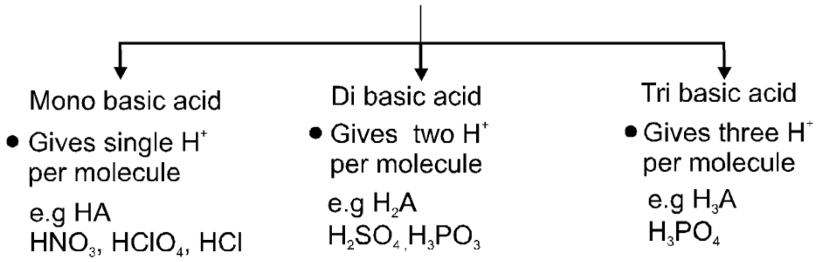
# Ionic Equilibrium

## SECTION (A) : ACID BASE CONCEPT

### Introduction

- **Arrhenius Acid :** Substance which gives $H^+$ ion on dissolving in water ($H^+$ donor)
  eg. $HNO_3$, $HClO_4$, $HCl$, $HI$, $HBr$, $H_2SO_4$, $H_3PO_4$ etc.

**Types of acids**



○ $H_3BO_3$ is not Arrhenius acid.

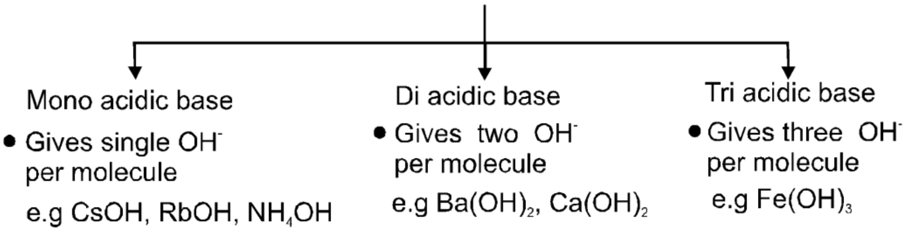
○ $H^+$ ion in water is extremely hydrated (in form of $H_3O^+$, $H_5O_2^+$, $H_7O_3^+$) and have high charge density.

○ The structure of solid $HClO_4$ is studied by X-ray, It is found to be consisting of $H_3O^+$ and $ClO_4^-$.

$$HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^- \text{ (better representation)}$$

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

**Types of base**



○ $OH^-$ ion also in hydrated form of $H_3O_2^-$, $H_7O_4^-$, $H_5O_3^-$

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

**Bronsted - Lowry concept : (Conjugate acid - base concept) (Protonic concept)**

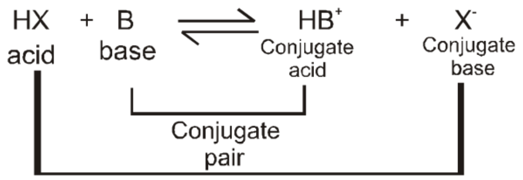
**Acid :** Substances which donate $H^+$ are Bronsted Lowry acids ($H^+$ donor)

**Base :** Substances which accept $H^+$ are Bronsted Lowry bases ($H^+$ acceptor)

**Conjugate acid - base pairs**

In a typical acid base reaction

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



○ Forward reaction – Here HX being a proton donor is an acid

B being a proton acceptor is a base.

○ Backward reaction – Here $HB^+$ being a proton donor is an acid

$X^-$ being a proton acceptor is a base.

| | **Acid** | | **Base** | | **Conjugate Acid** | | **Conjugate Base** |
|---|---|---|---|---|---|---|---|
| ○ | $HCl$ | + | $H_2O$ | $\rightleftharpoons$ | $H_3O^+$ | + | $Cl^-$ |
| ○ | $HSO_4^-$ | + | $NH_3$ | $\rightleftharpoons$ | $NH_4^+$ | + | $SO_4^{-2}$ |
| ○ | $[Fe(H_2O)_6]^{3+}$ | + | $H_2O$ | $\rightleftharpoons$ | $H_3O^+$ | + | $[Fe(H_2O)_5(OH)]^{2+}$ |

- Conjugate acid-base pair differ by only one proton
- Strong acid will have weak conjugate base and vise versa
- Reaction will always proceed from strong acid to weak acid or from strong base to weak base.

**Amphoteric (amphiprotic) :** Substances which can act as acid as well as base are known as amphoteric

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

base

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

acid

## Solved Examples

**Ex-1.** Write the conjugate bases of $HCl$, $H_2SO_4$ , $HSO_4^-$, $H_2O$ and conjugate acids of $NH_3$ , $H_2O$ and $RNH_2$.

