# Ionic Equilibrium

## CONCEPT OF ACIDS AND BASES Section - 1

### Concept of Acids and Bases

Three main concepts in defining the acids and bases are :

1. The Arrhenius concept
2. Bronsted-Lowry concept
3. Lewis concept

### 1. The Arrhenius concept :

According to this concept, an acid and a base can defined as follows :

**Acid :** It is a substance that produces hydrogen ions $(H^+)$ in water.

**Base :** It is a substance that produces hydroxyl ions $(OH^-)$ in water.

HCl, $H_2SO_4, HNO_3$ etc. are the examples of Arrhenius acids while NaOH, KOH, $Mg(OH)_2$ etc. are the examples Arrhenius bases.

Let us represent an acid as HX and a base as BOH.

The ionization of acid as (HX) can be represented by the following equation :

$$HX(aq) + H_2O(\ell) \rightarrow \underset{\text{(hydronium ion)}}{H_3O^+(aq)} + X^-(aq)$$

or simply, $HX(aq) \rightarrow H^+(aq) + X^-(aq)$

Hydronium ion $(H_3O^+)$ is used to represent a hydrated $H^+$ ion i.e., $H^+$, ion surrounded by water molecules.

*Note* : The Arrhenius concept of acids and bases is only limited to aqueous solutions.

### Limitations of Arrhenius Concept

(i) It is applicable only to aqueous solutions. For the acidic or basic properties, the presence of water is absolutely necessary. Dry HCl shall not act as an acid.

(ii) The concept does not explain acidic or basic properties of acids and bases in non-aqueous solvents respectively.

(iii) It fails to explain the acidic nature of the non-protic compounds such as $SO_2, NO_2, CO_2, P_2O_5$ etc. which do not have OH in the molecules to furnishing $H^+$ ions.

**(iv)** It fails to explain the basic nature of compounds like $NH_3, Na_2CO_3$ etc. which do not have OH in the molecules to furnish $OH^-$ ions.

**(v)** It fails to explain the acidic nature of certain salts such as $AlCl_3$ in aqueous solution.

## 2. Bronsted-Lowry Acids and Bases

According to this concept, an acid and a base can defined as follows :

**Acid :** It is a substance that can donate a proton.

**Base :** It is a substance that can accept a proton.

***Example :***

When HCl is dissolved in water, it donates a proton to $H_2O$ which behaves as a base.

$$HCl(aq) + H_2O(\ell) \rightarrow Cl^-(aq) + H_3O^-(aq)$$

Other examples of Bronsted Lowry acids (underlined) are :

**(a)** $\underline{NH_4^+}(aq) + H_2O(\ell) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

**(b)** $\underline{HSO_4^-}(aq) + H_2O(\ell) \rightarrow SO_4^{2-}(aq) + H_3O^+(aq)$

**(c)** $\underline{HCl}(aq) + NH_3(aq) \rightleftharpoons Cl^-(aq) + NH_4^+(aq)$

**(d)** $\underline{HCO_3^-}(aq) + NH_3(aq) \rightleftharpoons CO_3^{2-}(aq) + NH_4^+(aq)$

Some examples of Bronsted Lowry bases (underlined) are :

**(a)** $\underline{O^{2-}}(aq) + H_2O(\ell) \rightleftharpoons OH^-(aq) + OH^-(aq)$

**(b)** $\underline{NH_3}(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

**(c)** $\underline{CO_3^{2-}}(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

***Note :***

- This theory requires that an acid must contain transferable hydrogen and it offers great freedom in defining what constitutes base.
- When an acid has donated its proton, the remaining portion of the molecule or ion is a base.
- When a base accepts a proton, it forms an acid.
- The base must have an unshared pair of electrons so as to accept a proton.

The base formed from an acid is known as the *conjugate base of the acid*. Correspondingly, the acid formed from a base is called the *conjugate acid of the base*.

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{NH_3} \rightleftharpoons \underset{\text{Base}_1}{Cl^-} + \underset{\text{Acid}_2}{NH_4^+}$$

In the above reaction, $Cl^-$ is the conjugate base of HCl and $NH_4^+$ is the conjugate acid $NH_3$.

**Note :** **(i)** The conjugate acid always has one more proton than its conjugate base.

**(ii)** To obtain a conjugate acid of a compound, add a proton $(H^+)$ from it and to obtain the conjugate base of the same, remove a proton to the compound, e.g., Conjugate acid of $NH_3$ is $NH_4^+$ while the conjugate base of $NH_3$ is $NH_2^-$.

**(iii)** This concept has the advantage that it can be applied to a solvent other than water, having the tendency to accept or lose a proton.

**(iv)** The terms acid and base are comparative. A substance can behave as an aid in one solvent and as a base in another.

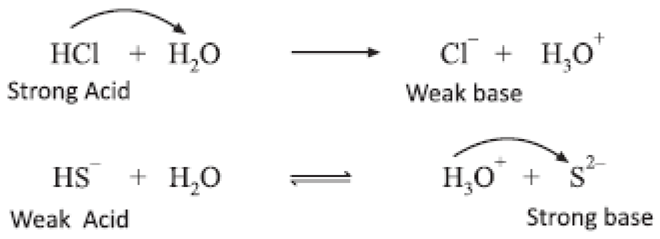
**For example :** Acetic acid $(CH_3COOH)$ behaves as an acid in water but as a base in HF.

$$\underset{\text{Acid}}{CH_3COOH(aq)} + \underset{\text{Base}}{H_2O(aq)} \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$\underset{\text{Base}}{CH_3COOH(aq)} + \underset{\text{Acid}}{HF(aq)} \rightleftharpoons CH_3COOH_2^+ + F^-(aq)$$

## Strength of Bronsted-Lowry Acid and Bases :

The strength of an acid or base is measured by its tendency to lose or gain proton. A strong acid is a substance which loses a proton easily to a base. Consequently, the conjugate base of a strong is a weak base.



The ability of an acid to lose a proton is experimentally measured by its equilibrium constant know as $K_a$. The larger the value of $K_a$, the more complete reaction or higher the concentration of $H_3O^+$ and the stronger is the acid Similarly: For bases, we have the equilibrium constant, $K_b$ which determines the extent of the completion of the reaction.

## Acid-Base Chart Containing Some Common Conjugate Acid-Base Pairs

| | Acid | Conjugate Base | | $K_a$ | $pK_a$ |
|---|---|---|---|---|---|
| Increasing order of acid strength ↑ | HI | $I^-$ | Increasing order of basic strength ↑ | $10^{11}$ | –11 |
| | $HClO_4$ | $ClO_4^-$ | | $10^{10}$ | –10 |
| | HBr | $Br^-$ | | $10^9$ | –9 |
| | HCl | $Cl^-$ | | $10^7$ | –7 |
| | $H_2SO_4$ | $HSO_4^-$ | | $10^2$ | –2 |
| | $H_3O^+$ | $H_2O$ | | 1 | 0.0 |
| | $H_2SO_3$ | $HSO_3^-$ | | $1.5 \times 10^{-2}$ | 1.81 |
| | $HSO_4^-$ | $SO_4^{2-}$ | | $1.2 \times 10^{-2}$ | 1.92 |
| | $H_3PO_4$ | $H_2PO_4^-$ | | $7.5 \times 10^{-3}$ | 2.12 |
| | HF | $F^-$ | | $3.5 \times 10^{-4}$ | 3.45 |
| | $CH_3COOH$ | $CH_3COO^-$ | | $1.8 \times 10^{-5}$ | 4.7 |
| | $H_2S$ | $HS^-$ | | $1.0 \times 10^{-7}$ | 7.0 |
| | $NH_4^+$ | $NH_3$ | | $5.6 \times 10^{-10}$ | 9.3 |
| | HCN | $CN^-$ | | $4.0 \times 10^{-10}$ | 9.4 |
| | $H_2O$ | $OH^-$ | | $1.0 \times 10^{-14}$ | 14.0 |

***Note :*** In general, solvents can be of four types :

**(a)** Protophillic : Solvents having a tendency to accept protons. For example water, alcohol, liq. Ammonia etc.

**(b)** Protogenic : Solvents having a tendency to donate protons. For example water, liq. HF, liq. HCl etc.

**(c)** Amphiprotic : Solvents having a tendency to accept or donate. For example water, liq. ammonia etc.

**(d)** Aprotic : Solvents which neither accept nor donate protons. For example benzene, carbon tetrachloride etc.

## Amphoteric Compounds :

The compounds which can act either as acids or as bases, $H_2O$, $NH_3$ and $CH_3COOH$ are some of the examples.

**(a) Water :**

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{NH_3} \rightleftharpoons OH^- + NH_4^+ \qquad \underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{H_2O} \rightleftharpoons H_3O^+ + OH^-$$

**(b) BIcarbonate :** $\underset{\text{Acid}}{HCO_3^-}+\underset{\text{Base}}{NH_3}\rightleftharpoons CO_3^{2-}+NH_4^+$  $\underset{\text{Acid}}{HCl}+\underset{\text{Base}}{HCO_3^-}\rightleftharpoons Cl^-+H_2CO_3$

> ***Note :*** The reaction $H_2O+H_2O\rightleftharpoons H_3O^++OH^-$ is known as *auto-ionization of water.*

## Limitations of Bronsted Concept :

**(i)** A substance is termed as an acid or base if it reacts with some other substance, i.e., if it donates proton to other substance, it is an acid and if it accepts proton from substance, it is a base.

**(ii)** There are number of acid-base reaction in which no proton transfer takes place, e.g.,

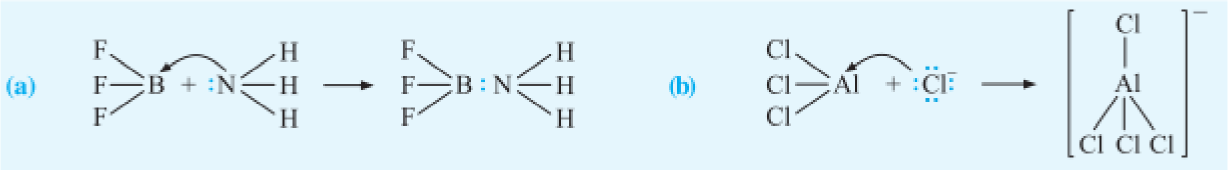
$$\underset{\text{Acid}_1}{SO_2}+\underset{\text{Base}_2}{SO_2}\rightleftharpoons\underset{\text{Acid}_2}{SO^{2+}}+\underset{\text{Base}_1}{SO_3^{2-}}$$

Thus, the protonic definition cannot be used to explain the reaction occurring in nonprotonic solvents such as $COCl_2, SO_2, N_2O_4$ etc.

## 3. Lewis Acid and BasesAcid :

**Acid :** It is a substance that can form a covalent bond by accepting a shared pair of electrons.

**Base :** It is a substance that possess at least one unshared pair of electrons.



**Monoprotic Acids :** Acids that give up one proton per molecule.

**Polyprotic Acids :** Acids that can give up more than one proton per molecule.

Substance that are bases in the Bronsted sysem are also bases according to the Lewis concept. However the Lewis definition of an acid considerably expands that number of substances that are classified as acid. A Lewis acid must have an empty orbital capable of receiving the electron pair of the base.

Lewis acids include molecules or atoms that have incomplete octets. For example molecules like $BF_3, AlCl_3$ etc., act as Lewis Acid.

Many simple cations can act as Lewis acids :

$$Cu^{2+}+4\,\overset{\cdot\cdot}{N}H_3\to Cu(NH_3)_4^{2+} \qquad Fe^{3+}+6:C\equiv N:\to Fe(C\equiv N)_6^{3-}$$

Some metal atoms can function as acids in the formation of compounds such as:

$$Ni+4\ C\equiv O\to Ni(CO)_4$$

Compounds that have central atoms capable of expanding their valence shells are Lewis acids in reactions in which this expansion occurs.

$$SnCl_4 + 2\,Cl^- \rightarrow SnCl_6^{2-} \qquad SiF_4 + 2\,F^- \rightarrow SiF_6^{2-} \qquad PF_5 + F^- \rightarrow PF_6^-$$

Some compounds have an acidic site because of one or more multiple bonds in the molecule.

## BASICS OF IONIC EQULIBRIUM — Section - 2

The type of equilibrium studied in *Chemical Equilibrium is known as molecular equilibrium* (the involvement of molecules only). Now, we will study reversible reactions involving formation of ions in water under *Ionic Equilibrium*.

Ionic Equilibrium is the study of equilibrium in the reactions where formation of ions takes place in aqueous solution.

Ions in solution arises mainly from two ways :

- When solute is ionic compound i.e., strong electrolyte (*a compound whose aqueous solution conducts* electricity) e.g. NaCl, $MgCl_2$, KBr, $NaNO_3$, NaOH etc. In such compounds, ions maintain their identity even in solid state. As such solutes are dissolved in water, ions get separated. In solution, whole of electrolyte is ionised i.e., ionisation is almost 100% complete.
- When solute is polar covalent compound and reacts with water to form ions. These may be *strong or weak electrolytes* depending upon their respective degree of ionizations ($\alpha$) e.g., HCl, $NH_3$, $H_2SO_4$, $HNO_3$, $CH_3COOH$, HCN, $NH_4OH$ etc.

Dissociation (or ionisation) of *strong electrolytes* and some *weak electrolytes* such as $HNO_3$, HCl, $H_2SO_4$ etc. is nearly complete in dilute solution i.e. almost 100% of electrolyte is converted to ions *or* one can say that degree of ionisation ($\alpha$) is nearly 1.

Let BA be an electrolyte and dissolved in water. It ionises as follows : $BA + aq. \rightleftarrows B^+(aq.) + A^-(aq.)$

### Case - I : $(\alpha \sim 1)$

The extent of forward reaction is very high (i.e. such reactions are nearly complete). So, it is of no use to study equilibrium in such reactions.

### Case - II : $(\alpha << 1)$

In aqueous solution of these compounds, only slight amount of reactant (i.e. electrolyte) undergoes dissociation and there exists an equilibrium between ionised molecules and unionized molecules (ions). Such electrolytes are weak electrolytes.

$$BA + aq. \rightleftharpoons B^+(aq.) + A^-(aq.)$$

$$\text{unionised molecules} \rightleftharpoons \text{ionised molecules (ions)}$$

Weak Electrolytes are categorized into three types for easy understanding :

1. **Weak Acids :** $CH_3COOH$ , HCN (and all organic acids)
2. **Weak Bases :** $NH_4OH$ and all organic bases
3. **Sparingly soluble salts :** AgCl, $PbCl_2$, $Ag_2C_2O_4$, MnS, $H_2S$, PbS etc.

## Weak Acids (HA) and Weak Bases (BOH)

### Weak Acids :

Let HA be a monoprotic (monobasic) acid whose equilibrium is to be studied. The aqueous solution of HA can be studied in either of two ways :

$$HA + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq) \quad (H_3O^+ = \text{hydronium ion})$$

or simply as : $$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The equilibrium constant for the above reaction is known as *ionisation constant* for an acid ($K_a$).

[ ] = concentration in mol/L

e.g., $$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \qquad K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

***Note :*** The ion $A^-$ formed due to the ionization of HA is known as its Conjugate base. Thus, to find a conjugate base of any acid, simply remove a Proton ($H^+$) ion from that acid.

⇒ Conjugate base of $CH_3COOH$ is $CH_3COO^-$ ; of $H_2PO_4^-$ is and so on.

Lets study the equilibrium of a weak acid HA in an aqueous solution as follows :

If 'c' be the molar concentration of weak acid HA and 'α' be its degree of dissociation (i.e. the fraction of total concentration which exist in ionic state), then : $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

| Moles | HA | $H^+$ | $A^-$ |
|---|---|---|---|
| Initial | $c$ | 0 | 0 |
| at equilibrium | $c - c\alpha$ | $c\alpha$ | $c\alpha$ |

$$\Rightarrow \quad K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(c\alpha)(c\alpha)}{(c-c\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

Also, $$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{c-[H^+]} \qquad (\because [H^+]=[A^-]=c\alpha)$$

For weak acids having $\alpha << 1$, we can take $1 - \alpha \approx 1$

$$\Rightarrow \quad K_a = c\,\alpha^2 \quad \Rightarrow \quad \alpha = \sqrt{\frac{K_a}{c}}$$

***Note :*** **(i)** In general, if $K_a < 10^{-5}$ and 'c' is fairly high (generally 0.1 M or 0.01 M) then $1 - \alpha$ can be taken as unity.
If c is very low (i.e. for very dilute solutions), $\alpha$ is higher. In that case, we can't take $1 - \alpha$ as 1. In such cases we have to solve a quadratic equation in $\alpha$. i.e. $(1 - \alpha)\,K_a = c\,\alpha^2$.

**(ii)** Basically, if decision on whether to go for approximation or not, is not easy, then just use approximation and solve but remember that you should always validate your approximation before reaching to a final answer. We will see more on this in illustrations and examples.

### Weak Bases :

Let BOH be the weak base, its aqueous solution is represented as follows :

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$$

The equilibrium constant for the above equilibrium is known as ionisation constant of a base ($K_b$).

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad [\ ] = \text{concentration in mol/L}$$

For : $NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = \frac{[NH_4^+]\,[OH^-]}{[BOH]}$

***Note :*** Similar to the concept of Conjugate base, there is a concept of Conjugate acid. e.g. $NH_4^+$ is a conjugate acid of base $NH_3$. Thus, to find a conjugate acid of any base, simply add a Proton ($H^+$) ion to that.

- $H_2PO_4^-$ : Its conjugate base is $H_2PO_4^{2-}$ and its conjugate acid $H_3PO_4$
- $H_2O$ : Its Conjugate base is $OH^-$ and its conjugate acid is $H_3O^+$

A substance is known as amphiprotic if it can both donate or accept a proton e.g. , $H_2O$

Now, if 'c' be the molar concentration of BOH and '$\alpha$' be its degree of dissociation, then :

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$$

| Moles | BOH | $B^+$ | $OH^-$ |
|---|---|---|---|
| Initial | $c$ | 0 | 0 |
| at equilibrium | $c - c\alpha$ | $c\alpha$ | $c\alpha$ |

$$\Rightarrow \quad K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{(c\alpha)(c\alpha)}{(c - c\alpha)} = \frac{c\alpha^2}{1 - \alpha}$$

Also, $K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{[OH^-]^2}{c-[OH^-]}$ $\quad (\because [B^+]=[OH^-]=c\alpha)$

For weak bases having $\alpha << 1$, $1-\alpha \approx 1$

$$\Rightarrow \quad K_b = c\,\alpha^2 \qquad \text{or} \qquad \alpha = \sqrt{\frac{K_b}{c}}$$

**Note :** At a given temperature, $K_a$ and $K_b$ are directly proportional to $\alpha$ i.e. comparing $K_a$ of different acids ($K_b$ for bases), one can compare their strengths or comparing '$\alpha$' of different acids (or bases) at a given temperature and given concentrations, acids strengths (base strengths) can be compared.

For example in case of bases :

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$ (two bases having same concentrations)

or $K_b = c_1\alpha_1^{\,2} = c_2\alpha_2^{\,2}$ (two samples of same base have same value of $K_b$)

$$\Rightarrow \quad \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{c_2}{c_1}}$$

In the above relations, it has been assumed that the degree of dissociation is small as compared to unity.

