightarrow [H^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$$

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

### *(e) pH of a solution of a polyprotic weak acid :*

◆ Diprotic acid is the one, which is capable of giving 2 protons per molecule in water. Let us take a weak diprotic acid ($H_2A$) in water whose concentration is c M.

In an aqueous solution, following equilbria exist.

If

$\alpha_1$ = degree of ionization of $H_2A$ in presence of $HA^-$ $\quad$ $K_{a_1}$ = first ionisation constant of $H_2A$

$\alpha_2$ = degree of ionisation of $HA^-$ in presence of $H_2A$ $\quad$ $K_{a_2}$ = second ionisation constant of $H_2A$

***I step*** $\qquad$ ***II step***

| | $H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$ | | | $HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+$ | | |
|---|---|---|---|---|---|---|
| at eq. | $c(1-\alpha_1)$ | $c\alpha_1(1-\alpha_2)$ | $(c\alpha_1 + c\alpha_1\alpha_2)$ | at eq. $c\alpha_1(1-\alpha_2)$ | $c\alpha_1\alpha_2$ | $(c\alpha_1 + c\alpha_1\alpha_2)$ |

$$(K_{eq})_1[H_2O] = \frac{[H_3O^+][HA^-]}{[H_2A]} = K_{a_1} \qquad (K_{eq})_2[H_2O] = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = K_{a_2}$$

$$\therefore \; K_{a_1} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1(1-\alpha_2)]}{c(1-\alpha_1)} \qquad K_{a_2} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1\alpha_2)]}{c\alpha_1(1-\alpha_2)}$$

$$= \frac{[c\alpha_1(1+\alpha_2)][\alpha_1(1-\alpha_2)]}{1-\alpha_1} \quad \text{..... (i)} \qquad = \frac{[c\alpha_1(1+\alpha_2)]\alpha_2}{1-\alpha_2} \quad \text{..... (ii)}$$

Knowing the values of $K_{a_1}$, $K_{a_2}$ and c, the values of $\alpha_1$ and $\alpha_2$ can be calculated using equations (i) and (ii) After getting the values of $\alpha_1$ and $\alpha_2$, $[H_3O^+]$ can be calculated as

$$[H_3O^+]_T = c\alpha_1 + c\alpha_1\alpha_2$$

Finally, for calculation of pH

◆ If the total $[H_3O^+] < 10^{-6}$ M, the contribution of $H_3O^+$ from water should be added.

◆ If the total $[H_3O^+] > 10^{-6}$ M, then $[H_3O^+]$ contribution from water can be ignored.

Using this $[H_3O^+]$, pH of the solution can be calculated.

***Approximation :***

For diprotic acids, $K_{a_2} << K_{a_1}$ and $\alpha_2$ would be even smaller than $\alpha_1$

$\therefore \quad 1 - \alpha_2 \approx 1$ and $1 + \alpha_2 \approx 1$

Thus, equation (i) can be reduced to $K_{a_1} = \frac{C\alpha_1 \times \alpha_1}{1-\alpha_1}$

This is expression similar to the expression for a weak monoprotic acid.

- Hence, for a diprotic acid (or a polyprotic acid) the $[H_3O^+]$ can be calculated from its first equilibrium constant expression alone provided $K_{a_2} << K_{a_1}$

➢ ***SALTS :***

Salts are the ionic compounds formed when its positive part (Cation) come from a base and its negative part (Anion) come from an acid.

***Classification of salts :***

***(1) Simple salts***

***(2) Normal salt :*** (i) Acid salts (ii) Basic salts

***(3) Double salts***

***(4) Complex salts***

***(5) Mixed salts***

➢ ***TYPES OF SALT HYDROLYSIS :***

***(1) Hydrolysis of strong acid - weak base [SA - WB] type salt –***

***Ex.*** $CaSO_4$, $NH_4Cl$, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

➢ ***Summary :***

(1) $K_h = \frac{K_w}{K_b}$ (2) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \times C}}$

(3) $\left[H^+\right] = Ch = \sqrt{\frac{K_w \times C}{K_b}}$ (4) pH = – log $[H^+]$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

***(2) Hydrolysis of [WA – SB] type salt –***

***Ex.*** KCN, NaCN, $K_2CO_3$, $BaCO_3$, $K_3PO_4$

$$NaCN + H_2O \rightleftharpoons NaOH + HCN$$

$$Na^+ + CN^- + H_2O \rightleftharpoons Na^+ + OH^- + HCN$$

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

➢ ***Summary :***

(1) $K_h = \frac{K_w}{K_a}$ (2) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \times C}}$

(3) $[OH^-] = Ch = \sqrt{\frac{K_w \times C}{K_a}}$ (4) $[H^+] = \sqrt{\frac{K_w \times K_a}{C}}$

(5) $pH = -\log [H^+]$

$$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

***(3) Hydrolysis of (WA - WB) type salt :***

***Ex.*** $NH_4CN$, $CaCO_3$, $(NH_4)_2 CO_3$, $ZnHPO_3$

➢ ***Summary :***

(1) $K_h = \frac{K_w}{K_a \times K_b}$ (2) $h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}}$

(3) $[H^+] = \sqrt{\frac{K_w \times K_a}{K_b}} = K_a.h$ (4) $pH = -\log [H^+]$

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

***(4) Hydrolysis of [SA – SB] type salt –***

***Ex.*** NaCl, $BaCl_2$, $Na_2SO_4$, $KClO_4$ etc.

(i) Hydrolysis of salt of [SA – SB] is not possible

(ii) Solution is neutral in nature (pH = pOH = 7)

(iii) pH of the solution is 7

➢ ***BUFFER SOLUTIONS :***

A solution that resists change in pH value upon addition of small amount of strong acid or base (less than 1 %) or when solution is diluted is called buffer solution.

The capacity of a solution to resist alteration in its pH value is known as buffer capacity and the mechanism of buffer solution is called buffer action.

***Types of buffer solutions***

(A) Simple buffer solution

(B) Mixed buffer solution

➢ ***SIMPLE BUFFER SOLUTION :***

A salt of weak acid and weak base in water e.g. $CH_3COONH_4$, $HCOONH_4$, AgCN, $NH_4CN$.

***Buffer action of simple buffer solution***

$$\boxed{pH = 7 + \frac{1}{2} pk_a - \frac{1}{2} pk_b}$$

➢ ***MIXED BUFFER SOLUTIONS*** :

***(a) Acidic buffer solution :***

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

*(b) Basic buffer solution :*

A basic buffer solution consists of a mixture of a weak base and its salt with strong acid. The best known example is a mixture of $NH_4OH$ and $NH_4Cl$.

◆ *Condition for maximum buffer action :*

$[NH_4OH]$ : $[NH_4Cl]$

1 1

$$pOH = pK_b + \log\frac{1}{1}$$

$pOH = pK_b$ and $pH = 14 - pK_b$

➢ *SOLUBILITY (s) AND SOLUBILITY PRODUCT ($K_{sp}$) :*

This is generally used for sparingly soluble salts. We will be dealing with the solubilities in the following type of solution.

***Solubility product ($K_{sp}$) is a type of equilibrium constant, so will be dependent only on temperature for a particular salt.***

◆ *Simple solubility*

Let the salt is $A_xB_y$, in solution in water, let the solubility in $H_2O$ = 's' M, then

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{-x}$$

– xs ys $\therefore K_{sp} = (xs)^x (ys)^y = x^x, y^y.(s)^{x+y}$

◆ *Condition of precipitation*

◆ For precipitation ionic product [IP] should be greater than solubility product $k_{sp}$.