**Sol.**

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

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## Lewis concept (electronic concept) :

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

Acid → $e^-$ pair acceptor

e.g. Electron deficient molecules : $BF_3$, $AlCl_3$

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

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

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

Base → (One electron pair donate)

e.g. Molecules with lone pairs : $NH_3$, $PH_3$, $H_2O$, $CH_3OH$

## Solved Examples

***Ex-2.*** In which of the following reactions does $NH_3$ act as an acid ?

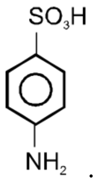
(1) $NH_3 + H^+ \longrightarrow NH_4^+$ (2) $NH_3 + Na \longrightarrow NaNH_2 + \frac{1}{2} H_2$

(3) $NH_3 + HCl \longrightarrow NH_4Cl$ (4) None of these

***Sol.*** (2) In the following reaction, $NH_3$ changes to $NaNH_2$ which contains $NH_2^-$ ion. This means that $NH_3$ has donated a proton to Na and hence acts as an acid.

***Ex-3.*** Sulphanilic acid is a / an

(1) Arrhenius acid (2) Lewis base (3) Neither (1) or (2) (4) Both (1) and (2)

***Sol.*** (4) Sulphanilic acid is  .

The $SO_3H$ group is capable of donating $H^+$ and hence it acts as arrhenius acid while nitrogen in the $NH_2$ group contains lone pair of electrons and hence can act as lewis base by donating it.

***Ex-4.*** Ammonium ion is

(1) A Lewis acid (2) Lewis base (3) Bronsted acid (4) Bronsted base

**Sol.** Correct answer is (3).

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## Section (B) : Ostwald dilution concept, property of water, pH definition

### Degree of dissociation :

- When an electrolyte is dissolved in a solvent ($H_2O$), it spontaneously dissociates into ions.
- It may dissociate partially ($\alpha << < 1$ ) or sometimes completely ($\alpha \cong 1$ )

**eg.** $NaCl(aq) \rightleftharpoons Na^+ (aq) + Cl^- (aq)$ ($\alpha \approx 1$)

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+ (aq)$ ($\alpha < < < 1$)

- The degree of dissociation of an electrolyte ($\alpha$) is the fraction of one mole of the electrolyte that has dissociated under the given conditions.

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{No. of moles taken initially}}$$

The value of $\alpha$ depends :

**(a)** **Nature of electrolyte :** Strong electrolyte dissociate completely where as weak electrolytes dissociate partially.

**(b)** **Nature of solvent :** A solvent having high value of **dielectric constant** and high **solvation (in** water **hydration)** will favour dissociation.

**(c)** **Dilution :** For some electrolytes degree of dissociation will increase by dilution (**Ostwald's dilution law**)

**(d)** **Temperature :** On increasing temperature generally degree of dissociation increases.

**(e)** **Presence of other solute :** When a substance is present it may affect the solubility of the another solute. Generally common ion present in both the substance affects most.

### Ostwald's Dilution Law (for weak electrolyte's)

- For a weak electrolyte $A^+B^-$ dissolved is water, if $\alpha$ is the degree of dissociation then

$$AB \rightleftharpoons A^+ + B^-$$

| | | | |
|---|---|---|---|
| initial conc | C | 0 | 0 |
| conc-at eq. | $C(1 - \alpha)$ | $C\alpha$ | $C\alpha$ |

Then according to law of mass action,

$K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \;.\; C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$ = dissociation constant of the weak electrolyte

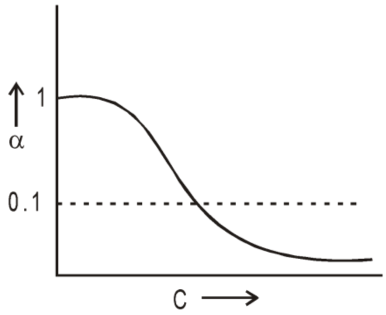
$[C] = \frac{1}{V}$ , then V = 1/C(volume of Solution in which 1 mole is present) is called **dilution**, so

$k_{eq} = \frac{\alpha^2}{(1-\alpha)V}$ ]

If α is negligible in comparison to unity then, $1 - \alpha \simeq 1$. So $k_{eq} = \alpha^2 C \;\Rightarrow\; \alpha = \sqrt{\frac{k_{eq}}{c}} = \sqrt{k_{eq}.\;V}$ .