## Self Ionisation of Water

Water ionises as follows : $H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq)$

The equilibrium constant here is denfined in a different way, and is called as ionic product ($K_w$) of water and is given by :

$$\Rightarrow \quad K_{w0} = [H^+]\,[OH^-]$$ where $K_w = K_a[H_2O]$

$K_a$ : ionisation constant of $H_2O$ and $[H_2O]$ is constant at a given temperature

At 25°C (298 K) ; $K_w = 1.0 \times 10^{-14}$

Since pure water is neutral, $[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7}$ M at 25°C.

- If a strong acid is added to it, $[H^+]$ increases and hence $[OH] < 10^{-7}$ M (at 25°C) and solution is said to be acidic.
- If a strong base is added to it, $[OH^-]$ increases and hence $[H^+]$ must decrease in order to keep $K_w$ constant. Now $[OH^-] > 10^{-7}$ M and solution is basic (or alkaline)

**Note :** The dissociation of water is an endothermic reaction. Thus, increasing the temperature will increase $K_w$ of water and thereby increasing the $[OH^-]$ and $[H^+]$.

## pH Scale :

*Sorensen*, a French chemist developed a scale to measure the acidity in terms of concentrations of $H^+$ in a solution. As defined by him :

*pH of a solution* is the negative logarithm to the base 10 of the concentration of $H^+$ ions which it contains.

(Basically "p" acts as a mathematical operator : $p(A) = -\log_{10} [A]$)

$\Rightarrow$ $pH = -\log_{10} [H^+]$ and $pOH = \log_{10} [OH^-]$

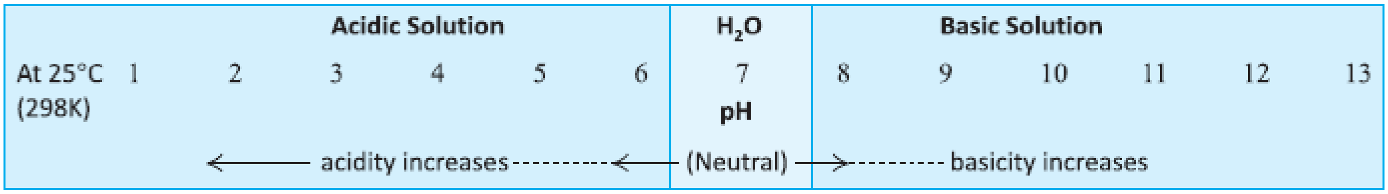
At 25°C, using this definition, a scale called pH Scale is developed as follows:

For pure $H_2O$ ; $[H^+] = [OH^-] = 10^{-7}$ M

$pH = -\log_{10} (10^{-7}) = 7 = pOH$ $\Rightarrow$ For pure water at 25°C ; $pH = pOH = 7$

**(i)** If $[H^+] > 10^{-7}$ M in a solution i.e., solution is acidic then $pH < 7$

**(ii)** If $[H^+] < 10^{7}$ M (or $[OH^-] > 10^{-7}$ M) i.e. solution is basic then $pH > 7$



In general, we talk about pH of a solution, whether it is basic or acidic.

For an aqueous solution : $pH + pOH = pK_W$ [Use $K_w = [H^+][OH^-]$ and take "$\log_{10}$ on both sides]

At 25°C, $pH + pOH = pK_w = 14$ [$K_w = 1 \times 10^{-14}$ at 25°C]

Now one can very easily re-define pH of a basic solution as : $pH = 14 + \log_{10} [OH^-]$

***Note :*** "p" operator is generally applied on any variable whose value is < 1. In most of the cases, we will use $pK_w$, $pK_a$, $pK_b$ etc.

Also, we can see that as temperature increases, both pH and pOH of pure water will decrease since there will be an increase in $[H^+]$ and $[OH^-]$ due to increased dissociation.

## Dissociation constant $(K_a$ and $K_b)$ of conjugate ion of weak acid and weak base :

HA is a weak acid and $A^-$ is its conjugate base.

Dissociation equilibrium of HA :

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) : \; K_a = \frac{[H^+][A^-]}{[HA]} \qquad \ldots(i)$$

Dissociation equilibrium of conjugate base $A^-$ :

$$A^-(aq) + H_2O(\ell) \rightleftharpoons HA(aq) + OH^-(aq):\ K_b = \frac{[HA][OH^-]}{[A^-]} \qquad \text{...(ii)}$$

$$H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq) : K_W$$

$$\underline{H^+(aq) + A^-(aq) \rightleftharpoons HA(aq) : \frac{1}{K_a}}$$

$$A^-(aq) + H_2O(\ell) \rightleftharpoons HA(aq) + OH^-(aq): K_b$$

$$K_{a_{acid}} \times K_{b_{conjugate\,base}} = K_W \quad \Rightarrow \quad \boxed{pK_{a(HA)} + pK_{b(A^-)} = pK_w}$$

Similarly for dissociation constant of weak base $(K_b)$ and dissociation constant of conjugate acid $(K_a)$ we can write

$$K_{b_{weak\,base}} \times K_{a_{conjugate\,base}} = K_W \quad \Rightarrow \quad \boxed{pK_{b(BOH)} + pK_{a(B^+)} = pK_w}$$

## pH of a Weak Acid and Weak Base :

### Weak acid (HA)

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

For c molar HA, we have : $[H^+] = c\alpha$ $\Rightarrow$ $pH = -\log_{10} c\alpha$

Also : $\alpha = \sqrt{\frac{K_a}{c}}$ [If the approximation $1 - \alpha \approx 1$ is valid]

$$\Rightarrow \boxed{pH = -\log_{10}\sqrt{K_a c} = \frac{1}{2}(pK_a - \log_{10} c)}$$

### Weak base (BOH) :

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$$

For c molar BOH, we have : $[OH^-] = c\alpha$ $\Rightarrow$ $pH = 14 + \log_{10}[OH^-] = 14 + \log_{10} c\alpha$

Also : $\alpha = \sqrt{\frac{K_b}{c}}$ [If the approximation $1 - \alpha \approx 1$ is valid]

$$\Rightarrow \boxed{pH = 14 + \log_{10}\sqrt{K_b c} = 14 - \frac{1}{2}(pK_b - \log_{10} c)}$$

**Illustration - 1** *Determine the hydrogen ion concentration in* 1.0 *M solution of HCN, if its dissociation constant is* $4.0 \times 10^{-10}$

**SOLUTION :**

$$\begin{array}{lccc} & HCN\,(aq) & \rightleftharpoons H^{+}\,(aq) & + \; CN^{-}\,(aq) \\ & C & 0 & 0 \\ & C - C\alpha & C\alpha & C\alpha \end{array}$$

$[H^+] = c\alpha$ and $[H^+] = [CN^-]$

Use $\quad K_a = \dfrac{[H^+]^2}{c-[H^+]} \quad ; \quad c = 1.0\ M$

Neglecting $[H^+]$ against c, as the given acid is very weak ($K_a = 4.0 \times 10^{-10}$) and c is quite high.

i.e. $\quad c - [H^+] \approx c = 1.0\ M$ (given)

$$\Rightarrow \quad [H^+] = \sqrt{K_a c} = 2 \times 10^{-5} M$$

Now, check the approximation : $c - [H^+] \approx c$

$$\Rightarrow \quad c - [H^+] = 1''\ 2 \times 10^{-5} \approx 1.0\ M = c$$

Thus, the answer obtained as above is correct.

★★

**Illustration - 2** *What is the pH of a* 0.2 *M solution of acetic acid ? To what volume must one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value ?*
*Given :* $K_a = 2.0 \times 10^{-5}$

**SOLUTION :**

$$\begin{array}{lcc} CH_3COOH(aq) \rightleftharpoons & CH_3COO^-(aq) + & H^+(aq) \\ C & 0 & 0 \\ C - C\alpha & C\alpha & C\alpha \end{array}$$

$$\Rightarrow \quad K_a = \frac{[H^+]^2}{c-[H^+]} \approx \frac{[H^+]^2}{c}$$

(as $K_a$ is too Low)

Thus, $\quad [H^+] = \sqrt{K_a\,c} = 2 \times 10^{-3}\ M \quad ;$

Also, $\quad \alpha = \dfrac{[H^+]}{c} = 0.01 \Rightarrow c - [H^+] \approx c$

$\Rightarrow \quad pH = 2.7 \qquad (pH = -\log_{10}[H^+])$

Now solution is diluted to make pH = 5.4 (twice the original)

**Note :** *On dilution, α increases, so 1 – α can't be taken as unity. So solve the quadratic in α.*

For pH = 5.4, $[H^+] = 4 \times 10^{-6}$ M

(Doubling the pH value is simply equivalent to squaring the $[H^+]$)

Using : $\quad K_a = \dfrac{[H^+]^2}{c-[H^+]}$

$$\Rightarrow \quad c = [H^+] + \frac{[H^+]^2}{K_a} 4.8 \times 10^{-6}\ M$$

Check yourself that new degree of dissociation of acetic acid = $\alpha_{new} = \dfrac{[H^+]_{new}}{c_{new}} = 0.83$

which clearly suggests that using approximations would have generated poor/wrong results.

Originally the solution was 0.2 M and 1 L, using molarity equation we have :

$$4.8 \times 10^{-6} \times V = 0.2 \times 1$$

$$(C_1V_1 = C_2V_2)$$

$$\Rightarrow \quad V = 4.17 \times 10^{4}\ L3$$

**Illustration - 3** *Calculate* $[H^+]$ *and % dissociation of* 0.1 *M solution of ammonium hydroxide solution. The ionisation constant for* $NH_4OH$ *is* $K_b = 2.0 \times 10^{-5}$.

**SOLUTION :**

$$\begin{array}{lcccc} NH_4OH & \rightleftharpoons & NH_4^+ & + & OH^- \\ C & & 0 & & 0 \\ C - C\alpha & & C\alpha & & C\alpha \end{array}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{c\alpha^2}{1-\alpha} \approx c\alpha^2$$

(Neglecting $\alpha$, in denominator i.e. $1 - \alpha \sim 1$)

$$\Rightarrow \quad \alpha = \sqrt{\frac{K_b}{c}} = \sqrt{2 \times 10^{-4}}$$

$= 1.41 \times 10^{-2}$ $= 1.41$ %

[Check that $1 - \alpha \;\; 1$ holds]

and $[OH^-] = C\alpha = 0.1 \times 1.41 \times 10^{-2}$

$= 1.41 \times 10^{-3}$ M

$$\Rightarrow \quad [H^+] = \frac{K_w}{[OH^-]} = 7.09 \times 10^{-12} \text{ M}$$

**Illustration - 4** *Calculate the pH of* $10^{-8}$ *M HCl solution.*

**SOLUTION :**

$[HCl] = 10^{-8}$ M

$\Rightarrow$ $[H^+] = 10^{-8}$ M

$\Rightarrow$ pH = 8 which is absolutely wrong since the solution must be acidic as it is an acidic solution i.e., pH < 7

The catch here is that since HCl has been added in water (which also dissociates) so we need to consider $[H^+]$ from dissociation of $H_2O$ as well. In the earlier illustrations, we didn't consider this because $[H^+]$ from acid comes out to be much higher than that furnished by water but in this case we can not neglect the water contribution.

$$\begin{array}{lcccc} H_2O & \rightleftharpoons & H^+ & + & OH^- \\ & & x & & x \end{array}$$

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

$[H^+]_{total} = [H^+]_{acid} + [H^+]_{water} = 10^{-8} + x$

$\Rightarrow$ $K_w = (x + 10^{-8})\, x = 10^{-14}$

$\Rightarrow$ $x^2 + 10^{-8}\, x - 10^{-14} = 0$

Solve the above quadratic equation to get :

$x = 9.52 \times 10^{-8}$ M

Now, $[H^+]_{total} = 10^{-8} + 9.52 \times 10^{-8}$

$= 1.05 \times 10^{-7}$ M

$\Rightarrow$ pH $= -\log_{10} [1.05 \times 10^{-7}] = 6.978$

## COMMON ION EFFECT

The addition of an ionic salt having a common ion (anion or cation) to weak acids or weak bases, suppresses their degree of dissociation (following *LeChatelier's principle*).

### Weak Acids :

Let HA be a weak acid (like $CH_3COOH$, HCN etc) and $B^+A^-$ be the ionic salt (100% dissociation in solution) containing common anion ($A^-$) that is added to the acid.

$$\text{HA (aq)} \rightleftharpoons \text{H}^+\text{(aq)} + \text{A}^-\text{(aq)}$$

$$\text{BA (aq)} \longrightarrow \text{B}^+\text{(aq)} + \text{A}^-\text{(aq)}$$

Now, the solution has excess of $A^-$ ions. This means increasing concentration of products, in an equilibrium state, (following *LeChatelier's principle*) the reaction ($HA \rightleftharpoons H^+ + A$) must go in backward direction, in order to nullify the effect of added $A^-$ ions. As a consequence, amount of $H^+$ in new equilibrium state will be less than before, *or* one can see that the degree of dissociation of acid (HA) is decreased.

## Quantitative Aspect :

Consider a weak acid HA which dissociates as : $\quad \text{HA(aq)} \rightleftharpoons \text{H}^+\text{(aq)} + \text{A}^-\text{(aq)}$

Its degree of dissociation = $\alpha = \sqrt{\dfrac{K_a}{c}}$ [Assuming $K_a$ to be small]

Let M molar BA be added to it and $\alpha'$ be its new degree of dissociation

$$\begin{array}{lcccc} \text{BA} & \longrightarrow & \text{B}^+\text{(aq)} & + & \text{A}^-\text{(aq)} \\ & & \text{M} & & \text{M} \end{array}$$

(Assuming BA to be 100% ionised)

$$\begin{array}{lcccc} \text{HA} & \rightleftharpoons & \text{H}^+\text{(aq)} & + & \text{A}^-\text{(aq)} \\ c - c\alpha' & & c\alpha' & & c\alpha' \end{array}$$

Now in solution : $\quad [\text{HA}] = c - c\alpha' \quad ; \quad [\text{H}^+] = c\alpha'$

$$[\text{A}^-]_{\text{total}} = [\text{A}^-]_{\text{From HA}} + [\text{A}^-]_{\text{From BA}} = c\alpha' + \text{M}$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(c\alpha')(c\alpha' + \text{M})}{(c - c\alpha')} = \frac{\alpha'(c\alpha' + \text{M})}{1 - \alpha'}$$

$\Rightarrow \quad K_a = c\alpha'^2 + \text{M}\alpha' \quad$ (Assuming $1 - \alpha' \approx 1$)

$\Rightarrow \quad K_a = \text{M}\alpha' \quad$ (Neglecting $c\alpha'^2$ in comparison to $\text{M}\alpha'$ as $\alpha' << 1 \Rightarrow \alpha'^2 <<< 1$]

$\Rightarrow \quad \alpha' = \dfrac{K_a}{\text{M}}$

By looking at the expressions of $\alpha$ and $\alpha'$, we can clearly figure out that $\alpha' >> \alpha$]

***Note :*** On similar lines, you can find $\alpha'$ for a weak base, BOH and adding $B^+$ ions to it.

Also, expression for $K_a$ becomes : $K_a = \dfrac{[H^+][A^-]_{ext.}}{[HA]}$ where $[A^-]_{ext.}$ is the externally added salt

## Buffer Solutions

A solution whose pH does not change very much when $H^+$ ($H_3O^+$) or $OH^-$ are added to it is referred to as a *buffer solution*.

A *buffer solution* is prepared by mixing a weak acid and its salt having common anion (i.e. HA + BA forms an acidic Buffer) *or* a weak base and its salt having common cation (i.e. BOH + BA forms a Basic Buffer).

It can be prepared to have a desired value of pH by controlling the amounts of acids and their salts in case of acidic buffer and of bases and their salts in basic buffer.

**Acidic buffer :** $CH_3COOH + CH_3COONa$, $HCN + NaCN$

**Basic buffer :** $NH_4OH + NH_4Cl$

***Note :*** See yourself that buffer solutions are actually conjugate acid-base pairs.

Consider an *acidic buffer* containing an acid HA and say common ions $A^-$. Now, any $H^+$ (or $H_3O^+$) added externally to this solution with in certain limits are neutralized by $A^-$ ions as :

$$\underset{\text{external}}{H^+} + \underset{\text{from salt}}{A^-} \rightleftharpoons \underset{\text{undissociated acid}}{HA}$$

While, addition of $OH^-$ ions externally (with in certain limits) are neutralised by acid HA as :

$$HA + OH^- \rightleftharpoons H_2O + A^-$$

Hence in both the cases, effect of addition of $H^+$ or $OH^-$ is almost compensated for (i.e. pH almost remains constant).

Such a system (may be acidic or basic) finds enormous use not only in industrial processes but also (most importantly) in biological reactions. Like the pH of normal blood is 7.4 and for good health and even for the survival, it should not change below 7.1 or greater than 7.7, the body maintains it through a buffer system made of carbonate and bicarbonate ions and $H_2PO_4^-$ and $HPO_4^{2-}$. Similarly, the pH of gastric juice is kept constant in order to operate good digestive functions.

## pH of an Acidic Buffer

If [acid] = concentration of a weak acid and [salt] = concentration of the salt that is mixed with acid to make the buffer

We have : $[H^+] = \dfrac{K_a\,[HA]}{\left[A^-\right]_{ext.}} = \dfrac{K_a\,[acid]}{[salt]}$ [See the derivation in the Common Ion effect section]

$\Rightarrow$ $pH = pK_a + \log_{10}\dfrac{[salt]}{[acid]}$ $(pK_a = -\log_{10} K_a)$

## pH of a Basic Buffer

We have : pH = 14 – pOH

If [base] = concentration of weak base and [salt] = concentration of salt that is mixed to make the buffer

$$\Rightarrow \quad [OH^-] = \frac{K_b\,[BOH]}{\left[B^+\right]_{ext.}} = \frac{K_b\,[base]}{[salt]}$$

$$\Rightarrow \quad pOH = pK_b + \log_{10}\frac{[salt]}{[base]} \qquad (pK_b = -\log_{10} K_b)$$

$$\Rightarrow \quad pH = 14 - pK_b - \log_{10}\frac{[salt]}{[base]}$$

**Note :** The above equations representing the pH of a buffer are known as *Henderson's Equations*.

## pH of a Buffer (*When an acid or a base is added*)

We have just discussed that addition of $H^+$ ions or $OH^-$ ions to an acidic buffer ($HA/A^-$) does not appreciably changes the pH of buffer. Similarly, we can analyse the same for a basic buffer ($BOH/B^+$).

In actual, pH of a buffer solution changes by a small quantity. Let us calculate this change in pH quantitatively.

- Consider an acidic buffer $HA/A^-$ where [salt] = $[A^-]$ and [acid] = [HA]

An acidic buffer is rich in $A^-$ ions. Let us add *x* mole per litre of HCl to it. This added HCl ($H^+$) reacts with

$A^-$ (salt) to give undissociated acid as : $\quad H^+ + \underset{[salt]}{A^-} \longrightarrow \underset{[acid]}{HA}$

After adding *x* M $H^+$ ions : $\quad [salt - x] \qquad [acid + x]$

Now using *Henderson's Equation* : $pH\,(\text{original buffer}) = pK_a + \log_{10}\frac{[salt]}{[acid]}$ and pH (new)

$$= pK_a + \log_{10}\frac{[salt - x]}{[acid + x]}$$

$\Rightarrow$ pH of buffer *decreases*.