$\alpha \propto \frac{1}{\text{concentration}}$ **{ Thumb rule }**

- ○ As **concentration increases ⇒ α decreases**
- ○ **At infinite dilution α reaches its maximum value, unity**.



## PROPERTIES OF WATER :

- **Amphoteric (amphiprotic) Acid/base nature:**

**Water :** An acid as well as base according to Arrhenius and Bronsted-Lowry theory but according to Lewis concept it can only be taken as base.

**In pure water $[H^+] = [OH^-]$ so it is Neutral.**

- **Molar concentration / Molarity of water :**

**Molarity** = No. of moles/litre = $\frac{1000\text{gm/litre}}{18\text{gm/mole}}$ = 55.55 mole /litre **= 55.55 M** (density = 1 gm/cc)

- **Ionic product of water :** According to Arrhenius concept

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

- ○ dissociation of water, is endothermic, so on increasing temperature $K_{eq.}$ increases

$K_w$ increases with increase in temperature.

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

$$\left.\begin{array}{lcl} pH = 7 = pOH & \Rightarrow & \text{neutral} \\ pH < 7 \text{ or } pOH > 7 & \Rightarrow & \text{acidic} \\ pH > 7 \text{ or } pOH < 7 & \Rightarrow & \text{Basic} \end{array}\right\} \text{at } 25°C$$

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

- **Degree of dissociation of water :**

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

  $$\Rightarrow \alpha = \frac{\text{no. of moles dissociated}}{\text{Total No. of moles initially taken}} = \frac{10^{-7}}{55.55} = 18\text{x}10^{-10} \text{ or } 1.8\text{x } 10^{-7}\%$$

- **Absolute dissociation constant of water :**

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

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

## pH definition :

- Acidic strength means the tendency of an acid to give $H_3O^+$ or $H^+$ ions in water.
  So greater the tendency to give $H^+$ , more will be the acidic strength of the substance.

- Basic strength means the tendency of a base to give $OH^-$ ions in water.
  So greater the tendency to give $OH^-$ ions, more will be basic strength of the substance.

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

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

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

- For dilute Solutions $[H^+] \leq 1M$ concentration can be taken as activity of $H^+$ ions while for higher concentrations the activity would be much less than the concentration itself, so it is calculated experimentally.

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

- If the temperature is changed, the pH range of the scale will also change. For ***Example***

| | | |
|---|---|---|
| 0 – 14 | at 25°C | Neutral point, pH = 7 |
| 0 –13 | at 80°C ($K_w = 10^{-13}$) | Neutral point, pH = 6.5 |

- pH can also be negative or > 14.

## Solved Examples

***Ex*-5.** For which temperature the $pK_w$ of pure water can be greater than 14.
(1) 20ºC (2) 30ºC (3) 40ºC (4) 50ºC **Ans.** (1)

***Ex*-6.** For pure water at 10ºC and 60ºC , the correct statement is
(1) $pOH_{10^oC} = pOH_{60^oC}$ (2) $pOH_{10^oC} > pOH_{60^oC}$ (3) $pOH_{60^oC} > pOH_{10^oC}$ (4) Can't say **Ans.** (2)

***Ex*-7.** For pure water at 25ºC and 50ºC the correct statement is
(1) $pH_{25^oC} = pH_{50^oC}$ (2) $pH_{25^oC} > pH_{50^oC}$ (3) $pH_{50^oC} > pH_{25^oC}$ (4) Can't say **Ans.** (2)

## pH Calculations of different types of solutions :

## Section (C) : Strong Acid, Strong Base and their mixture

**(a)** **Strong acid** Solution **:**

(i) If concentration is greater than $10^{-6}$ M, in this case $H^+$ ions coming from water can be neglected. So $[H^+]$ = normality of strong acid Solution

(ii) If concentration is less than $10^{-6}$ M, in this case $H^+$ ions coming from water cannot be neglected. So $[H^+]$ = normality of strong acid + $H^+$ ions coming from water in presence of this strong acid

## Solved Examples

***Ex-8.*** Calculate pH of $10^{-8}$M HCl Solution.

***Sol.*** $H_2O \rightleftharpoons H^+ + OH^-$

$10^{-8} + x$

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

$10^{-14} = x(x \times 10^{-8})$

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

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \quad x \quad 10^{-14}}}{2} = \frac{-10^{-8} + 10^{-7}\sqrt{4 + \frac{1}{100}}}{2} = \frac{(\sqrt{401} - 1)10^{-8}}{2} = 0.95 \text{ x } 10^{-7}$$

$[H^+] = 10.5 \text{ x } 10^{-8} = 1.05 \text{ x } 10^{-7}$

$[pH] = 7 - \log 1.05 \approx 6.98$

$10^{-9}$ M HCl pH $\approx 7$

$10^{-16}$ M HCl pH $\approx 7$

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**(b)** **Strong base** Solution **:**

Calculate the $[OH^-]$ which will be equal to normality of the strong base solution and then use $K_W = [H^+] \times [OH^-] = 10^{-14}$ , to calculate $[H^+]$.