Change or difference in pH = pH (new) – pH (original)

Let us add $x$ M NaOH to the buffer. This added NaOH ($OH^-$ ions) react with acid (HA) to produce salt and $H_2O$.

$$OH^- + \underset{[\text{acid}]}{HA} \longrightarrow \underset{[\text{salt}]}{A^-} + H_2O$$

After adding $x$ M $OH^-$ ions : [acid – $x$] [salt + $x$]

$$\Rightarrow \quad \text{pH (new)} = pK_a + \log_{10}\frac{[\text{salt}+x]}{[\text{acid}-x]} \quad \Rightarrow \quad \text{pH of buffer } \textit{increases}.$$

Change in pH = pH (new) – pH (original)

***Note :*** **(i)** In exactly similar manner, we can calculate the change in pH of a basic buffer ($BOH/B^+$). Try to get a relation like this for basic buffer. Remember, it is not to be used as standard result.

**(ii)** A buffer solution is assumed to be destroyed if on addition of strong acid or base, its pH changes by ± 1 unit i.e.,
pH (new) = $pK_a \pm 1$ [if the initial pH of the buffer solution was $pK_a$].

This means the ratio $\frac{[\text{salt}]}{[\text{acid}]}$ OR $\frac{[\text{salt}]}{[\text{base}]}$ = 10 or 1/10.

## Illustration - 5

*To 1.0 L of a decimolar solution of acetic acid, how much dry sodium acetate be added (in moles) so as to decrease the concentration of $H^+$ ion to 1/10th of its previous value ?* $K_a = 2.0 \times 10^{-5}$.

**SOLUTION :**

$$CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-\ (aq) + H^+\ (aq)$$

$\Rightarrow \quad [H^+] = c\,\alpha = \sqrt{K_a c} = \sqrt{2.0\times10^{-5}\times0.1} = 1.41\times10^{-3}$ M [Ceck yourself that approximations are valid]

Note that when salt, $CH_3COONa$ is added, the solution will behave just like an acidic Buffer solution.

Using, Henderson equation : $pH = pK_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]} \quad \Rightarrow \quad [H^+] = K_a\frac{[\text{acid}]}{[\text{salt}]}$ or $[\text{salt}] = K_a\frac{[\text{acid}]}{[H^+]}$

Now, $[H^+]_{new} = \frac{1}{10}\times1.41\times10^{-3}\,M = 1.41\times10^{-4}$ M

$$\Rightarrow \quad [\text{salt}] = \frac{(2.0\times10^{-5})(0.1)}{1.41\times10^{-4}} = 0.0142\ M$$

$\Rightarrow$ moles of salt, sodium acetate = 0.0142 (≡ 14.2 mmoles) per 1.0 L is required. (V = 1.0 L)

**Illustration - 6** **(a)** *A buffer solution of pH value = 4 is to be prepared, using $CH_3COOH$ and $H_3COONa$. How much amount of sodium acetate is to be added to 1.0 L of M/10 acetic acid ?* $K_a = 2.0 \times 10^{-5}$.

**(b)** *What will be the pH if 0.01 mol of HCl is dissolved in the above Buffer solution ? Find the change in pH value.*

**(c)** *How will the pH be affected if 1.5 L of $H_2O$ is added to above buffer ?*

**SOLUTION :**

**(a)** For an acidic buffer containing acetic acid, $CH_3COOH$ and sodium acetate, $CH_3COONa$, we have :

$$[H^+] = \frac{K_a\,[\text{acid}]}{[\text{salt}]}$$

Use this rather than : $pH = pK_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]}$

$[CH_3COOH] = 0.1$ M ;

$[H^+] = 10^{-4}$ M and let $[CH_3COONa] = x$ M

$$\Rightarrow \quad [H^+] = 10^{-4} = \frac{2\times10^{-5}\times0.1}{x}$$

$\Rightarrow$ $x = 0.02$ moles i.e. 0.02 moles of $CH_3COONa$ is required.

**(b)** Now 0.01 mol of HCl ($[H^+] = 0.01$ M) is added to 1 L of buffer, this will react with acetate ion ($CH_3COO^-$ ) as :

$$\begin{array}{ccccc} CH_3COO^- & + & H^+ & \longrightarrow & CH_3COOH \\ 0.02 & & 0.005 & & 0.1 \\ 0.015 & & & & 0.105 \end{array}$$

$\Rightarrow$ [acid] = 0.11 M and [salt] = 0.01 M [V = 1.0 L]

$$\Rightarrow \quad pH_{new} = pK_a + \log_{10}\frac{0.015}{0.105}$$

$= 4.7 + (-0.84) = 3.86$ [Use $\log_{10}7 = 1.0.84$]

$\Rightarrow$ Change in pH = 3.86 – 4.0 = -0.14

**(c)** Now, if 1.5 L of $H_2O$ is added, it just increases the volume, thereby decreasing concentrations of both acid and salt. The ratio $\log_{10}\frac{[\text{salt}]}{[\text{acid}]}$ remains constant.

Hence pH remains same.

**Illustration - 7** *How many of the following combination can act as buffer.*

**(i)** $HCl + NaOH$

**(ii)** $HCl + CH_3COO^-Na^+$

**(iii)** $H_2SO_4 + NaHSO_4$

**(iv)** $H_2CO_3 + NaOH$

**(v)** $NaOH + PhCOOH$

**(vi)** $HBr + NH_4OH$

**(vii)** $CH_3COOH + NH_4OH$

**(viii)** $NaOH + NH_4OH$

**(ix)** $HCl + CH_3COOH$

**(x)** *Borax* $(Na_2B_4O_7)$ + *Boric acid* $(H_3BO_3)$

**(xi)** $NaH_2PO_4 + Na_2HPO_4$

**(xii)** $Na_2CO_3 + NaHCO_3$

**SOLUTION :**

As we know that buffer is a mixture having weak acid and its salt with strong base or weak base and its salt with strong acid. Further a mixture of acid and base may also acid and base may also acts as buffer depend -ing on the nature of acid and base (strong or weak) and their moles taken for preparation of mixture, because acid and base reacts to form salt. The combination (i) and (iii) can't acts as buffer because it does not contain weak electrolyte (weak acid or base) but combination (ii) can act as buffer if axcess of $CH_3COONa$ is mixed with limited amount of HCl.

$$CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$$

| | | | | | |
|---|---|---|---|---|---|
| Initially | a | b | 0 | 0 | (a > b) |
| After mixing | (a − b) | 0 | b | b | |

Resulting mixture contains weak acid $(CH_3COOH)$ and its salt with strong base $(CH_3COONa)$. Similarly combinations $(H_2CO_3 + NaOH), (PhCOOH + NaOH), (NH_4OH + HBr)$ can also act as buffer.

$$H_2CO_3 + 2\,NaOH \longrightarrow Na_2CO_3 + H_2O$$

| | | | | |
|---|---|---|---|---|
| Initially | a | 2b | 0 | – |
| After mixing | (a − b) | 0 | b | – |

$$H_2CO_3 + NaOH \longrightarrow NaCO_3 + H_2O$$

| | | | | |
|---|---|---|---|---|
| Initially | a | b | 0 | – |
| After mixing | (a − b) | 0 | b | – |

$$PhCOOH + NaOH \longrightarrow PhCOONa + H_2O$$

| | | | | |
|---|---|---|---|---|
| Initially | a | b | 0 | – |
| After mixing | (a − b) | 0 | b | – |

$$NH_4OH + HBr \longrightarrow NH_4Br + H_2O$$

| | | | | |
|---|---|---|---|---|
| Initially | a | b | 0 | – |
| After mixing | (a − b) | 0 | b | – |

The combinations(viii) and (ix) can't acts as buffer because salt component is missing.
Mixture of two salts of weak polyprotic acid can also acts as buffer because because in such cases we will visualize a mixture of acid and its conjugate base as salt.

$NaHCO_3$ [having weak acid $HCO_3^-$ ] and $Na_2CO_3$ [having conjugate base $CO_3^{2-}$ ] acts as buffer.

Hence the combination (ii), (iv), (v), (vi), (vii), (x), (xi) and (xii) can acts as buffer.

**Illustration - 8** *The pH of blood stream is maintained by a proper balance of* $H_2CO_3$ *and* $NaHCO_3$ *concentrations. What volume of* 5*M* $NaHCO_3$ *solution, should be mixed* with 10 *mL sample of blood which is* 2*M in* $H_2CO_3$ *in order to maintain a pH of* 7.4 $K_a$ *for* $H_2CO_3$ *in blood is* $4.0 \times 10^{-7}$ ?

**SOLUTION :**

$[H_2CO_3]$ in blood = 2M

Volume of blood = 10 mL

$[NaHCO_3]$ = 5M

Let volume of $NaHCO_3$ used = V mL

$$[H_2CO_3] \text{ in mixture} = \frac{2 \times 10}{(V + 10)}$$

$$[NaHCO_3] \text{ in mixture} = \frac{(5 \times V)}{(V + 10)}$$

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

$$7.4 = \log 7.8 \times 10^7 + \log \frac{(5 \times V)/(V+10)}{(2 \times 10)/(V+10)}$$

V = 40 mL

**Illustration - 9** *Consider a buffer solution containing* 0.1 *mole each of acetic acid and sodium acetate in* 1.0 *L of solution.* 0.01 *mole of NaOH is gradually added to this buffer solution. Calculate the new* $[H^+]$ *is the resulting solution.* $[K_a = 2 \times 10^{-5}]$

**SOLUTION :**

pH of the solution is given by :

$$pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$$

Initial pH of solution :

$$pH = pK_a + \log_{10} \frac{0.1}{0.1} = 4.7$$

When 0.01 M NaOH is added,

[salt] = 0.11 M and [acid] = 0.09 M

⇒ Final pH of solution :

$$pH = pK_a + \log_{10} \frac{0.11}{0.09} = 4.787$$

$$\Rightarrow \quad [H^+] = K_a \frac{[acid]}{[salt]}$$

$$= 2 \times 10^{-5} \times \frac{0.09}{0.11} = 1.64 \times 10^{-5} M$$

**Illustration - 10** 500 ml of 0.2 *m aqueous solution of acetic acid is mixed with* 500 *ml of* 0.2 *M HCl at* 25°*C*.

**(i)** *Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.*

**(ii)** *If 6g of NaOH is added to the above solution, determine the final pH.* $[K_{a\,\text{acetic acid}} = 2 \times 10^{-5}]$

**SOLUTION :**

**(i)** $$[CH_3COOH]_{\text{Just after mising}} = \frac{0.2}{2} = 0.1M$$

$$[HCl]_{\text{just after mising}} = \frac{0.2}{2} = 0.1M = [H^+]_{\text{From HCl}}$$

**Note :** Equal volumes added.

$$\begin{array}{lcccc} & CH_3COOH & \rightleftharpoons CH_3COO^- & + & H^+ \\ \underset{\text{(conc.)}}{i=0} & c & 0 & & 0 \\ t=i_{eq} & c-c\alpha & c\alpha & & c\alpha \end{array}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha.(c\alpha+0.1)}{c-c\alpha}$$

$$\left[\because [H^+]_{Total} = [H^+]_{From\ CH_3COOH} + [H^+]_{From\ HCl}\right]$$

$\Rightarrow \quad c\alpha + 0.1 \sim 0.1\ ;\ c - c\alpha \sim c$

[ $\because$ $\alpha$ will be small due to common ion effect]

$\Rightarrow \quad K_a \sim \alpha \times 0.1$

$\Rightarrow \quad \alpha = \dfrac{\mathrm{K_a}}{0.1} = 2\times10^{-4}$ [Check : $1-\alpha = 1-2\times10^{-4} \sim 1$] and

$$[\mathrm{H^+}]_{\mathrm{Total}} = c\alpha + 0.1 = 0.1\times2\times10^{-4} + 0.1 \sim 0.1\mathrm{M}$$

$\Rightarrow \quad \mathrm{pH} = 1$

**(ii)** 6gm NaOH $\equiv \dfrac{6}{40/1} = 0.15$ gmeq $\equiv 150$ mmoles NaOH

Mmoles HCl = $500 \times 0.2 = 100$ mmoles.

NaOH will first react with HCl and if there is a leftover then it will react with $\mathrm{CH_3COOH}$

$\Rightarrow$ Mmoles NaOH left $= 150 - 100 = 50$

These will react with $\mathrm{CH_3COOH}$ as :

$$\begin{array}{ccccccc} \mathrm{NaOH} & + & \mathrm{CH_3COOH} & \rightleftharpoons & \mathrm{CH_3COONa} & + & \mathrm{H_2O} \\ 50 & & 100 & & - & & \\ - & & 50 & & 50 & & \end{array}$$

$\Rightarrow$ Formation of an acidic buffer

$$\Rightarrow \quad \mathrm{pH} = \mathrm{pK_a} + \log_{10}\frac{[\mathrm{Salt}]}{[\mathrm{Acid}]}$$

$$= 4.7 + \log_{10}\frac{50/\mathrm{V_{Total}}}{50/\mathrm{V_{Total}}} = 4.7$$

## HYDROLYSIS OF SALTS

It involves the study of the reactions between a salt and water to yield an acid and a base. The salts are generally ionised in water. Here we will deal with salts which are almost fully soluble (not sparingly soluble salts).

Water in the presence of ionic impurites is visualized as follows :

$$H_2O\,(aq) \rightleftharpoons H^+\,(aq) + OH^-\,(aq) \text{ with } [H^+] = [OH^-] \text{ (i.e neutral)}$$

Now, when a salt is put in the water, there is an interaction between ions of salt and ions of water. The phenomenon of interaction of cations and anions of the salts with $H^+$ and $OH^-$ ions furnished by water so that there is some net change in the pH of the resulting solution is known as *Hydrolysis of a salt.*

Four cases have been discussed here to understand the behavior of various type of salts.

### 1. Salts of strong acids and strong bases [SA-SB]

When such salts are dissolved in water, they do not undergo hydrolysis. They simply ionises and fail to change the $H^+$ ion concentration of solution and hence the pH of the solution remains same. e.g. NaCl, $CaCl_2$, $BaCl_2$, KCl, $NaNO_3$, $Na_2SO_4$, $Ca(NO_3)_2$

$$NaCl\,(aq) \rightleftharpoons Na^+\,(aq) + Cl^-\,(aq)$$

$$H_2O\,(aq) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

The final pH of the solution remains 7 at 25°C.
(*If NaOH and HCl are formed, they neutralises each other to keep the pH same*)

### 2. Salts of weak acids and strong bases [WA-SB]

Such salts give alkaline solutions in water. Some of such salts are : $CH_3COONa$, $Na_2CO_3$, $K_2CO_3$, KCN etc . For our discussion, we consider $CH_3COONa$ (sodium acetate) in water. When $CH_3COONa$ is put in water, it completely ionises to give $CH_3COO^-$ (acetate) ions and $Na^+$ ions.

Now acetate ions ($CH_3COO^-$) absorb some $H^+$ ions from weakly dissociated $H_2O$ molecules to form undissociated $CH_3COOH$. $Na^+$ remains in ionic state in water.

Now for $K_w$ (ionic product) of water to remain constant, $H_2O$ further ionises to produce more $H^+$ and $OH^-$ ions. $H^+$ ions are taken up by $CH_3COO^-$ ions leaving $OH^-$ ions in excess and hence an alkaline solution.

Let BA represents such a salt. As it is put in water ;

$$BA\,(aq) + H_2O\,(aq) \rightleftharpoons BOH\,(aq) + HA\,(aq)$$

BA dissociates into ions and BOH being strong base also ionises.

$$B^+ + A^- + H_2O \rightleftharpoons B^+\,(aq) + OH^-\,(aq) + HA\,(aq)$$

So, the net reaction is : $A^-\,(aq) + H_2O \rightleftharpoons OH^-\,(aq) + HA\,(aq)$ [Anionic Hydrolysis]

The above equation is known as *equation of hydrolysis* and equilibrium constant for such reactions is called as *Hydrolysis Constant* ($K_h$).

$$K_h = \frac{[OH^-][HA]}{[A^-]}$$

## Degree of Hydrolysis :

It is defined as the fraction of total salt that has undergone hydrolysis on attainment of equilibrium. It is denoted by *h*.

Let *c* be the concentration of salt and *h* be its degree of hydrolysis.

$$\begin{array}{lllllllll} A^- & + & H_2O & \rightleftharpoons & OH^- & + & HA & & \text{(Equation of hydrolysis)} \\ c & & & & & & & & \\ c - ch & & & & ch & & ch & & \end{array}$$

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

$$\Rightarrow \quad K_h = ch^2 \qquad [\text{assuming } h << 1] \qquad \Rightarrow \quad h = \sqrt{\frac{K_h}{c}}$$

Now considering, dissociations of weak acid HA and $H_2O$

$$HA \rightleftharpoons H^+ + A^- \quad ; \quad K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{. . . . (i)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad ; \quad K_w = [H^+][OH^-] \qquad \text{. . . . (ii)}$$

$$\Rightarrow \quad K_h = \frac{K_w}{K_a}$$

(Subtracting (i) from (ii), we get equation of hydrolysis)

**Note :**
- Weaker is the acid, greater is the hydrolysis constant.
- Degree of hydrolysis increases when 'c' decreases i.e. with dilution.

Now substituting the value of $K_h$ in expression of *h*,

$$\Rightarrow \quad h = \sqrt{\frac{K_w}{K_a c}}$$

## pH of solution :

pH of a basic solution is given as :

$$pH = 14 + \log[OH^-] \qquad \text{and} \qquad [OH^-] = ch = \sqrt{K_h c}$$

Substituting for $K_h$ , we get :

$$[OH^-] = \sqrt{\frac{K_w c}{K_a}} \quad \Rightarrow \quad pH = 14 + \log_{10}\sqrt{\frac{K_w c}{K_a}}$$

$$\Rightarrow \quad pH = \frac{1}{2}(pK_w + pK_a + \log_{10} c) \quad \text{or} \quad pH\ (\text{at } 25°C) = 7 + \frac{1}{2}(pK_a + \log_{10} c)$$

## 3. Salts of strong acids and weak bases [SA-SB]

Such salts give acidic solutions in water. Some of such salts are : $NH_4Cl$, $ZnCl_2$, $FeCl_3$ etc. For the purpose of discussion, we will consider hydrolysis of $NH_4Cl$.

When $NH_4Cl$ is put in water, it completely ionises in water to give $NH_4^+$ and $Cl^-$ ions. $NH_4^+$ ions combine with $OH^-$ ions furnished by weakly dissociated water to form $NH_4OH$ (weak base). Now for keeping $K_w$ constant, water further ionises to give $H^+$ and $OH^-$ ions, where $OH^-$ ions are consumed by $NH_4^+$ ions leaving behind $H^+$ ions in solution to give an acidic solution.