***Ex-9.*** Calculate pH of $10^{-7}$ M of NaOH Solution

***Sol.*** $[OH^-]$ from NaOH = $10^{-7}$

$[OH^-]$ from water = $x < 10^{-7}$ M (due to common ion effect)

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

$- \quad (x + 10^{-7}) \quad x$

$K_w = [H^+][OH^-] = 10^{-14} = x(x + 10^{-7})$

$x^2 + 10^{-7}x - 10^{-14} = 0$

$\Rightarrow \quad x = \frac{\sqrt{5} - 1}{2} \times 10^{-7} = 0.618 \times 10^{-7}$ ($\sqrt{5} = 2.236$)

$[OH^-] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$

$pOH = 7 - \log(1.618) = 6.79$

$pH = 14 - 6.79 = 7.21$

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**(c)** **pH of mixture of two strong acids :**

If $V_1$ volume of a strong acid solution of normality $N_1$ is mixed with $V_2$ volume of another strong acid solution of normality $N_2$, then

Number of $H^+$ ions from I-solution = $N_1V_1$

Number of $H^+$ ions from II-solution = $N_2 V_2$

If final normality is N and final volume is V, then

$$NV = N_1 V_1 + N_2 V_2$$

[dissociation equilibrium of none of these acids will be disturbed as both are strong acid]

$$[H^+] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

**(d) pH of mixture of two strong bases :**

Similar to above calculation

$$[OH^-] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2} \qquad [H^+] = \frac{10^{-14}}{[OH^-]}$$

## Solved Examples

***Ex-10.*** Calculate pH of mixture of (400ml , $\frac{1}{200}$ M $H_2SO_4$) + (400ml, $\frac{1}{100}$ M HCl) +( 200 ml of water)

***Sol.*** $N_1V_1 = \frac{1}{100} \times \frac{400}{1000} = \frac{4}{1000}$ , $N_2 V_2 = \frac{4}{1000}$ , $H^+$ ions from water will be neglected

$N_1V_1 + N_2V_2 = 8 \times 10^{-3}$ $\qquad [H^+] = \frac{8 \times 10^{-3}}{1} = 8 \times 10^{-3}$

pH = 3 – log 8 =2.1

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**(e) pH of mixture of a strong acid and a strong base :**

- ❍ Acid Base neutralisation reaction will take place.
- ❍ The solution will be acidic or basic depending on which component has been taken in excess.
- ❍ If $V_1$ volume of a strong acid solution of normality $N_1$ is mixed with $V_2$ volume of a strong base solution of normality $N_2$ , then

Number of $H^+$ ions from I-solution = $N_1V_1$

Number of $OH^-$ ions from II-solution = $N_2 V_2$

If $N_1V_1 > N_2V_2$

$$[H^{+}] = N = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

solution will be acidic in nature

If $N_2V_2 > N_1V_1$

$$[OH^{-}] = N = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

solution will be basic in nature

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

## Solved Examples

***Ex-11.*** Calculate pH of mixture of (400ml, $\frac{1}{200}$ M $Ba(OH)_2$) + (400ml, $\frac{1}{50}$ M HCl) + ( 200ml of Water)

***Sol.*** $[H^+] = \frac{400 \times \frac{1}{50} - 400 \times \frac{1}{200} \times 2}{1000} = 4 \times 10^{-3}$ , so pH = 3 – 2 log 2 = 2.4

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## Section (D) : Weak Acid, Weak Base and their pH, Polyprotic acid :

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

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

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

t = 0 C 0 0

t = $t_{eq}$ C(1–α) Cα Cα $K_a = \dfrac{[H^+]\ \ [OH^-]}{[HA]} = \dfrac{C\ \ \alpha^2}{1-\alpha}$

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

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

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

### Solved Examples

***Ex-12.*** Calculate pH of $10^{-1}$ M $CH_3COOH$

Take $K_a = 2 \times 10^{-5}$.