Let BA be one of such salts. When it is put into water, the reaction is as follows.

$$B^+ + A^- + H_2O \rightleftharpoons BOH + H^+(aq) + A^-(aq) \qquad [\text{HA is strong acid}]$$

The net reaction of hydrolysis is :

$$\underset{c-ch}{B^+} + H_2O \rightleftharpoons \underset{ch}{BOH\,(aq)} + \underset{ch}{H^+(aq)} \qquad [\text{Cationic Hydrolysis}]$$

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

Considering ionisation of weak base BOH and $H_2O$.

$$BOH \rightleftharpoons B^+ + OH^- \quad ; \quad K_b = \frac{[B^+][[OH^-]}{[BOH]}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad ; \quad K_w = [H^+]\,[OH^-]$$

From expressions for $K_h$, $K_b$ and $K_w$ , we have : (As done in previous case)

$$K_h = \frac{K_w}{K_b} \quad \Rightarrow \quad h = \sqrt{\frac{K_w}{K_b c}}$$

## pH of solution :

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

$$\text{and} \quad [H^+] = ch = c\sqrt{\frac{K_h}{c}} = \sqrt{K_h c} \quad \Rightarrow \quad [H^+] = \sqrt{\frac{K_w c}{K_b}}$$

$$\Rightarrow \quad pH = -\log_{10}\sqrt{\frac{K_w c}{K_b}}$$

$$\Rightarrow \quad pH = \frac{1}{2}\left(pK_w - pK_b - \log_{10} c\right) \qquad \text{or} \qquad pH\ (\text{at } 25°C) = 7 - \frac{1}{2}\left(pK_b + \log_{10} c\right)$$

***Try Your Self :***

**1.** Calculate pH of M/100 solution of $CH_3COONa$ at 25°C where $K_a$ of $CH_3COOH$ is $2.0 \times 10^{-5}$.
[Ans : 8.37]

**2.** Calculate pH of M/100 solution of $NH_4Cl$ at 25°C where $K_b$ for $NH_4Cl$ is $2.0 \times 10^{-5}$.
[Ans : 5.63]

**3.** In above two cases, find the degree of hydrolysis taking $K_w = 10^{-14}$.

***Note :*** The results of above two cases of hydrolysis of salts can be used directly.

## 4. Salts of weak acids and weak bases [WA-WB]

Let us consider ammonium acetate ($CH_3COONH_4$) for our discussion. Both $NH_4^+$ ions and $CH_3COO^-$ ions react respectively with $OH^-$ and $H^+$ ions furnished by water to form $NH_4OH$ (weak base) and $CH_3COOH$ (acetic acid).

Let BA represents such a salt.

$$B^+ + A^- + H_2O \rightleftharpoons \underset{(\text{weak base})}{BOH} + \underset{(\text{weak acid})}{HA}$$

| | $B^+$ | $A^-$ | $BOH$ | $HA$ |
|---|---|---|---|---|
| Initially | c | c | 0 | |
| At equilibrium | c – ch | c – ch | ch | ch |

$$\Rightarrow \quad K_h = \frac{[BOH][HA]}{[B^+][A^-]} = \frac{(ch)(ch)}{(c-ch)^2}$$

$$\Rightarrow \quad K_h = \frac{h^2}{(1-h)^2} \ ;$$

Taking square root on both sides to get :

$$h = \frac{\sqrt{K_h}}{1+\sqrt{K_h}} \qquad (\text{Here, } 1-h \neq; \text{ Think why?})$$

Hence the degree of hydrolysis of such salts is independent of concentration of salt solution.

Now considering the dissociation of both weak base and acid.

$$HA \rightleftharpoons H^+ + A^- \quad ; \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$BOH \rightleftharpoons B^+ + OH^- \quad ; \quad K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad ; \quad K_w = [H^+][OH^-]$$

Combining $K_h$, $K_b$, $K_a$ and $K_w$, we have

$$K_h = \frac{K_w}{K_a K_b} \quad \text{and} \quad h = \sqrt{\frac{K_h}{1+\sqrt{K_h}}} \qquad \text{[Cation - Anionic Hydrolysis]}$$

(Observe that $1-h \neq 1$)

## pH of Solution :

Consider, $K_a = \dfrac{[H^+][A^-]}{[HA]} \quad \Rightarrow \quad [H^+] = K_a \dfrac{[HA]}{[A^-]}$

Since, base and acids are weaker, hence,

$$[BOH] = [HA] \quad \Rightarrow \quad [B^+] = [A^-]$$

$$\Rightarrow \quad K_h = \frac{[BOH][HA]}{[B^+][A^-]} = \frac{[HA]^2}{[A^-]^2} \quad \Rightarrow \quad [H^+] = K_a\sqrt{K_h} = \sqrt{\frac{K_w K_a}{K_b}}$$

$$pH = -\log[H^+] = -\log\sqrt{\frac{K_w K_a}{K_b}}$$

$$\Rightarrow \quad pH = \frac{1}{2}\left(pK_w + pK_a - pK_b\right) \quad \text{or} \quad \text{at } 25°C, \quad pH = 7 + \frac{1}{2}\left(pK_a - pK_b\right)$$

### *Illutrating the concept* :

*What is the pH of a* 0.50 *M aqueous NaCN solution* ? $pK_b$ *of* $CN^-$ *is* 4.70.

### SOLUTION :

NaCN is a salt of weak acid and strong base. The pH of its aqueous solution is given by :

$$pH\ (\text{at } 25°C) = 7 + \frac{1}{2}\ (pK_a + \log_{10} c)$$

Remember that for any acid and its conjugate base or vice-versa : $pK_a + pK_b = pK_w$

e.g. For acid (say HA), $pK_a$ corresponds to HA and $pK_b$ corresponds to its conjugate base : $A^-$

Thus, $pK_a$ of HCN = 14 – 4.7 = 9.3

So, $pH\ (\text{at } 25°C) = 7 + \frac{1}{2}\ (pK_a + \log_{10} c) = 7 + \frac{1}{2}(9.3 + \log_{10}\ 0.5) = 11.5$

**Illustration - 11** *Calculate the degree of hydrolysis of a mixture of aniline and acetic acid each of them being 0.01 M. $K_a$ of acetic acid = $1.8 \times 10^{-5}$ and $K_b$ (aniline) = $4.5 \times 10^{-10}$. Also calculate pH of the mixture.*

**SOLUTION :**

$$\mathrm{C_6H_5NH_2 + CH_3COOH \rightleftharpoons \underset{(Acetanilide)}{C_6H_5NHCOCH_3} + H_2O}$$

Now when we mix equal concentrations of aniline and acetic acid, they will neutralise each other to form acetanilide (salt). The salt is of weak base and weak acid, so hydrolysis takes place. The degree of hydrolysis of the salt of weak acid and weak base is given by :

$$h = \frac{\sqrt{K_h}}{1+\sqrt{K_h}}$$

Here, $K_h = \dfrac{K_w}{K_a \cdot K_b} = \dfrac{10^{-14}}{1.8 \times 10^{-5} \times 4.5 \times 10^{-10}}$

$= 1.23$

$\Rightarrow$ $h = 0.52$

However the pH of solution can be calculated by using the standard result :

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

$$\Rightarrow \quad pH = 7 + \frac{1}{2}\left[-\log_{10} 1.8\times10^{-5} - \left(-\log_{10} 4.5\times10^{-10}\right)\right]$$

$$\Rightarrow \quad pH = 7 + \frac{1}{2}\log_{10}\frac{4.5 \times 10^{-10}}{1.8 \times 10^{-5}} = 4.7$$

**Note :**

- Solution in this case is acidic. In such salts, pH depends upon which of two i.e. weak acid or weak base is stronger than the other, i.e. by comparing $K_a$ and $K_b$; one can theoretically get an idea about the pH of solution.
- The formula $pH = 7 + \frac{1}{2}(pK_a - pK_b)$ is applicable even when '*h*' is large as no approximation of '*h*' comparison with unity, has been taken in the derivation (see derivation yourself).

★★

**Illustration - 12** *2.5 mL of 0.4 M weak mono-acidic base* $\left(K_b = 1\times10^{-12}\ at\ 25^\circ C\right)$ *is titrated with 2/15 M HCl in water at 25°C. Find the concentration of H⁺ ions at equivalence point.* $\left(K_w = 1\times10^{-14}\ at\ 25^\circ C\right)$

**SOLUTION :**

First find the volume of HCl required to reach the equivalence point.

meq. of Base = meq of HCl

$$\Rightarrow \qquad 2.5\times(0.4\times1) = \left(\frac{2}{15}\times1\right)V_{HCl}$$

$$\Rightarrow \qquad V_{HCl} = 7.5\,mL$$

The net volume of the solution at the equivalent point = $V_{base} + V_{HCl} = 2.5 + 7.5 = 10$ mL

$$\Rightarrow \qquad [salt] = c = \frac{0.4\times2.5}{10} = 0.1M$$

pH of an aqueous solution of such a salt is given by :

$$pH = 7 - \frac{1}{2}\left(pK_b + \log_{10} c\right) = 7 - \frac{1}{2}\left(12 + \log_{10} 0.1\right) = 1.5$$

$$\Rightarrow \qquad \left[H^+\right] = 10^{-1.5} = \frac{1}{10\sqrt{10}} \approx 3.2\times10^{-2}\ M$$

Please note that the above solution is Incorrect. (Why?)

Actually, $pH = 7 - \frac{1}{2}\left(pK_b + \log_{10} c\right)$ is valid only when $1 - h \approx 1$

To check, calculate *h* using :

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_b\,c}} = \sqrt{\frac{10^{-14}}{10^{-12}\times0.1}} = \sqrt{0.1} \qquad \Rightarrow \qquad 1 - \sqrt{0.1} \neq 1$$

So we have solve from basics as follows :

$$\begin{array}{lcccc} B^+ + H_2O & \rightleftharpoons & BOH & + & H^+ \\ c - ch & & ch & & ch \end{array}$$

$$\Rightarrow \qquad K_h = \frac{[BOH][H^+]}{[B^+]} = \frac{(ch)(ch)}{c - ch} \qquad \Rightarrow \qquad K_h = \frac{K_w}{K_b} = 10^{-2} = \frac{[H^+]^2}{c - [H^+]} \qquad \left(ch = [H^+]\right)$$

$$\Rightarrow \qquad [H^+] = -\frac{10^{-2} + \sqrt{10^{-4} + 4\times10^{-3}}}{2} = 2.7\times10^{-2}\ M$$

## SOLUBILITY PRODUCT ($K_{sp}$) AND PRECIPITATION OF SALTS — Section - 5

Here, we will study those salts which are generally considered as insoluble in water. (e.g. AgCl, $BaSO_4$, $Ag_2S$, PbS etc) Actually no insoluble salt is actually completely insoluble, they have a very small solubility. Consider a vessel containing water with a sufficient amount of AgCl being put into it. A very small amount of it dissolves in water (*because generally salts are composed of ions or contain polarised atoms*). The small amount which is soluble is almost 100% ionised.

The situation achieved at this stage is *Dynamic* in nature; with same of ions (soluble) being solidifying and some solid always dissolving. Thus a state of equilibrium exists (like in earlier cases). This means at a given temperature, the concentration of $Ag^+$ ions and $Cl^-$ ions in aqueous solution remains constant. The following equilibrium exists. In this equilibrium, the equilibrium state is known as *Saturated state*.

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^- \qquad [\text{insoluble} \rightleftharpoons \text{soluble (ions)}]$$

The equilibrium constant for this reaction is known as *solubility product* ($K_{sp}$) and is written as :

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

$K_{sp}$ is expressed in concentration units. The reaction coefficient, Q in such system is known as ionic product (I.P)

**Note :**

- The solubility of a salt in water depends upon other substances (ions) present is water (at that time) and the solubility product is a constant value (at a given temperature) and is independent of presence of any other ion present. Like other equilibrium constants such as : $K_p$, $K_c$, $K_a$ and $K_b$ , it is also constant at a certain temperature and can change only when temperature changes.
- The salts like AgCl are regarded as sparingly soluble salts. Some of them are : $Ag_2SO_4$, $Ag_2CO_3$, $PbCl_2$, $PbCrO_4$, PbS, ZnS, $Al(OH)_3$, $Ca_3(PO_4)_2$, $BaSO_4$, $CaSO_4$, MnS etc.

$K_{sp}$ for $Ag_2SO_4$ :

$$Ag_2SO_4(s) + aq. \rightleftharpoons 2Ag^+ + SO_4^{2-}(aq)$$

$$K_{sp} = [Ag^+]^2[SO_4^{2-}]$$

$K_{sp}$ for $Ca_3(PO_4)_2$ :

$$Ca_3(PO_4)_2(s) + aq. \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}(aq)$$

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

**Note :** In the solubilities of sparingly soluble salts, we will deal with mainly two types of problems : one to find out the solubility in water if $K_{sp}$ of a salt is given and vice-versa. Second, to find out solubility of a salt in presence of other (common) ions in water.

**Illustration - 13** *If $K_{sp}$ of calcium iodate $Ca(IO_3)_3 = 6.3 \times 10^{-7}$ at 18°C, find the solubility of salt in (i) gm/L (ii) mol/L in water at 18°C.*

**SOLUTION :**

In questions, solubility is sometime asked (or given) to be expressed in gm/L.

Now the following equilibrium is established :

$$Ca(IO_3)_2 \rightleftharpoons Ca^{2+}(aq) + 2IO_3^-(aq)$$

Let $x$ mole/L be solubility of $Ca(IO_3)_2$ in water

$\Rightarrow \quad [Ca^{2+}] = x\text{ M} \quad$ and $\quad [IO_3^-] = 2x\text{ M}$

Now, $\quad K_{sp} = [Ca^{2+}][IO_3^-]^2$

$\Rightarrow \quad 6.3 \times 10^{-7} = (x)(2x)^2$

$\Rightarrow \quad 4x^3 = 6.3 \times 10^{-7}$

$\Rightarrow \quad x = 5.4 \times 10^{-3}$ M.

Now answer is to expressed in gm/L

$\Rightarrow \quad$ solubility $= x \times M_0$

$= (5.4 \times 10^{-3}) \times 390 = 2.106$ g/L

**Illustration - 14** *The $K_{sp}$ of AgCl at 25°C is $1.5 \times 10^{-10}$. Find the solubility of AgCl (in gm/L) in an aqueous solution containing 0.01 M $AgNO_3$.*

**SOLUTION :**

Now this is quite similar to finding the degree of dissociation of a weak acid or weak base in presence of its common ion (Le Chatelier's principle).

Here 0.01 M $AgNO_3$ will give 0.01 M $Ag^+$ ions in solution before the addition of AgCl.

($AgNO_3$ is 100% soluble in water).

Let the solubility be c mol/L in $AgNO_3$.

$$\underset{}{AgCl} \rightleftharpoons \underset{c}{Ag^+} + \underset{c}{Cl^-}$$

$$AgNO_3 \longrightarrow \underset{0.01M}{Ag^+} + NO_3^-$$

In solution :

$[Ag^+] = c + 0.01 \quad$ and $\quad [Cl^-] = c$

Now $K_{sp}$ is a constant and is independent of presence of any ion in water.

$\Rightarrow \quad K_{sp} = [Ag^+][Cl^-] = (0.01 + c)(c) = 1.50 \times 10^{-10}$

(Now assuming $0.01 + c \sim 0.01$ as $c << 1$ for sparingly soluble salt)

$$\Rightarrow \quad c = \frac{K_{sp}}{0.01} = 1.5 \times 10^{-8}\text{ M}$$

[Check that $c + 0.01 \approx 0.01$ M]

or $\quad$ solubility $= (1.5 \times 10^{-8}) \times 143.5 = 2.15 \times 10^6$ g/L

***Note :*** The solubility of AgCl in water containing $Ag^+$ (a common ion) is much less than in pure water.

**Illustration - 15** *The solubility of $BaSO_4$ in water is $2.33 \times 10^{-4}$ gm/100 mL. Calculate the % age loss in weight when 0.2 gm of $BaSO_4$ is washed with*

**(a)** *1 L of water* **(b)** *1 L of 0.01 N $H_2SO_4$.* $\left[M_{0\ BaSO_4} = 233\ gm/mol\right]$

**SOLUTION :**

**(a)** Solubility is in general expressed in gm/L,

so solubility of $BaSO_4 = 2.33 \times 10^{-3}\ g/L$

Loss in weight of $BaSO_4$ = amount of $BaSO_4$ soluble.

$$\Rightarrow \quad \%\ \text{loss} = \frac{2.33 \times 10^{-3}}{0.2} \times 100 = 1.16\ \%$$

**(b)** $0.01\ N\ H_2SO_4 \equiv 0.01\ N\ SO_4^{2-}$ ions

$\equiv 0.005\ M\ SO_4^{2-}$ ions

Now presence of $SO_4^{2-}$ prior to washing $BaSO_4$ will suppress the solubility of $BaSO_4$ (*due to common ion effect*). The suppression will be governed by $K_{sp}$ value of $BaSO_4$. So first calculate $K_{sp}$ of $BaSO_4$.

Solubility of $BaSO_4$ in fresh water

$= 2.33 \times 10^{-3}$ g/L

$$\equiv \frac{2.33 \times 10^{-3}}{233}\ \text{mol/L} = 10^{-5}\ M$$

$K_{sp} = [\ Ba^{2+}]\ [\ SO_4^{2-}] = (10^{-5})^2 = 10^{10}$

Now let $x$ be solubility in mol/L in $H_2SO_4$

$\Rightarrow \quad [Ba^{2+}]$ in solution $= x$ mol/L

and $\quad [\ SO_4^{2-}]$ in solution $= (x + 0.005)$ mol/L

Ionic product $= [\ Ba^{2+}]\ [SO_4^{2-}]$

$= (x)\ (x + 0.005)$

$K_{sp}$ = Ionic Product at equilibrium (saturation)

$\Rightarrow \quad 1.0 \times 10^{-10} = (x)\ (x + 0.005)$

Assuming $x$ to be a small number

$x + 0.005 \sim 0.005$

$$\Rightarrow \quad x = \frac{10^{-10}}{0.005} = 2 \times 10^{-8}\ \text{mol/L}$$

$= 2 \times 10^{-8} \times 233$ g/L

$= 4.66 \times 10^{-6}$ g/L

$\Rightarrow \quad 4.66 \times 10^{-6}$ gm of $BaSO_4$ are washed away.

$$\Rightarrow \quad \%\ \text{loss} = \frac{4.66 \times 10^{-6} \times 100}{0.2}$$

$= 2.33 \times 10^{-3}\ \%$

**Note :** Third type of problem are related to the precipitation of salts (sparingly soluble). To understand and solve such problems, let us read following article carefully.

## Precipitation of salts

Now we will study (application of $K_{sp}$) how to determine whether or not a precipitate will form when we mix known concentrations of ions which combine to give a sparingly soluble salt. To understand and solve such problems let us analyse the expression of solubility product.

For a salt (sparingly soluble) when dissolved in water : $\quad BA \rightleftharpoons B^+\ (aq) + A^-\ (aq)$

At equilibrium (saturation) : $\quad K_{sp} = [B^+]\ [A^-]$

When we mix ions or if there be two or more ions in water, we define reaction coefficient ($Q$) called as *ionic-product (I.P.)*, giving the products of ions in water (ions of soluble salts and other common ions).

I.P. is product of ionic concentration due to ions already present in water or from a salt. It may be and may not be equal to $K_{sp}$. To illustrate it more clearly, consider a case when 500 ml of 0.005 M solution of $AgNO_3$ is added to 500 ml of 0.001 M solution of KCl. Now in solution (mixture), there are $Ag^+$, $NO_3^-$, $K^+$ and $Cl^-$ ions. The concentration of $[Ag^+] = [NO_3^-] = 0.005/2 = 0.0025$ M (*equal volumes are mixed*) and $[K^+] = [Cl^-] = \frac{0.001}{2} = 0.0005\,M$ as equal volumes of two solutions are mixed.

Now, we know that $Ag^+$ will react with $Cl^-$ ions to form AgCl since :

$AgCl \rightleftharpoons Ag^+ + Cl^-$ is a reversible reaction with a high tendency towards left (solidifying or precipitating).

Now, question is, whether AgCl will be formed or not (precipitation of $Ag^+$ and $Cl^-$ as AgCl) and if it formed, how much of it will be formed ? For this we define some rules.

1. If Ionic Product (IP) > $K_{sp}$ ; precipitation takes place till I.P. equals $K_{sp}$.
2. If Ionic Product < $K_{sp}$ ; a precipitate will not be formed and the solution will be *unsaturated*.
3. If Ionic Product = $K_{sp}$ ; a precipitate will not be formed and the solution is saturated in that salt. (or *we can say that solution is at a critical stage*, *when precipitation just begins*, *but actually has not occurred*)

In present case, I.P. $= [Ag^+]\,[Cl^-] = (0.0025)\,(0.0005) = 1.25 \times 10^{-7}$

(Only for the salt which is sparingly soluble not for $KNO_3$)

Ionic product > $K_{sp}$ in this case ($K_{sp}$ AgCl $= 1.56 \times 10^{-10}$) which mean precipitation takes place.

## Illustration - 16

*When* 15*mL of* 0.05 *M* $AgNO_3$ *is mixed with* 45.0 *mL of* 0.03 *M* $K_2CrO_4$, *predict whether precipitation of* $Ag_2CrO_4$ *occurs or not ?* $K_{sp}$ *of* $Ag_2CrO_4$ $= 1.9 \times 10^{-12}$.

### SOLUTION :

First find the concentrations of $Ag^+$ and $CrO_4^{2-}$ ions in the resulting mixture.

$$[Ag^+] = \frac{15 \times 0.05}{15+45} = 1.25 \times 10^{-2}\,M$$

$$[CrO_4^{2-}] = \frac{45 \times 0.03}{15+45} = 2.25 \times 10^{-2}\,M$$

The ionic product for $Ag_2CrO_4$ is given as follows.

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

Ionic product (I.P.) $= [Ag^+]^2[CrO_4^{2-}]$

$= (1.25\ \ 10^{-2})^2\,(2.25 \times 10^{-2})$

$= 3.51 \times 10^{-6} > K_{sp}$

Hence precipitation occurs.

**Illustration - 17** *The concentration of $Ni^{2+}$ ions in a given NiS solution is* $2.0 \times 10^{-6}$ *moles/L. Find the minimum $S^{2-}$ ions necessary to cause precipitation of NiS. The solubility product, $K_{sp}$ of NiS* $= 1.4 \times 10^{-14}$.

**SOLUTION :**

***Note :*** Solubility product, $K_{sp}$ gives an idea of maximum possible concentration of an ion which can be retained in solution.

Ksp = ionic product (I.P.) for saturated solution

For $\quad NiS \rightleftharpoons Ni^{2+} + S^{2-}$

Now, $\quad K_{sp} = [Ni^{2+}][S^{2-}]$

$$\Rightarrow \quad [S^{2-}] = \frac{K_{sp}}{[Ni^{2+}]}$$

*It is the maximum permissible concentration of $S^{2-}$ ion in solution.*

➤ For $[S^{2-}] = \dfrac{K_{sp}}{[Ni^{2+}]}$, NiS will just start to precipitate and

➤ If $[S^{2-}] > \dfrac{K_{sp}}{[Ni^{2+}]}$, NiS will precipitate.

This means $\dfrac{K_{sp}}{[Ni^{2+}]}$ is minimum concentration of $S^{2-}$ ion above which precipitation occurs.

$$\Rightarrow \quad [S^{2-}]_{min} = \frac{1.4\times10^{-14}}{2\times10^{-6}} = 7\times10^{-9}\,M$$

**Illustration - 18** *A solution contains* 0.01 *M each of $CaCl_2$ and $SrCl_2$. A* 0.005 *M solution of $SO_4^{2-}$ is slowly added to the given solution.*

**(a)** *Which substance begins to precipitate first* ?

**(b)** *If $H_2SO_4$ is continuously added, determine when will other salt be precipitated* ?

**(c)** *When second salt starts to precipitate, find the concentration of cation of first salt.*

*Assume that $CaCl_2$ and $SrCl_2$ are* 100% *ionised and volume of the solution remains constant.*

$K_{sp}$ *of* $CaSO_4 = 1.3 \times 10^{-4}$ *and* $K_{sp}$ *of* $SrSO_4 = 3.2 \times 10^{-7}$.

**SOLUTION :**

The solution contains 0.01 M $Ca^{2+}$ ion and 0.01 M $Sr^{2+}$ ions (100% ionization). Now $SO_4^{2-}$ ions are added gradually and slowly……………..

**(a)** First calculate the minimum $[SO_4^{2-}]$ ions required to start precipitation of $CaSO_4$ and $SrSO_4$

$$\left[SO_4^{2-}\right]_{\text{Min. for } CaSO_4} = \frac{K_{sp}[CaSO_4]}{[Ca^{2+}]}$$

$$= \frac{1.3\times10^{-4}}{0.01} = 1.3\times10^{-2}\,M$$

$$\left[SO_4^{2-}\right]_{\text{Min. for } SrSO_4} = \frac{K_{sp}[SrSO_4]}{[Sr^{2+}]}$$

$$= \frac{3.2\times10^{-7}}{0.01} = 3.2\times10^{-5}\,M$$

Since $[SO_4^{2-}]$ for $SrSO_4$ is much lower that required for $CaSO_4$, so $SrSO_4$ will precipitate FIRST.

**(b)** Now, if i.e., $SO_4^{2-}$ ions are continuously added, at some instant, its concentration will become equal to that minimum required for precipitating out $Ca^{2+}$ ions.

Hence $CaSO_4$ will start precipitating if $[SO_4^{2-}]$ $= 1.3 \times 10^{-2}$ M.

**(c)** Now, find the concentration of $Sr^{2+}$ ions when $[SO_4^{2-}] = 1.3 \times 10^{-2}$ M in the solution.

$$\left[Sr^{2+}\right] = \frac{K_{sp}\ SrSO_4}{[SO_4^{2-}]} = \frac{3.2\times10^{-7}}{1.3\times10^{-2}}$$

$$= 2.46\times10^{-5}\ M$$

$$\left[2.46\times10^{-5} M <<< 0.01M\right]$$

Can you observe that when $CaSO_4$ starts to precipitate, $SrSO_4$ is almost precipitated out as the value of $Sr^{2+}$ is very very low ?

***Note :*** The above illustration represents a case of selective precipitation (or separation of metals cations) by adding a common anion. Observe that there is a vast difference in the $K_{sp}$ values of two sulphates, and hence in the minimum values of sulphate ion for precipitating out the two metals ions.

**Illustration - 19** *How much the concentration of $Ag^+$ ions in a saturated solution of AgCl diminish if such an amount of HCl is added to it that the concentration of $Cl^-$ ions in the solution becomes equal to* 0.03 *M* ? *Also fine the amount of AgCl precipitated at the given concentration*. *$K_{sp}$ of AgCl* $= 1.8 \times 10^{-10}$.

**SOLUTION :**

HCl is added to a solution containing $Ag^+$ ions in saturated solution. First find the concentration of $Ag^+$ ion in this solution.

$$AgCl\,(s) \rightleftharpoons Ag^+ + Cl^-$$

$\Rightarrow$ $K_{sp} = [Ag^+][Cl^-] = x^2$ where $x$ is solubility of AgCl in mol/L

$$\Rightarrow \quad [Ag^+] = \sqrt{K_{sp}} = \sqrt{1.8\times10^{-10}}$$

$$= 1.34 \times 10^{-5}\ M$$

When HCl is added, the ionic product of AgCl approaches the $K_{sp}$ value of AgCl, the precipitation of $Ag^+$ ions will occur. As ionic product increases (i.e. becomes greater than $K_{sp}$ value), an appreciable amount of AgCl precipitates out, and precipitation continues till ionic product (I.P.) equals solubility product ($K_{sp}$).

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

$$\Rightarrow \quad [Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8\times10^{-10}}{(0.03)} = 6.0\times10^{-9}\ M$$

Now this is the amount of $Ag^+$ ions left un-precipitated.

$\Rightarrow$ $[Ag^+]$ diminishes in the solution by

$$\frac{6.0\times10^{-9}}{1.34\times10^{-5}} = \left(\frac{1}{2233}\right) \text{times}$$

The concentration of AgCl precipitated out of the solution

$= [Ag^+]_{initial} - [Ag^+]_{left}$

$= 1.34 \times 10^{-5} - 6.0 \times 10^{-8}$ M

It means almost whole of AgCl is precipitated out of the solution at $[Cl^-] = 0.03$ M.

## Precipitation through $H_2S$

The most typical technique used in precipitating the metals ions or selectively precipitating (separation) the two metal ions, is passing $H_2S$ gas in a solution of metal ion (s) whose acidity is externally controlled (or preset by adding HCl). First consider the ionisation (equilibrium) of $H_2S$ gas in an aqueous solution and then in an acidic solution.

### ➢ Passing $H_2S(g)$ in an aqueous solution :

$H_2S$ is a dibasic acid. We have to visualize two stage ionisation for it as follows:

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq)\ ; \quad K_1 \qquad \ldots \text{(i)}$$

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq)\ ; \quad K_2 \qquad \ldots \text{(ii)}$$

$K_1$ and $K_2$ are Ist and IInd ionisation constants respectively for $H_2S$ (aq). Since $K_2 << K_1$ (due to common ion effect), we usually neglect the concentration of $H^+$ ions from second equilibrium.

$$\Rightarrow \quad [H^+]_{\text{in Solution}} = [H^+]_{\text{from } H_2S} + [H^+]_{\text{from } HS^-} \approx [H^+]_{\text{from } H_2S}$$

Now, $K_1 = \dfrac{[H^+][HS^-]}{[H_2S]}$ and $K_2 = \dfrac{[H^+][S^{2-}]}{[HS^-]}$

From (i), $[H^+] = [HS^-]$ and neglecting $[H^+]$ from (ii), we have from second ionisation constant :

$$K_2 = \frac{[H^+][S^{2-}]}{[HS^-]} \approx [S^{2-}] \quad \text{or} \quad [S^{2-}] \approx K_2$$

So if we pass $H_2S$ in an aqueous solution, sulphide ion concentration is simply equal to the value of second ionisation constant. We can determine whether precipitation of metal sulphide will occur or not by comparing ionic product (I.P.) with solubility constant ($K_{sp}$).

### ➢ Passing $H_2S(g)$ in an acidic solution :

Now if we pass $H_2S$ in an acidic solution of a metal ion till saturation, we simply neglect the concentration of $H^+$ ion from $H_2S$ (both from first and second ionisations) totally as the concentration of $H^+$ from acid (strong acid added externally) is very high. In that case we can simply add two equilibriums (i) and (ii) to get :

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)\ ;\ K_a\,(H_2S)$$

$$K_a = K_1 \times K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

Note that in a saturated solution of $H_2S$ at 25°C, $[H_2S]$ is constant at 0.1 M.

$$\Rightarrow \quad K_a \times (0.1\ M) = [H^+]^2\,[S^{2-}]$$

$$([H^+][S^{2-}] = K_{sp} \text{ of } H_2S)$$

$$\Rightarrow \quad [S^{2-}] = \frac{K_a \times (0.1\ M)}{[H^+]^2} = \frac{K_1 \times K_2 \times (0.1\ M)}{[H^+]^2}$$

In this way, we now know the concentration of sulphide ion in an acidic solution, so accordingly we can plan precipitation of metal ions. The important aspect of this method is that we can always increase or decrease the concentration of sulphide ion by controlling the amount of acid.

★★

**Illustration - 20** *Calculate the maximum possible concentration of $Mn^{2+}$ in water that is saturated with $H_2S$ (which is 0.1 M at 300K) and maintained at pH = 3 with HCl. The equilibrium constant(s) for dissociation of $H_2S$ are :*

$$H_2S \rightleftharpoons H^+ + HS^- ; \qquad K_1 = 9 \times 10^{-8}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} ; \qquad K_2 = 1 \times 10^{-12} \text{ and } K_{sp} \text{ of MnS} = 3 \times 10^{-22}.$$

**SOLUTION :**

Note that solution contains $S^{2-}$ ions (from $H_2S$).

So $Mn^{2+}$ will react with $S^{2-}$ ions to give a precipitate of MnS (being sparingly soluble salt). Hence the concentration of $S^{2-}$ at saturation will determine the maximum possible concentration of $Mn^{2+}$ ions in solution that will not be precipitating. So first calculate $[S^{2-}]$ at saturation.

Calculate $K_a$ for dissociation of $H_2S$.

$$K_a \text{ of } H_2S = K_1 \times K_2 = 9 \times 10^{-20}$$

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$\Rightarrow \quad K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \qquad \Rightarrow \quad [S^{2-}] = \frac{K_a[H_2S]}{[H^+]^2}$$

Note that pH of solution is maintained at 3 (externally).

$$\Rightarrow \quad [H^+] = 10^{-3}\ M$$

$$\Rightarrow \quad [S^{2-}] = \frac{9 \times 10^{-20} \times 0.1}{\left(10^{-3}\right)^2} = 9 \times 10^{-15}$$

In a saturated solution, ionic product = $K_{sp}$

Now ionic product = $[Mn^{2+}][S^{2-}] = [Mn^{2+}](9 \times 10^{-15})$

$$\Rightarrow \quad [Mn^{2+}](9 \times 10^{-15}) = 3 \times 10^{-22}$$

$$\Rightarrow \quad [Mn^{2+}] = 3.33 \times 10^{-8}\ M$$

★★

## ACID BASE TITRATIONS Section - 6

### pH of Mixtures of Acids and Bases

Let us take $x$ millimoles of acid (HA) and $y$ millimoles of base (BOH). Note that acid is monobasic and base is monoacidic.

### (a) Strong acid and strong base

- If $x = y$, then complete neutralization takes place and we get $x$ (= y). Millimoles of salt (BA) of strong acid and strong base which means no hydrolysis takes place and pH of solution = 7.
- If $x > y$, then there is an excess of strong acid and resulting solution is acidic with millimoles of acid left in excess = $x - y$. Now if V (in cc) be the volume of mixture, then :

$$\Rightarrow \quad M = \frac{x-y}{V}.$$ Now calculate pH using the equation $pH = -\log_{10}[H^+]$

- If $x < y$, then there is an excess of strong base and resulting solution is basic with millimoles of base left in excess = $y - x$. Now if $V$ (in cc) be the volume of mixture, then :

$$\Rightarrow \quad M = \frac{y-x}{V}.$$ Now calculate pH using the equation $pH = 14 - \log_{10}[OH^-]$

### (b) Strong base and weak acid

- If $x = y$, first of all neutralization takes place to give $x$ (= $y$) millimoles of salt (BA). The salt will now undergo *hydrolysis* to give an alkaline solution. Calculate pH by using the standard result :

$$pH = 7 + \frac{1}{2}(pK_a + \log_{10} c) \quad ; \qquad \text{c is concentration expressed in M (mol/L)}$$

- If $x > y$, there is excess of weak acid whose millimoles = $x - y$ and $y$ millimoles of salt is formed. This will give an *acidic buffer solution*. Calculate pH of buffer solution using *Henderson's Equation*.

$$pH = pK_a + \log_{10}\frac{[salt]}{[acid]} = pK_a + \log_{10}\frac{y}{x - y}$$

- If $x < y$, the solution in this case contains excess of strong base whose millimoles are $y - x$.

$$M = \frac{y - x}{V}$$ Calculate pH using the equation $pH = 14 - \log_{10}[OH^-]$

### (c) Strong acid and weak base

- If $x = y$, first of all complete neutralisation takes place to produce $x$ (= $y$) millimoles of salt (BA). The salt (BA) is of strong acid and weak base, hence *hydrolysis* takes place to give an acidic solution. Calculate its pH by using standard result.

$$pH = 7 - \frac{1}{2}(pK_b + \log_{10} c) \quad ; \qquad c : \text{mol/L}$$

- If $x > y$, then solution contain excess of strong acid whose millimoles = $x -$ y.

$M = \frac{x-y}{V}$ Now calculate pH using the equation $pH = -\log_{10}[H^+]$

- If $x < y$, then there is an excess of weak base whose millimoles are $y - x$ and millimoles of salt (BA) are $x$. This will give a *basic buffer solution*. Calculate the pH by using Henderson's *Equation*.

$$pH = 14 - pK_b - \log_{10}\frac{[salt]}{[base]} = 14 - pK_b - \log_{10}\frac{x}{y-x}$$

## (d) Weak acid and weak base

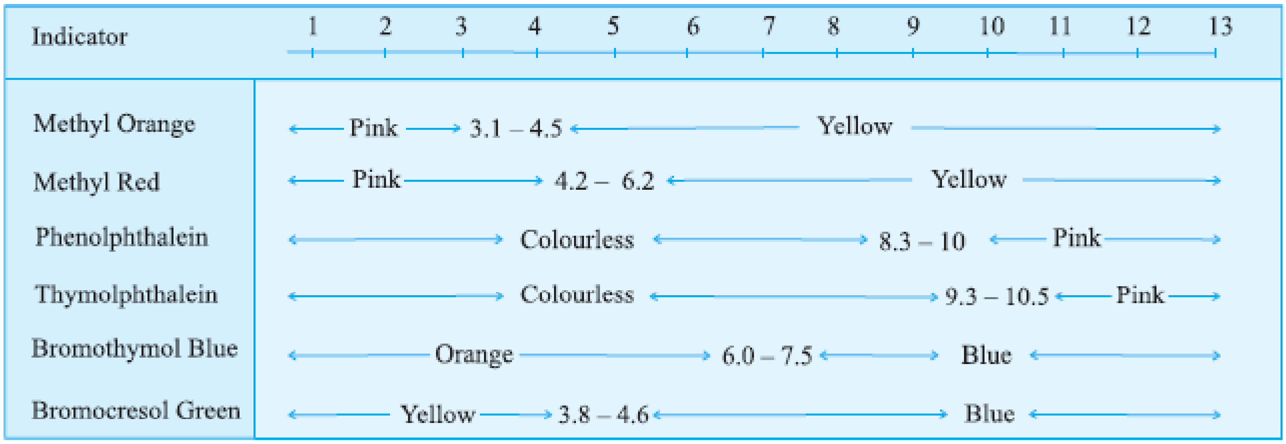
- If $x = y$, neutralisation takes place completely with the formation of $x$ (= $y$) millimoles of salt (BA) of weak acid and weak base. So hydrolysis takes place. Calculate the pH by using :

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

## Indicators

***Definition :*** An "indicator" is a dye (or substance) which change color over a short pH range.

***Example:*** Methyl orange changes color in the pH range of 3.1 to 4.5



**pH Range and color change of some common Acid-base indicators**

***End Point :*** It is the point at which the reaction between an acid and a base is "*observed*" to be complete i.e. the pH at which an indicator changes it color.

***Equivalence Point:*** It is the point at which the reaction between an acid and a base is "*theoretically*" complete (as per the balanced equation for the reaction).

***Note :***

- At "*equivalence point*", meq. of acid = meq. of base but the "*end point*" can only be detected by measuring the pH at different points of time during the titration. It is usually more convenient to add an indicator to the solution and detect the "*observed end*" of the reaction through a color change in the solution.
- An indicator is usually a weak acid or a weak base for acid-base titration. The color change occurs when protons are transferred to form a conjugate base or a conjugate acid of a different color.

Let us represent an indicator as HIn (Weak Acid)

$$\underset{\substack{\text{Acid}\\ \text{(color 1)}}}{HIn + H_2O} \rightleftharpoons \underset{\substack{\text{Conjugate Base}\\ \text{(color 2)}}}{H_3O^+ + In^-}$$

or simply, $$\underset{\text{(color 1)}}{HIn} \rightleftharpoons \underset{\text{(color 2)}}{H^+ + In^-}$$

**Necessary property of Indicator :** Color of ionised form must be remarkably different from that of unionized form.

Now, $K_{In}$ = Equilibrium Constant for the dissociation of the indicator $= \dfrac{[H^+][In^-]}{[HIn]}$

$$\Rightarrow \quad pH = pK_{In} + \log_{10}\frac{[In^-]}{[HIn]}$$

**Note :**

- An indicator changes color over a pH range (the so called "*transition range*"). It is the range over which color change in the solution is detectable by the "*observer*".
- The smaller the transition range, the better the indicator in detecting "*equivalence point*". (*Equivalence Point ≠ End Point*)

With indicator in which both the forms, ionized and unionized form are colored, generally one colored is visible if the ratio of the concentration of the two forms is 10 : 1.