***Sol.*** $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

C 0 0

C(1–α ) Cα Cα

$K_a = \dfrac{C\alpha^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\dfrac{K_a}{C}} = \sqrt{\dfrac{2\times10^{-5}}{10^{-1}}} = \sqrt{2\times10^{-4}}$ ($\alpha << 0.1$)

So, $[H^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow pH = 3 - \dfrac{1}{2}\log 2 = 2.85$ **Ans.**

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- **At very low concentration (at infinite dilution) weak electrolyte will be almost 100% dissociated, so behave as strong electrolyte**

  (pH) of $10^{-6}$ M HCl $\simeq$ pH of $10^{-6}$ M $CH_3COOH$ $\simeq$ 6)

**(g)** **pH of a mixture of weak acid(monoprotic) and a strong acid** Solution **:**

- Weak acid and Strong acid both will contribute $H^+$ ion.
- For the first approximation we can neglect the $H^+$ ions coming from the weak acid Solution and calculate the pH of the Solution from the concentration of the strong acid only.
- To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.

  If [SA] = $C_1$ and [WA] =$C_2$ , then $[H^+]$ from SA = $C_1$

  the weak acid will dissociate as follows.

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

$C_2$ 0 0

$C_2(1-\alpha)$ $\quad C_2\alpha + C_1$ $\quad C_2\alpha$ $\quad K_a = \dfrac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)}$ $\quad (\alpha <<< 1)$

(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

$K_a = (C_2\alpha + C_1)\alpha$

Total $H^+$ ion concentration = $C_1 + C_2\alpha$

○ If the total $[H^+]$ from the acid is less than $10^{-6}$ M, then contribution from the water can be neglected at 25ºC temp., if not then we have to take $[H^+]$ from the water also.

**(h) pH of a** Solution **of a polyprotic weak acid :**

○ Diprotic acid is the one, which is capable of giving 2 protons per molecule in water.

Let us take a weak diprotic acid ($H_2A$) in water whose concentration is cM.

In an aqueous Solution , following equilbria exist.

If

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

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

**I step**

$$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$$

at eq. $c(1-\alpha_1)$ $\quad c\alpha_1(1-\alpha_2)$ $\quad (c\alpha_1 + c\alpha_1\alpha_2)$

$$(K_{eq})_1\,(H_2O) = \frac{[H_3O^+][HA^-]}{[H_2A]} = K_{a_1}$$

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

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

**II step**

$$HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+$$

at eq. $c\alpha_1(1-\alpha_2)$ $\quad c\alpha_1\alpha_2$ $\quad (c\alpha_1 + c\alpha_1\alpha_2)$

$$[K_{eq}]_2\,[H_2O] = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = K_{a_2}$$

$$K_{a_2} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)(c\alpha_1 c\alpha_2)}{c\alpha_1\ (1-\alpha_2)}$$

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

Knowing the values of $K_{a_1}$, $K_{a_2}$ and c, the values of $\alpha_1$ and $\alpha_2$ can be calculated using equations (i) and (ii).

After getting the values of $\alpha_1$ and $\alpha_2$ $[H_3O^+]$ can be calculated as.

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

**Finally, for calculating pH**

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

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

**Approximation**

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

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

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

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

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

## Solved Examples

***Ex-13.*** Calculate pH, $[HS^-]$, $S^{2-}$ , $[Cl^-]$ in a Solution which is 0.1 M HCl & 0.1 M $H_2S$ given that $Ka_1$ $(H_2S) = 10^{-7}$, $Ka_2$ $(H_2S) = 10^{-14}$ also calculate $\alpha_1$ & $\alpha_2$

***Sol.*** HCl + $H_2S$

0.1 0.1 C = 0.1

∴ pH = 1 (most of $[H^+]$ comes from HCl)

$$H_2S \rightleftharpoons H^+ + SH^-$$

$C_1$ $+0.1$

$C_1 - C_1\alpha_1$ $C_1\alpha_1$, $C_1\alpha_1$

$$Ka_1 = \frac{C_1\alpha_1 \times 10^{-1}}{C_1(1-\alpha_1)}$$

$$\alpha_1 = \frac{10^{-7}}{10^{-1}} = 10^{-6}$$

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

$C_1\alpha_1(1-\alpha_2)$ $C_1\alpha_1\alpha_2$ 0.1

$10^{-14} = 0.1 \times \alpha_2$

⇒ $\alpha_2 = 10^{-13}$

$[S_2^{2-}] = C\alpha_1\,\alpha_2 = 10^{-1} \times 10^{-6} \times 10^{-13} = 10^{-20}$ M