Thus, when only the color of un-ionized (HIn) form is seen : $\dfrac{[HIn]}{[In^-]} = \dfrac{10}{1}$

$$\Rightarrow \quad pH_1 = pK_a + \log_{10}\frac{1}{10} = pK_a - 1$$

and when only the color of ionized ($In^-$) form is seen: $\dfrac{[In^-]}{[HIn]} = \dfrac{10}{1}$

$$\Rightarrow \quad pH_2 = pK_a + \log_{10}\frac{10}{1} = pK_a + 1$$

Thus, pH change required in going from one color to other is $\Delta pH = pH_2 - pH_1 = 2$

In the midway between the two colors (i.e. in the transition range), one can assume that $[HIn] = [In^-]$

$$\Rightarrow \quad pH = pK_a + \log_{10} 1 = pK_a \quad \Rightarrow \quad pH = pK_a$$

⇒ The $pK_a$ of the indicator should be close to the pH of the equivalence point

For weak-base indicators, same transition range is observed and $pOH = pK_b$ at the midway.

**(i) Phenophthalein :** It is a weak acid represented by PhH.

$$\underset{\text{Colorless}}{PhH} \rightleftharpoons \underset{\text{Pink in base}}{Ph^- + H^+} \qquad \text{.... (i)}$$

- Phenolphthalein is colorless in acid solution and pink in basic solution.
- When a strong base like NaOH is added, it displaces the equilibrium (I) towards left direction and there is a color change.

**(ii) Methyl Orange :** It is a weak base represented as MeOH.

$$\underset{\text{Yellow in base}}{MeOH} \rightleftharpoons \underset{\text{Red in acid}}{Me^+ + OH^-} \qquad \text{.... (ii)}$$

- When a strong acid is added, equilibrium (II) is shifted towards right and color change to red is detected..

### *Illustrating the concept* :

**(a)** *What is the equivalence point of* 0.1 *M $NH_4Br$ solution* ?

$$[(pK_b)_{NH_4OH} = 4.74]$$

When a strong acid reacts with a strong base, equivalence point is the neutralisation point (i.e pH of the solution = 7 if both of acid and base have same meq.) but when a strong acid reacts with a weak base or vice-versa, pH at the equivalence point ≠ 7 as the salt formed will get hydrolysed and pH of the solution > 7 or < 7 at the equivalence point. $NH_4Br$ is a salt of Strong acid and Weak base.

$$\Rightarrow \quad pH = 7 - \frac{1}{2}(pK_b + \log_{10} c) = 7 - \frac{1}{2}(4.74 + \log_{10} 0.1) = 5.13$$

**(b)** *What will be the color of the mehtyl red indicator in the solution of $NH_4Br$ in part* (*a*) ? *At pH* < 3.1, *the indicator methyl red is colored pink, at pH* > 6.3, *it is yellow and at the intermediate values of the pH it is orange*.

Since the pH of $NH_4Br$ solution is 5.13 and it lies in the intermediate range of methyl orange, its color will be orange. (3.1 < pH < 6.3)

**(c)** *An acid indicator has $pK_{In}$* = 5.3. *In a certain solution, this indicator is found to be* 80% *ionised. What is the pH of the solution* ?

$$\begin{array}{lcll} HI_n & \rightleftharpoons & H^+ & + \; In^- \\ 1 & & 0 & \quad 0 \\ 1-x & & x & \quad x \end{array}$$

Indicator is 80% ionized in acid form : $\Rightarrow x = 0.8$

$$\Rightarrow \quad pH = pK_a + \log_{10}\frac{[In^{-1}]}{[HIn]} \qquad \Rightarrow \quad pH = 5.3 + \log_{10}\frac{0.8}{0.2} = 5.9$$

## ★★ Acid Base titration curves :

*Titration Curve :* It is a curve in which pH of the solution is titrated against volume of the titrate added.

## (i) Strong Acid and Strong Base :

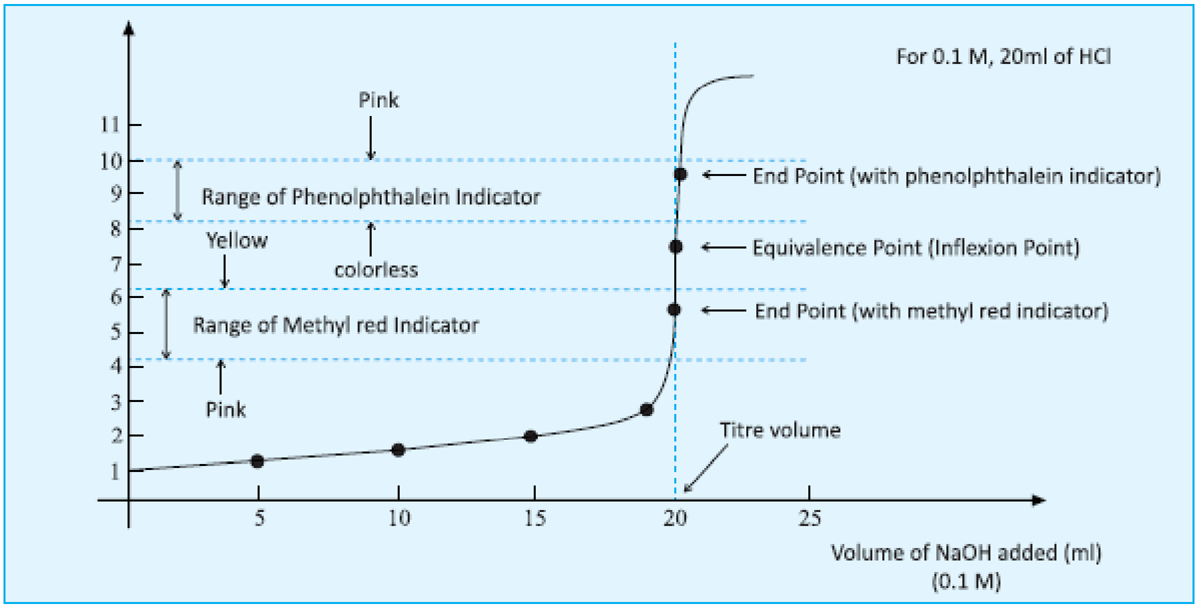
(HCl) (NaOH)

In this case, both the titrants are completely ionized.

$$HCl + NaOH \rightleftharpoons NaCl + H_2O$$

As $OH^-$ is added to an acid solution, $[H^+]$ decreases and $[OH^-]$ increases $\Rightarrow$ pH goes on increasing. As the equivalence point is reached, $[H^+]$ is rapidly reduced. Above this point, $[OH^-]$ increases rapidly from $10^{-7}$ M and after that pH of the solution remains fairly constant. Thus, there is an inflexion point at the equivalence point.

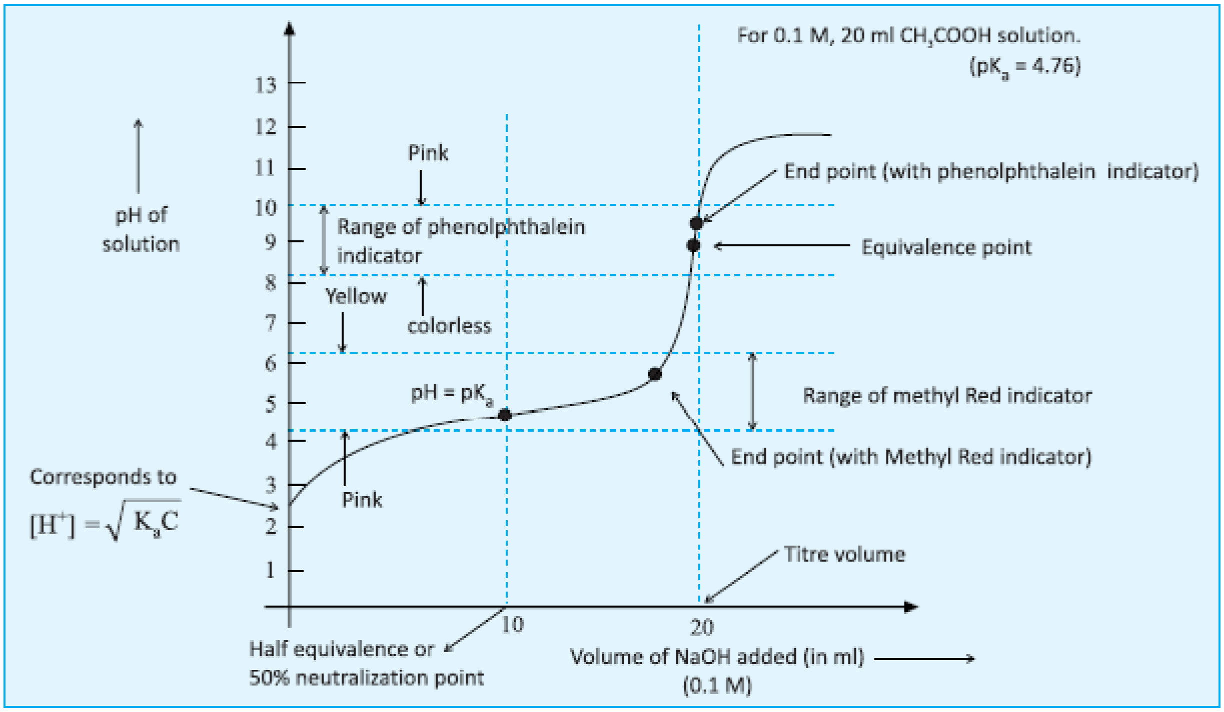
The difference in the volume of NaOH solution between the *end point* and the *equivalence point* is not significant for most of the commonly used indicators as there is a large change in the pH value around the equivalence point and most of them change their color across this pH change.



## (ii) Weak Acid and Strong Base :

($CH_3COOH$) (NaOH)

Initially, when a few drops of $OH^-$ are added to the weak acid, it forms an acidic buffer $CH_3COOH$/$CH_3COONa$ and thus, pH of the solution changes slowly. At the equivalence point, solution will be alkaline. If $OH^-$ addition is continued after the equivalence point, $[OH^-]$ will increase rapidly.



$$(\text{pH}) \text{ at equivalence point} = 7 + \frac{1}{2}\left(4.76 + \log_{10} c\right) = 7 + \frac{1}{2}\left(4.76 + \log_{10} 0.05\right) = 8.72$$

[Here c = concentration of the salt formed at equivalence point]

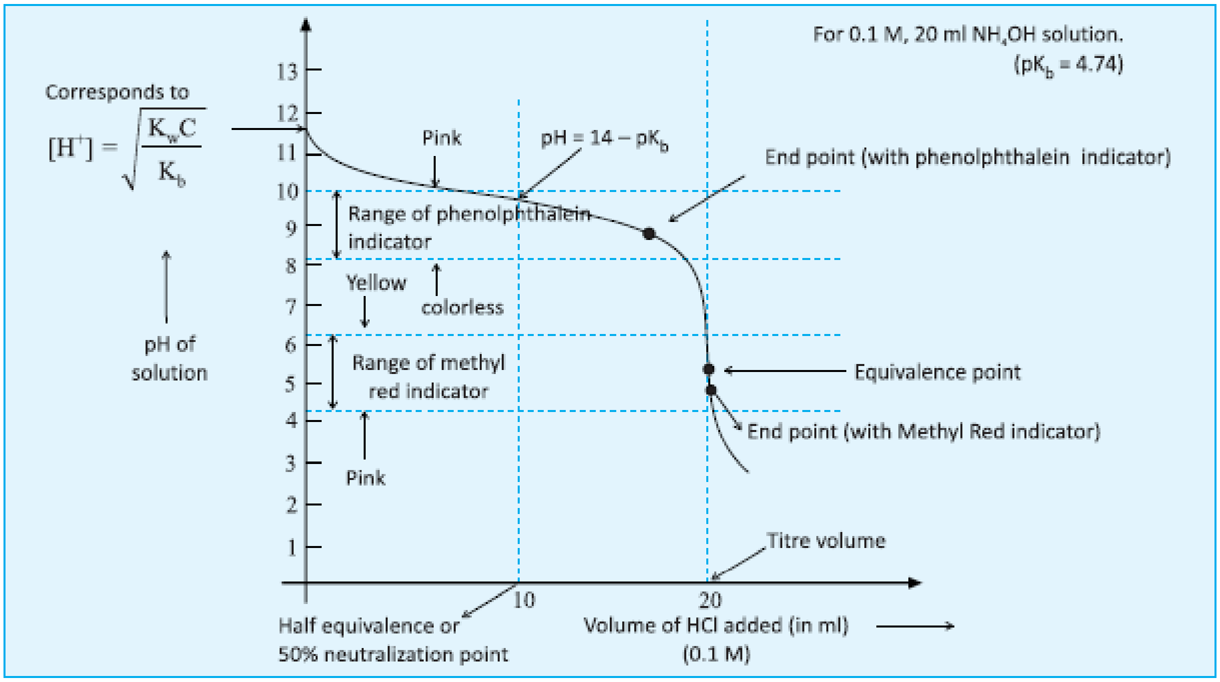
Thus, methyl red, methyl orange are inappropriate for use in the detection of the end point between a weak acid and a strong base.

Also note that the buffer capacity of the buffer solution will be maximum at 50% equivalence point i.e. when the volume of NaOH is 10 ml.

### (iii) Strong Acid and Weak Base :

(HCl) ($NH_4OH$)

Initially, when a few drops of $H^+$ are added to the weak acid, it forms a basic buffer $NH_4OH/NH_4Cl$ and thus, pH of the solution changes slowly. At the equivalence point, solution will be alkaline. If $H^+$ addition is continued after the equivalence point, $[H^+]$ will increase rapidly.



Thus, phenolphthalein, thymolphthalein are quite inappropriate to be used as an indicator to detect the end point between a strong acid and weak base neutralization.

Also note that the buffer capacity of the buffer solution will be maximum at 50% equivalence point i.e. when the volume of HCl is 10 ml.

**Note :** The selection of an indicator therefore is determined by the pH of the solution at the equivalence point.

**Illustration - 21** *0.1 M NaOH is titrated with 0.1 M, 20 ml HA till the end point.* $K_a(HA) = 6 \times 10^{-6}$ *and degree of dissociation of HA is negligible (small) as compared to unity. Calculate the pH of the resulting solution at the end point* [Use $\log_{10} 6 \sim 0.8$]

**SOLUTION :**

| | NaOH | + HA | $\longrightarrow$ NaA | + $H_2O$ |
|---|---|---|---|---|
| At end point (mmoles) | 2 | 2<br>(≡ 0.1 × 20) | - | |
| | - | - | 2 | - |

**Note :** 20ml of NaOH is required for the complete neutralisation of HA.

NaA is a salt of strong base and weak acid. Thus, will undergo hydrolysis and solution will become basic.

Here $\quad c = [NaA] = \frac{2}{20+20} = 0.05\,M$

and $\quad pK_a = -\log_{10}(6 \times 10^{-6}) = 5.2$

$$pH_{\text{at end point}} = 7 + \frac{1}{2}\left(pK_a + \log_{10} c\right)$$

$$= 7 + \frac{1}{2}\left(5.2 + \log_{10} 0.05\right) = 8.95$$

★★

**Illustration - 22** *The equivalence point in a titration of* 40.0 *mL of a solution of a weak monoprotic acid occurs when* 35.0 *mL of a* 0.10 *M NaOH solution has been added. The pH of the solution is* 5.5 *after the addition of* 2.0 *mL of NaOH solution. What is the dissociation constant of the acid* ?

**SOLUTION :**

Let x milimoles of HA are taken initially. Find $x$ :

Consider the equation of neutralization :

$$\begin{array}{llll} HA & + \; NaOH & \longrightarrow NaA & + \; H_2O \\ x & \quad y & \quad - & \\ x-y & \quad - & \quad y & \end{array}$$

At equivalent point, millimoles of acid = milimoles of aicd = NaOH [i.e. $x = y$]

$\Rightarrow$ millimoles HA = $x$ = 3.5 [35 ml of 0.1 M NaOH]

At pH = 5.5, millimoles of NaOH added = 2 = y [20 ml of 0.1 M NaOH]

$\Rightarrow$ millimoles of HA left $x - y = 1.5$

and millimoles of NaA formed = 2

Now such a solution will behave as an acidic buffer, whose pH is given as :

$$[H^+] = \frac{K_a[\text{acid}]}{[\text{salt}]} \quad \Rightarrow \quad 10^{-55} = K_a = \frac{1.5}{2}$$

$$\Rightarrow \quad K_a = 4.22 \times 10^{-6} \; [10^{-5.5} = \sqrt{10} \times 10^{-6}]$$

## SIMULTANEOUS EQUILIBRIUM

### Section - 7

When two slats having a common ion (either cation or anion) are together in water, then their respective solubilities are not independent of each other.

***Illustrating the concept*** **:**

Consider a solution containing two salt : $CaF_2$ ($K_{sp}$ = 3.4 × $10^{-11}$) and $SrF_2$ ($K_{sp}$ = 2.9 × $10^{-9}$). Compare their $K_{sp}$ values. Let us assume that most of $F^-$ ion concentration in the saturated solution is from $SrF_2$, as its $K_{sp}$ is much higher than that of $CaF_2$. It means that first $SrF_2$ will establish its equilibrium (as if there is no $CaF_2$), then $CaF_2$ will dissolve in presence of ions furnished only by $SrF_2$.

Let the solubility of $SrF_2$ bw $x$ mol/L.

$$SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2F^-(aq)$$

$$\Rightarrow \quad [Sr^{2+}] = x \text{ and } [F^-] = 2x$$

$$K_{sp} = [Sr^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3$$

$$\Rightarrow \quad x = \left(\frac{K_{sp}}{4}\right)^{1/3} = 9 \times 10^{-4}$$

Now the solubility of $CaF_2$ is determined in presence of $9\times10^{-4}$ M $F^-$ ions. It means neglect the contribution of $F^-$ ions from $CaF_2$.

$$K_{sp}=[Ca^{2+}][F^-]^2 \quad\Rightarrow\quad [Ca^{2+}]=\frac{K_{sp}}{[F^-]^2}=\frac{3.4\times10^{-11}}{(2\times9\times10^{-4})^2}=1.0\times10^{-5}\ \text{M}$$

Hence the solubility of $CaF_2$ is $1.0\times10^{-5}$ mol/ L.

**Note :** Let us check our assumption. $F^-$ ions from $CaF_2$ is twice the amount of $Ca^{2+}$ ions i.e., $2.0\times10^{-5}M$, whereas, $F^-$ ions from $SrF_2$ is $2\times9.0\times10^{-4}$ i.e. $1.8\times10^{-3}$ M, which is much higher than $2.0\times10^{-5}$ M.

## Illustration - 23

*Calculate the simultaneous solubilities of AgSCN and AgBr.*

$$K_{sp}(AgSCN)=1.0\times10^{-12} \quad ; \quad K_{sp}(AgBr)=5.0\times10^{-13}$$

**SOLUTION :**

In this case, please note that the $K_{sp}$ values of two salts are very similar. So the concentration of $Ag^+$ ions (the common ion) can not be calculated from a single salt alone and we have to consider the equilibrium of the two salts simultaneously.

Let the simultaneous solubilities of AgSCN and AgBr be x and y respectively in mol/L.

$$\underset{}{AgSCN(s)} \rightleftharpoons \underset{x}{Ag^+(aq)}+\underset{x}{SCN^-(aq)}$$

$$AgBr(s) \rightleftharpoons \underset{y}{Ag^+(aq)}+\underset{y}{Br^-(aq)}$$

At equilibrium :

$$[Ag^+]=x+y; \quad [SCN^-]=x\ ; \quad [Br^-]=y$$

$$[Ag^+][Br^-]=K_{sp\ AgBr}$$

and $\quad [Ag^+][SCN^-]=K_{sp\ AgSCN}$

Note that : $[Ag^+]=[Br^-]+[SCN^-]$

[This is an Electrical charge neutrality equation]

$$[Ag^+]=\frac{K_{sp\ AgBr}}{[Ag^+]}+\frac{K_{sp\ AgSCN}}{[Ag^+]}$$

$$\Rightarrow \quad [Ag^+]=\sqrt{K_{sp\ AgBr}+K_{sp\ AgSCN}}$$

$$=x+y=1.22\times10^{-6} \qquad \ldots\text{(i)}$$

$$\text{Also,}\quad \frac{[Br^-]}{[SCN^-]}=\frac{y}{x}=\frac{K_{sp\ AgBr}}{K_{sp\ AgSCN}}=0.5 \qquad \ldots\text{(ii)}$$

Using (i) and (ii), we get :

$$x=8.0\times10^{-7}\ ; \quad y=4.0\times10^{-7}$$

**Illustration - 24** *Two weak monobasic organic acids HA and HB have dissociation constants as* $3.0\times10^{-5}$ *and* $1.5\times10^{-5}$ *respectively at* $25°C$. *If* 500 *ml of* 1 *M solutions of each of these two acids are mixed to produce* 1 *litre of mixed acid solution, what is the pH of the resulting solution* ?

**SOLUTION :**

Note that $K_a$ of two acids is nearly same. In such cases, we have to consider $H^+$ from both HA and HB simultaneously. The concentration of HA and HB in the mixture = 5.0 M

[equal volume are mixed] = cM

$$\begin{array}{llll} HA \rightleftharpoons & H^+ & + & A \\ c & x & & x \end{array}$$

$$\begin{array}{llll} HB \rightleftharpoons & H^+ & + & B^- \\ c & & & \\ c-y & y & & y \end{array}$$

Now, $[H^+]_{\text{final}} = [H^+]_{from\ HA} + [H^+]_{from\ HB}$

$$\Rightarrow \quad K_{aHA} = \frac{(x+y)x}{c-x} \text{ and } K_{aHB} = \frac{(x+y)y}{c-y}$$

As $K_a$ of both acid $\sim 10^{-5}$ and $H^+$ from one acid acts as common ion for other's dissociation, $x$ and $y$ are very less as compared to c.

$$\Rightarrow \quad c-x \approx c \quad \text{and} \quad c-y \approx c$$

$$\Rightarrow \quad K_{a(HA)} \approx \frac{(x+y)x}{c} \text{ and}$$

$$K_{a(HB)} \approx \frac{(x+y)y}{c}$$

Divide the two expressions to get :

$$\frac{1}{2} = \frac{x}{y} \quad \Rightarrow \quad x = 2y$$

Substitute for $y = \frac{1}{2}x$ in $K_{a(HA)} = \frac{x^2+xy}{c}$

$$\Rightarrow \quad 3.0\times10^{-5} = \frac{x^2+0.5x^2}{0.5}$$

$$\Rightarrow \quad x = \sqrt{10}\times10^{-3}\text{ M}$$

$$\text{and } y = \frac{\sqrt{10}}{2}\times10^{-3}\text{ M}$$

$$[H^+] = x+y = \frac{3\sqrt{10}}{2}\times10^{-3}\text{ M}$$

$$pH = -\log_{10}\left(\frac{3\sqrt{10}}{2}\times10^{-3}\right) \quad \Rightarrow \quad pH = 2.32$$

**Illustration - 25** *Determine the solubility of AgCN in a buffer solution maintained at pH* = 3.

$$K_{sp}(AgCN) = 2.0\times10^{-16} \; ; \quad K_a(HCN) = 6.0\times10^{-10}$$

**SOLUTION :**

AgCN is a sparingly soluble salt in aqueous medium.

$$AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq)$$

Let the solubility of AgCN be x M. Thus,

$[Ag^+] = xM$ and $[CN^-] = x$ M *from salt but it will not be equal to x finally*.

The $\text{CN}^-$ ions will react with $H^+$ in the solution to form HCN. (a weakly dissociated acid) and we have to assume that in solution $[CN^-] = y$ M finally which will be decided by the dissociation of HCN as explained below : $AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq)$

$$\begin{array}{llll} H^+ & + & CN^- \longrightarrow HCN & \\ 10^{-3} & & x & \\ 10^{-3}-x & & & x \end{array}$$

$$\begin{array}{llll} HCN \rightleftharpoons & H^+ & + & CN \\ x & 10^{-3} & & \\ x-y & 10^{-3}+y & & y \\ & \approx 10^{-3} & & \end{array}$$

We have two equations now :

$$K_{sp\,(AgCN)} = [Ag^+][CN^-] = xy = 2\times10^{-16}$$

and

$$K_{a(HCN)} = \frac{[H^+][CN^-]}{HCN} = \frac{10^{-3}y}{x-y} = 6\times10^{-10}$$

Solve the equation to get :

$$x = [Ag^+] = \sqrt{\frac{K_{sp}}{K_a}\left([H^+]+K_a\right)} = 1.82\times10^{-5}\text{ M}$$

Note that in the solution :

$$[Ag^+] = [CN^-] + [HCN]$$

(Electrical charge neutrality equation)

**Note :** In this example, since the dissociation constant of acid is very low and pH of the solution is fairly high, we could have assumed that $[H^+]$ and $K_a$ in the expression for x.

**Illustration - 26** *How much AgBr could dissolver in* 1.0 *L of* 0.4 *M* $NH_3$? *Assume that* $Ag(NH_3)_2^+$ *is the only complex formed Given: The dissociation constant for* $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$ ; $K_d = 6.0\times10^{-8}$ *and* $K_{sp}(AgBr) = 5.0\times10^{-13}$.

**SOLUTION :**

Let solubility of AgBr be *x*M. Thus, $[Br^-] = x$ M but $[Ag^+] \neq x$ M since it will react with $NH_3$ to form a complex and thus, its concentration will be decided by the dissociation of the complex. So, let $[Ag^+] = y$ M.

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

$$\Rightarrow \quad K_{sp} = [Ag^+][Br^-] = y\,x = 5.0\times10^{-13}$$

Since the formation constant $(K_f)$ of the complex is very high, assume that whole of $Ag^+$ formed is consumed.

$$\begin{array}{llll} Ag^+ & + & 2NH_3 \longrightarrow & Ag(NH_3)_2^+ \\ x & & 0.4 & \\ & & 0.4-2x & x \end{array}$$

$$\begin{array}{lll} Ag(NH_3)_2^+ \rightleftharpoons & Ag^+ + 2NH_3\ ; & K_d = 5.0\times10^{-13} \\ x & & 0.4-2x \\ x-y & y & 0.4-2x+2y(\sim 0.4) \end{array}$$

$$K_d = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = \frac{y(0.4-2x+2y)^2}{x-y} = 6\times10^{-8}$$

Assuming $x - y \approx x$ since $K_d$ is low and << 0.4, we get :

$$K_d = \frac{y(0.4)^2}{x}$$

Solving for $x : x = 1.15 \times 10^{-3}$ M

(Verify the approximation yourself)

**Illustration - 27** *$HN_3$ (hydroazoic acid) is a weak acid dissociating as : $NH_3 \rightleftharpoons H^+ + N_3^-$. Find the concentration of $Ag^+$ ions, if excess of solid $AgN_3$ is added to a solution maintained at pH = 4. The ionization constant $K_a$ of $NH_3$ is $2.0 \times 10^{-5}$. The solubility of $AgN_3$ in pure water is found to be $5.4 \times 10^{-3}$ M at 25°C.*

**SOLUTION :**

$AgN_3$ is a sparingly soluble salt, dissociating in water as : $AgN_3 \rightleftharpoons Ag^+ + N_3^-$

$$K_{sp} = [Ag^+][N_3^-]$$

Since solubility of $AgN_3$ in water is $5.4 \times 10^{-3}$,

$$K_{sp} = (5.4 \times 10^{-3})^2 = 2.92 \times 10^{-5}$$

Now we have to find the solubility of $AgN_3$ in solution having pH = 4.

Let solubility of $AgN_3$ be $x$ M at pH = 4.

$\Rightarrow \quad [Ag^+] = xM$, but $[N_3^-] \neq x$M

($[N_3^-]$ *will be decided by dissociation of* $HN_3$ ).

Let $[N_3^-] = $ yM

First, assume that whole of $N_3^-$ (xM) formed from $AgN_3$ reacts with $H^+$ ions to form $HN_3$.

$\Rightarrow \quad [HN_3] = xM$

Now $HN_3$ dissociates as follows :

| $HN_3 \rightleftharpoons$ | $H^+$ | $N_3^-$ |
|---|---|---|
| $x$ | $10^{-4}$ | – |
| $x - y$ | $10^{-4} + y \approx 10^{-4}$ | $y$ |

[As pH is maintained at 4 hence $[H^+] = 10^{-4} M$ ]

Now we have a simultaneous equilibrium in aqueous solution involving dissociation of $AgN_3$ *and* $HN_3$.

$$K_{sp} \text{ of } AgN_3 = [Ag^+][N_3^-] = xy \quad \textbf{... (i)}$$

$$K_a \text{ of } HN_3 = \frac{[H^+][N_3^-]}{[HN_3]} = \frac{[H^+]y}{(x-y)} \quad \textbf{... (ii)}$$

Solving (i) and (ii) simultaneously, we have :

$$x = [Ag^+] = \sqrt{\frac{K_{sp}}{K_a}\left([H^+] + K_a\right)}$$

Substitute the values of $K_{sp}, K_a$ *and* $[H^+]$ to get x = 0.0132 mol/L

***Note*** : In this example, since the dissociation constant of acid is quite high and pH of the solution is quite low, we can not assumed that $x - y \approx x$. You can check the same by comparing $[H^+]$ *and* $K_a$ in the expression for $x$.

## ★★ SUBJECTIVE SOLVED EXAMPLES

**Example - 1** *A solution contains a mixture of* $Ag^+(0.1M)$ *and* $Hg_2^{2+}$ $(0.10\ M)$ *which are separated by selective precipitation. Calculate maximum concentration of Iodide ion at which one of them gets precipitated almost completely. What % age of that metal ion is precipitated ?*

$$\left(K_{sp\ AgI} = 8.5\times10^{-17}M;\ K_{sp\ HgI_2} = 2.5\times10^{-26}\right)$$

**SOLUTION :**

First determine, which ion starts precipitating. first

$$[I^-]_{\text{Min. for AgI}} = \frac{K_{sp}\text{ of AgI}}{[Ag^+]}$$

$$= \frac{8.5\times10^{-17}}{0.1} = 8.5\times10^{-16}\text{ M}$$

$$[I^-]_{\text{Min. for }Hg_2I_2} = \sqrt{\frac{K_{sp}\text{ of }Hg_2I_2}{[Hg_2^{2+}]}}$$

$$= \sqrt{\frac{2.5\times10^{-26}}{0.1}} = 5\times10^{-13}\text{ M}$$

This means that AgI will be precipitated first as $[I^-]$ required for AgI is less.

But when $[I^-]$ reaches $5\times10^{-13}$ M then precipitation of $Hg_2I_2$ also starts.

So $[Ag^+]$ left at that stage is given as :

$$[Ag^+] = \frac{K_{sp}\text{ of AgI}}{[I^-]_{Hg_2I_2}}$$

$$= \frac{8.5\times10^{-17}}{5.0\times10^{-13}} = 1.7\times10^{-4}\text{M}$$

% of $Ag^+$ left un-precipitated

$$= \frac{1.7\times10^{-4}}{0.1}\times100 = 0.17\%$$

$\Rightarrow$ % age of $Ag^+$ = 99.83 %

This means when $Hg_2I_2$ starts precipitating, $Ag^+$ is almost precipitated.

**Example - 2** *Carbonic acid,* $H_2CO_3$*, is a diprotic acid for which* $K_1 = 10^{-7}$ *and* $K_2 = 10^{-11}$*. Which solution will produce a pH closest to 9 ?*

**(A)** $0.1M\ H_2CO_3$

**(B)** $0.1M\ Na_2CO_3$

**(C)** $0.1\ M\ NaHCO_3$

**(D)** $0.1M\ NaHCO_3$ *and* $0.1\ M\ Na_2CO_3$

**SOLUTION :**

Amphiprotic salt is a salt that can donate proton well as can accept a proton. For example : NaHS, $NaHCO_3$ etc.

$$NaHS \longrightarrow Na^+ + HS^-$$

$$HS^- + H^+ \rightleftharpoons H_2S$$

$$HS^- \rightleftharpoons S^{2-} + H^+$$

pH of amphiprotic salt of weak acid is calculated by using following expression.

$$pH = \frac{1}{2}\left[pK_{a_1} + pK_{a_2}\right]$$

$$pH = \frac{1}{2}\left[pK_{a_1} + pK_{a_2}\right] = \frac{1}{2}[7+11] = 9$$

**Example - 3** *For the reaction* $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-$, *in an aqueous medium, the equilibrium constant* $K_C$ *at* $25°C$ *is* $4 \times 10^{-19}$. *Calculate the* $Ag^+$ *ion concentration in the solution which was originally* 0.1 *M in KCN and* 0.03 *M* $AgNO_3$.

**SOLUTION :**

0.1 M KCN and 0.03 M $AgNO_3$ are mixed.

Since $K_{eq}$ for $Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$ is very-very high $\left(K = \frac{1}{4} \times 10^{19}\right)$, first assume that whole of $Ag^+$ is converted to $Ag(CN)_2^-$.

| $Ag^+$ | + | $2CN^-$ | $\longrightarrow$ | $Ag(CN)_2^-$ |
|---|---|---|---|---|
| 0.03 M | | 0.1 M | | 0 |
| 0 | | 0.1 – 2 × 0.03 M | | 0.03 M |

Now, Let 0.03 M $Ag(CN)_2^-$ ($K_{eq} = 4 \times 10^{-19}$) to dissociate as follows :

| $Ag(CN)_2^-$ | $\rightleftharpoons$ | $Ag^+$ | + | $2CN^-$ |
|---|---|---|---|---|
| 0.03 M | | - | | 0.04 M |
| $0.03 - x$ | | $x$ | | $(0.04 + 2x)$ |

$$K_C = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = 4\times10^{-19}$$

$$\Rightarrow [Ag^+] = \frac{K_C[Ag(CN)_2^-]}{[CN^-]^2}$$

$$= \frac{4\times10^{-19}[0.03 - x]}{(0.04 + 2x)^2}$$

Solve the above equation by assuming '$x$' to be very small.

$$\Rightarrow [Ag^+] = \frac{4\times10^{-19}[0.03]}{(0.04)^2} = 7.5\times10^{-18}\ M$$

[Verify the approximation yourself]

**Example - 4** *Calculate* $[NH_4^+]$ *(derived from* $NH_4Cl$*) needed to prevent* $Mg(OH)_2$ *from precipitating in a litre of solution which contains* 0.2 *mole of ammonia and* 0.001 *mole of* $Mg^{2+}$ *ions. The ionisation constant of ammonia is* $2.0 \times 10^{-5}$ *and* $K_{sp}$ *of* $Mg(OH)_2$ *is* $1.0 \times 10^{-11}$.

**SOLUTION :**

Note that aq. ammonia is $NH_4OH$.

First check whether we need to add $NH_4Cl$.

$$[OH^-]_{\text{From } NH_3} = \sqrt{K_b c} = 2 \times 10^{-3}\ M$$

$$\left[\because \alpha = \sqrt{\frac{K_b}{c}} = 10^{-2} \Rightarrow 1 - \alpha \sim 1\right]$$

$$\Rightarrow I.P_{Mg(OH)_2} = 10^{-3} \times (2 \times 10^{-3})^2$$

$$= 4\times10^{-9} > K_{sp}$$

Thus, precipitation will take place if $NH_4Cl$ is not added and hence, $NH_4Cl$ is required to be added so as to suppress the dissociation of $NH_4OH$. As a result, $[OH^-]$ will decreases.

Now, calculate the concentration of $OH^-$ ions in equilibrium with $Mg^{2+}$ ions from Ksp of $Mg(OH)_2$.

$$K_{sp} \text{ of } Mg(OH)_2 = [Mg^{2+}]\,[OH^-]^2$$

$$\Rightarrow \quad [OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{1.0\times10^{-11}}{0.001}} = 1.0\times10^{-4}$$

If $[OH^-] \le 1.0 \times 10^{-4}$M, $Mg^{2+}$ ions will not be precipitated. So, maximum concentration of $OH^-$ in the solution should be $1.0 \times 10^4$ M. As $[OH^-]$ is derived from dissociation of ammonia.

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

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

$$\Rightarrow \quad [NH_4^+]_{min} = \frac{(2.0\times10^{-5})(0.2)}{[1.0\times10^{-4}]}$$

$$= 4.0\times10^{-2}\text{ M}$$

For this much concentration of $NH_4^+$ ions, $Mg^{2+}$ will not be precipitated.

**Example - 5** *When a* 40 *mL of a* 0.1 *M weak base, BOH is titrated with* 0.10 *M HCl, the pH of the solution at the end point is* 5.5. *What will be the pH if* 10 *mL of* 0.10 *M NaOH is added to the resulting solution* ?

**SOLUTION :**

At the end point, pH = 5.5 (i.e. an acidic solution). It means salt formed at the end of neutralisation undergoes hydrolysis.

For 4 millimoles (40 × 0.1) of weak base, 4 millimoles of acid is required at the end point.

$$\begin{array}{llll} BOH & + \; HCl & \rightleftharpoons & BCl + H_2O \\ 4 & \quad 4 & & \\ - & \quad - & & \quad 4 \end{array}$$

⇒ millimoles of salt (BCl) formed = 4

⇒ [BCl] = 4/V where $V = V_{HCl} + V_{base}$

At the end point : $4 = 0.10 \times V_{HCl}$

⇒ $V_{HCl} = 40$ mL

⇒ V = 40 + 40 = 80 mL

⇒ [BCl] = 4 / 80 = 0.05 M

Note that BCl is a salt of strong acid and weak base.

$$\Rightarrow \quad [H^+] = \sqrt{\frac{K_w c}{K_b}}$$

$$\Rightarrow \quad K_b = \frac{K_w c}{[H^+]^2} = \frac{(10^{-14})\times(0.05)}{(10^{-5.5})^2} = 5.0\times10^{-5}$$

When 10 mL of 0.12 M NaOH is added :

$$\begin{array}{llll} & BCl \; + \; NaOH & \longrightarrow & BOH \; + \; NaCl \\ \text{Initially} & 4 \text{ m.moles} \quad 10\times0.10 & & \\ \text{Finally} & 4 - 10\times0.10 & & \\ & 4 - 1 = 3.0 \qquad - & & 1.0 \end{array}$$

It means a basic buffer containing 3.0 m.moles of BCl and 1.0 m.moles of BOH is fomed. Find the pH by using Henderson's equation for basic buffer.

$$pOH = pK_b + \log\frac{[BCl]}{[BOH]}$$

$$\Rightarrow \quad pOH = -\log(5\times10^{-5}) + \log\frac{[3.0/V]}{[1.0/V]}$$

⇒ pOH = 4.77 $\qquad (pK_b = 4.3)$

⇒ pH = 14 – pOH = 9.22

**Example - 6** *It is given that 0.001 mol each of* $Cd^{2+}$ *and* $Fe^{2+}$ *ions are contained in 1.0 L of 0.02M HCl solution. This solution is now saturated with* $H_2S$ *gas at 25°C.*

**(a)** *Determine whether or not each of these ions will be precipitated as sulphide ?*

**(b)** *How much* $Cd^{2+}$ *ions remain in the solution at equilibrium ?*

$$K_1\,(H_2S) = 1.0 \times 10^{-7} \;\; ; \;\; K_2\,(H_2S) = 1.0 \times 10^{-14} \;\; ; \;\; K_{sp}\,(CdS) = 8 \times 10^{-27} \;\; ; \;\; K_{sp}\,(FeS) = 3.7 \times 10^{-19}$$

**SOLUTION :**

Note that two salts are of same type (i.e., AB type) and $K_{sp}$ of CdS is lower than that of FeS. This means CdS will precipitate first if at all any precipitation takes place.

Calculate the minimum concentration of Sulphide ion required to initiate the precipitation of each of the metal sulphide.

$$[S^{2-}]_{\text{Min for CdS}} = \frac{K_{sp}\ \text{CdS}}{[Cd^{2+}]} = \frac{8\times10^{-27}}{0.001} = 8\times10^{-24}\ \text{M}$$

$$[S^{2-}]_{\text{Min for FeS}} = \frac{K_{sp}\ \text{FeS}}{[Fe^{2+}]} = \frac{3.7\times10^{-19}}{0.001} = 3.7\times10^{-16}\ \text{M}$$

Now calculate the sulphide ion concentration in the saturated solution, using :

$$K_a = K_1 \times K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = 10^{-21}$$

$$\Rightarrow \quad [S^{2-}] = \frac{10^{-21}\times0.1}{0.02^2} = 2.5\times10^{-19}\ \text{M}$$

$$\Rightarrow \quad [Cd^{2+}]_{\text{Left}} = \frac{8\times10^{-27}}{2.5\times10^{-19}} = 3.2\times10^{-8}\ \text{M}$$

Thus, only CdS will get precipitated.

To calculate the remaining concentration of $Cd^{2+}$ ion (more accurately) ion in the solution, first assume that whole of the $Cd^{2+}$ has been precipitated as :

$$Cd^{2+} + H_2S \longrightarrow CdS + 2\,H^+$$

Thus, $[H^+]_{\text{new}} = 0.02 + 0.001 \times 2 = 0.022$ M

$$\Rightarrow \quad [S^{2-}]_{\text{At new equilibrium}} = \frac{10^{-21}\times0.1}{0.022^2}$$

$$= 2.07 \times 10^{-19}\ \text{M}$$

$$\Rightarrow \quad [Cd^{2+}]_{\text{Left}} = \frac{8\times10^{-27}}{2.07\times10^{-19}} = 3.86\times10^{-8}\ \text{M}$$

***Note :*** FeS will not be precipitated at all.

**Example - 7** *The solubility product,* $K_{sp}$ *of* $Ca(OH)_2$ *at* $25°C$ *is* $4.0\times10^{-6}$. *A 500 mL of saturated of* $Ca(OH)_2$ *is mixed with equal volume of 0.4 M NaOH solution. How much* $Ca(OH)_2$ *in milligrams is precipitated ?*

**SOLUTION :**

First find the concentration of $Ca^{2+}$ ions at saturation using $K_{sp}$ *of* $Ca(OH)_2$.

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

$$\Rightarrow \quad K_{sp} = [Ca^{2+}][OH^-]^2$$

Let $[Ca^{2+}] = x\ mol/L \qquad \Rightarrow \qquad [OH^-] = 2x$

$\Rightarrow \qquad K_{sp} = 4x^3$ or $x = \sqrt[3]{\dfrac{K_{sp}}{4}} = 0.01M$

$\Rightarrow \qquad [Ca^{2+}] = 0.01M$ and $\qquad [OH^-] = 0.02\,M$

As equal volumes of saturated solution and 0.4 M NaOH are mixed :

$$[Ca^{2+}] = \frac{0.01}{2} = 5\times10^{-3}M$$

and $\quad [OH^-]_{Total} = \dfrac{0.02}{2} + \dfrac{0.4}{2} = 0.21M$

$$[\because [OH^-]_{Total} = [OH^-]_{NaOH} + [OH^-]_{From\ Ca(OH)_2}]$$

Now, calculate I. $P_{Ca(OH)_2} = [Ca^{2+}][OH^-]^2 = (5\times10^{-3})(0.21)^2 = 2.2\times10^{-4} > K_{sp}$

Since concentration of $OH^-$ is quite high, $Ca^{2+}$ will be precipitated till a new saturation state is reached.

Let at new saturated state. $[OH^-] = 0.21M$ (Assuming no change in $[OH^-]$)

$$[Ca^{2+}]_{\text{left}} = \frac{K_{sp}}{[OH^-]^2} = \frac{(4\times10^{-6})}{(0.21)^2} = 9.07\times10^{-5}M$$

$\Rightarrow \qquad [Ca^{2+}]\text{precipitated} = 5\times10^{-3} - 9.07\times10^{-5}M = 4.91\times10^{-3}M$

$\Rightarrow \qquad amount\ of\ Ca^{2+} = 4.91\times10^{-3}\times74\times10^{3}mg/L = 363.3mg/L$

Check the approximation : $[OH^-]_{left} \sim 0.21M$. How ??

Find out the $[OH^-]_{used} = 2[Ca^{2+}]_{used}$ (see Reation's Stoichichiometry)

$$= 2\times4.91\times10^{-3}M = 9.8\times10^{-3}M$$

$\Rightarrow \qquad [OH^-]_{left} = 0.21 - 9.8\times10^{-3}M = 0.2M \approx 0.21M$

## Alternate Approach :

$$Ca(OH)_2 \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

| | | | |
|---|---|---|---|
| $t = t_{eq}$ : *concentration*: | $0.01$ | $0.02$ | $I.P. = K_{sp}$ |
| $t = 0(new)$ *concentration* : | $5\times10^{-3}$ | $0.21$ | $I.P. > K_{sp}$ |
| (*After mixing equal volumes with NaOH*) | | | |
| $t = t_{eq}(new)$ | $5\times10^{-3} - x$ | $0.21 - 2x$ | $I.P. = K_{sp}$ |

Now, $I.P. = K_{sp}$ at equilibrium

$$(5\times10^{-3} - x)(0.21 - 2x)^2 = 4\times10^{-6} \quad \Rightarrow \text{ This equation in '}x\text{' is clearly a cubic.}$$

To solve the above equation approximately, assume $0.21 - 2x \sim 0.21$ which is what has been done in the previous approach.

**Example - 8** *The solubility product of* $Ag_2C_2O_4$ *at* $25°C$ *is* $1.20\times10^{-11}$. *A solution of* $K_2C_2O_4$ *containing* 0.15 *moles in* 500 *ml water is mixed with excess of* $Ag_2CO_3$ *till the following equilibrium established :*

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3.$$

*At equilibrium, the solution contains* 0.03 *mole of* $K_2CO_3$. *Assuming that the degree of dissociation of* $K_2C_2O_4$ *and* $K_2CO_3$ *to be equal, calculate the solubility product of* $Ag_2CO_3$. [*Take* 100% *ionisation of* $K_2C_2O_4$ *and* $K_2CO_3$]

**SOLUTION :**

$$\underset{\text{initial}}{[K_2C_2O_4]} = \frac{0.15}{0.5} = 0.30\,M = P$$

and $$\underset{\text{final}}{[K_2CO_3]} = \frac{0.03}{0.5} = 0.06\,M = x$$

$$\begin{array}{ccccc} Ag_2CO_3 + & K_2C_2O_4 & \rightleftharpoons & K_2CO_3 & + Ag_2C_2O_4 \\ & P & & - & \\ & P-x & & x & \end{array}$$

1 mol $K_2CO_3 \equiv 1$ mole $K_2C_2O_4$ and since both are completely ionized :

Now find $[Ag^+]$ at equilibrium as :

$$[Ag^+] = \sqrt{\frac{K_{sp}\ of\ Ag_2C_2O_4}{[C_2O_4^{2-}]}}$$

$$= \sqrt{\frac{1.20\times10^{-11}}{P-x}} = \sqrt{\frac{1.20\times10^{-11}}{0.3-0.06}}$$

$$= 7.07\times10^{-6}\ \text{M}$$

$$[CO_3^{2-}]_{final} = x = 0.06\,M$$

Now, $K_{sp}\ of\ Ag_2CO_3 = [Ag^+]^2[CO_3{}^{2}]$

$$\Rightarrow \qquad K_{sp}\ of\ Ag_2CO_3 = (7.07\times10^{-6})^2 \times 0.06$$

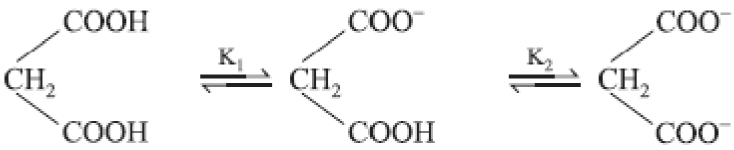
$$= 3\times10^{-12}$$

**Example - 9** *Malonic acid is an organic dibasic acid like* $H_2S$ *having first ionization constant,* $K_1 = 1.42 \times 10^{-3}$ *and second ionization constant,* $K_2 = 2.0 \times 10^{-6}$*. Compute the divalent malonate ion concentration in :*

**(a)** 0.001 *M Malonic acid* **(b)** *in a solution that is 0.0001 M in malonic acid and* 0.0004 *M HCl.*

**(c)** *in a solution that is* 0.0001 *M in malonic acid and* 0.1 *M HCl.*

**SOLUTION :**



**(a)** Consider malonic acid to be $H_2A$, where malonate ion is $A^{2-}$. For dibasis acids, we consider ionization in two stages as follows :

$H_2A \rightleftharpoons H^+ + HA^-$ ; First ionization constant $= K_t = 1.42 \times 10^{-3}$

$c - x \quad x \quad x$ c = initial concentration = 0.001 M.

$$\Rightarrow \qquad K_1 = \frac{[H^+][HA^-]}{[H_2A]} = \frac{x^2}{c - x} = 1.42 \times 10^{-3}$$

Solving the quadratic, $x^2 + 1.42 \times 10^{-3} x - 1.42 \times 10^{-6} = 0 \Rightarrow \qquad x = 6.75 \times 10^{-4} M$

Note that $K_1 >> K_2$. so concentration of $H^+$ in solution is considered only from dissociation i.e.,

$[H^+] = x\text{M}$ (neglect $H^+$ concentration from second ionization).

Consider second ionisation :

$HA^- \longrightarrow H^+ + A^{2-}$ ; Second ionisation constant $= K_t = 2.0 \times 10^{-6}$

$x \quad x \quad -$

$x - y \quad x + y \quad y$

$$\Rightarrow \qquad K_2 = \frac{[H^+][A^{2-}]}{[HA^-]} = \frac{(x+y)y}{x-y}$$

Note : $[H^+]$ $[H^+] = x + y = x$ $\qquad [HA^-] = x - y = x$ $(y << x)$

$$\Rightarrow \qquad K_2 = y = [A^{2-}] = 2.0 \times 10^{-6}\ \text{M}$$

***Note*** : Usually, $[A^{2-}]$ for $H_2A$ (dibasic acid) can be approximately taken to be $K_2$.

**(b)** Here $=10^{-4}M$, $[H^+]=4\times10^{-4}$ M (From HCl)

$$\Rightarrow \quad K_1=\frac{[H^+][HA]}{[H_2A]}=\frac{(4\times10^{-4}+x)(x)}{10^{-4}-x}=1.42\times10^{-3}$$

> ***Important :*** Note that, we can not go for approximation in this case, since the concentration of HCl is so low that $H^+$ is considered both from HCl and molonic acid.

Solving the quadratic, $x^2+1.82\times10^{-3}x-1.42\times10^{-7}=0 \Rightarrow \quad x=7.5\times10^{-5}M$

Now consider, second ionisation and substitute for value of x.

$$K_2=\frac{[H^+][A^{2-}]}{[HA]}=\frac{(4\times10^{-4}+x)}{x}=2.0\times10^{-6}$$

$$\Rightarrow \quad \frac{(4\times10^{-4}\times7.5\times10^{-5})y}{7.5\times10^{-5}}=2.0\times10^{-6}$$

$$\Rightarrow \quad y=[A^{2-}]=3.2\times10^{-7}\text{ M}$$

**(c)** Here $c=10^{-4}M$, $[H^+]=0.1$M

$$\Rightarrow \quad K_a=K_1K_2=\frac{[H^+]^2[A^{2-}]}{[H_2A]}=\frac{(0.1)^2[A^{2-}]}{10^{-4}}=2.84\times10^{-9}$$

$$\Rightarrow \quad [A^{2-}]=2.84\times10^{-11}\text{ M}$$

> ***Important*** : Note that, we will do the approximation in this case, since the concentration of HCl is so high that $H^+$ is considered from malonic acid is negligible. Recall the ionization of $H_2S$ (g) in an acidic solution.

**Example - 10** *Calculate the $[F^-]$ in a solution saturated with respect to $MgF_2$ and $SrF_2$.*

$$K_{sp}(MgF_2)=6.0\times10^{-9};\ K_{sp}(SrF_2)=3.0\times10^{-9}$$

**SOLUTION :**

In this case, please note that the $K_{sp}$ values of two salts are very similar. So the concentration of $F^-$ ions (the common ion) can not be calculated from a single salt alone.

Let the simultaneous solubilities of $MgF_2$ *and* $SrF_2$ be $x$ and $y$ respectively in mol/L.

$$MgF_2(s)\rightleftharpoons \underset{x}{Mg^{2+}} + \underset{2x}{2F^-}$$

$$\begin{array}{lll} SrF_2(s) \rightleftharpoons & Sr^{2+} & 2F^- \\ & y & 2y \end{array}$$

At eq : $[F^-] = 2x + 2y$ ; $[Mg^{2+}] = x$ ; $[Sr^{2+}] = y$

$\Rightarrow$ $[Mg^{2+}][F^-]^2 = K_{sp\ MgF_2}$

and $[Sr^{2+}][F^-]^2 = K_{sp\,Sr\,F_2}$

Note that : $[F^-] = 2\left([Mg^{2+}] + [Sr^{2+}]\right)$ [This is an Electrical charge neutrality equation]

$$[F^-] = 2\left(\frac{K_{sp\,MgF_2}}{[F^-]^2} + \frac{K_{sp\ SrF_2}}{[F^-]^2}\right)$$

$$\Rightarrow \quad [F^-] = \sqrt[3]{2\left(K_{sp\,MgF_2} + K_{sp\,SrF_2}\right)} = 2.62 \times 10^{-3} M$$

## THINGS TO REMEMBER

## 1. Weak Electrolyte

(a) **Weak Acid :** $K_a = \frac{[H^+]^2}{c-[H^+]} = \frac{c\alpha^2}{1-\alpha}$ ; $c = [H^+] + \frac{[H^+]^2}{K_a}$

If $1-\alpha \sim 1$, then $K_a = c\alpha^2$ and $[H^+] = \sqrt{K_a c}$

(b) **Weak Base :** $K_b = \frac{[OH^-]^2}{c-[OH^-]} = \frac{c\alpha^2}{1-\alpha}$ ; $c = [OH^-] + \frac{[OH^-]^2}{K_b}$

If $1-\alpha \sim 1$, then $K_b = c\alpha^2$ and $[OH^-] = \sqrt{K_b c}$

- For any acid – conjugate base pair, $K_a.K_b = K_w$
- "$\alpha$" of weak electrolytes increase on dilution.
- $H_2O \rightleftharpoons H^+ + OH^-$

  $K_w = [H^+][OH^-]$ or $pH + pOH = pK_w$

  $K_w$ increases as T increases and decreases as T decreases.

## 2. Buffer solution :

(a) **Acidic :** $HA + A^-$ $\Rightarrow$ $pH = pK_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]}$

(b) **Basic :** $BOH + B^+$ $\Rightarrow$ $pOH = pK_b + \log_{10}\frac{[\text{salt}]}{[\text{base}]}$

- Buffer capacity of the buffer solution is maximum at $pH = pK_a$ or $pOH = pK_b$.
- pH of a buffer solution does not change on dilution.

## 3. Hydrolysis :

- Salts of SA – SB do not get hydrolysed.
- Salts of SA – WB on hydrolysis give acidic solution.

$$K_h = \frac{ch^2}{1-h} = \frac{K_w}{K_b} \quad ; \quad pH = \frac{1}{2}\left[pK_w - (pK_b + \log_{10} c)\right]$$

- Salts of WA – SB on hydrolysis give basic solution.

$$K_h = \frac{ch^2}{1-h} = \frac{K_w}{K_a} \quad ; \quad pH = \frac{1}{2}\left[pK_w + (pK_a + \log_{10} c)\right]$$

- Salts of WA – SB on hydrolysis may give acidic, basic or neutral solution.

$$K_h = \frac{h^2}{(1-h)^2} = \frac{K_w}{K_a \cdot K_b} \quad ; \quad pH = \frac{1}{2}\left[pK_w + (pK_a - pK_b)\right]$$

$K_h$ : hydrolysis constant ; h : degree of hydrolysis

## 4. Sparingly soluble salts and Precipitation :

- Solubility of a sparingly soluble salt is expressed in mol / L or gm/L
- Solubility (in Mol/L) of any salt $A_xB_y$ in pure water is given by : $\text{Solubility} = \left[\frac{(K_{sp})}{x^x \cdot y^y}\right]^{1/(x+y)}$
- Solubility of a salt decreases in the presence of a common ion.

  In general, we can neglect the contribution of common ion from the sparingly soluble salt.

  e.g. solubility of AgCl in pM NaCl $= \frac{K_{sp}AgCl}{[Cl^-]} = \frac{K_{sp}AgCl}{p}$

- **Selective precipitation :** When difference in the minimum concentrations of common cation/anion required to start the precipitation is very high.

  To check, always calculate the conc. of the cation/anion left in the solution when the second cation/anion starts to precipitate, and so on..........

- **Simultaneous Solubility :** Solubility of two or more salts having a common cation / anion when their Ksp values are comparable. Solve the governing equations simultaneously.

## 5. Use of Indicators :

- Transition range of an indicator : $pK_{In} - 1$ to $pK_{In} + 1$
- For SA - SB titration, almost every indicator is effective.
- For SA - WB and WA - SB, indicator selection is important and depends on the pH at equivalence point.

## 6. Miscellaneous :

- For dissociation of $H_2A$, $[A^{2-}] \approx K_2$ ; For $H_3A$, $[A^{3-}] \approx K_3$ and so on.
- For any polyprotic acid, $K_{a_1} >> K_{a_2} >> K_{a_3}$ and so on.
- Solubility of a salt can be increased by adding a substance that makes a stable complex / compound with any of the cation / anion in the salt.

  e.g. AgCl dissolves more in aq. $NH_3$ solution due to the formation of $Ag(NH_3)_2^+$ and AgCN dissolves more in an acidic solution due to the formation of HCN (weak electrolyte)