***Ex-14.*** Calculate pH $10^{-1}$ M HCl in $10^{-3}$ M $CH_3COOH$ $[K_a = 2 \times 10^{-5}]$

***Sol.*** $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$C(1-\alpha)$ $C\alpha$ $10^{-1} + C\alpha$

; C ; $10^{-1}$

$H^+$ ion can be treated completely from HCl due to less dissociation of $CH_3COOH$ and its low conc.

$$2 \times 10^{-5} = \frac{C\alpha \times 10^{-1}}{C}$$

$\alpha = 2 \times 10^{-4}$

$[H^+]_{CH_3COOH}$ $C\alpha = 2 \times 10^{-7}$

---

- **All these steps can be followed for the calculation of pOH for weak base and their mixtures (we just have to replace $K_a$ with $K_b$).**

## Section (E) : Mixture of acid and bases :

**(k) pH of a mixture of a weak acid/ weak base with weak/strong base/acid respectively.**

For this type of mixtures there can be two cases in general,

(i) if the acids and bases are mixed in equal amounts (equivalents)

(ii) if the acids and bases are mixed in different amounts (equivalents)

First case will lead to phenomenon of **SALT HYDROLYSIS** and second case will lead to formation of **BUFFER** SOLUTION**S.**

## Section (F) : Salt Hydrolysis :

**Salt + Water $\rightleftharpoons$ acid +base**

When acids and bases are mixed in equal amounts(equivalents), then we will be having salt Solutions only in the water and we have to calculate pH of salt Solutions.

When a salt is added to water, the solid salt first dissolves and breaks into ions completely(unless otherwise specified). The ions of the salt may or may not react with water, the cations when react with water will always produce $H_3O^+$ ions and the anions on reaction with water will produce $OH^-$ ions. Depending on the extent of hydrolysis and on the amounts of $H_3O^+$ and $OH^-$ ions the Solution can be acidic, basic or neutral. If salt is BA, then

$BA(s) \longrightarrow BA(aq) \longrightarrow B^+(aq) + A^-(aq)$

$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$ (anionic hydrolysis)

$B^+ (aq) + 2H_2O(l) \rightleftharpoons BOH (aq) + H_3O^+ (aq)$ (cationic hydrolysis)

**ANIONIC HYDROLYSIS :**

Anions can function as a base on reaction with water and hydrolyse as follows :

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

The extent of hydrolysis of a given anion depends on its basic strength

**CATIONIC HYDROLYSIS :**

Cations can function as acid on reaction with water and hydrolyse as follows.

$B^+(aq) + 2H_2O(l) \rightleftharpoons BOH(aq)\ H_3O^+(aq)$

The extent of hydrolysis of a given cation depends on its acidic strength.

***There are four types of salt.***

(i) Salt of strong acid and strong base

(ii) Salt of strong acid and weak base

(iii) Salt of weak acid and strong base

(iv) Salt of weak acid and weak base

Salts of first type does not undergo hydrolysis and rest three types undergo hydrolysis.

**(i) Salt of strong acid and strong base :**

Neither of the ions will undergo hydrolysis so the Solution contain only the equilibrium of ionization of water.

$2H_2O(l) \rightleftharpoons H_3O^+ + OH^-$

Thus, **the pH of** Solution **will be 7(neutral** Solution**).**

**(ii) Salt of strong acid and weak base :**

The ***Example***s can be $NH_4Cl$,$(NH_4)_2\ SO_4$, $AlCl_3$

Only the cation will undergo hydrolysis and the Solution will be acidic in nature. for ***Example*** in the Solution of $NH_4Cl$ of concentration c, we will have

| | $NH_4^+$ | $+ H_2O \rightleftharpoons$ | $NH_4OH$ | $+ H^+$ | |
|---|---|---|---|---|---|
| t = 0 | c | 0 | 0 | 0 | |
| at eq. | c(1– h) | | ch | ch | (h - degree of hydrolysis) |

$K_h = \dfrac{[NH_4OH][H^+]}{[NH_4^+]}$ = called hydrolysis constant of the salt

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ , $K_b = \dfrac{[NH_4^+][OH^-]}{[NH_4OH]}$

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

From above equations we can get

$K_h \times K_b = K_w$

$K_h = \dfrac{ch\ .ch}{c(1-h)} = \dfrac{ch^2}{(1-h)}$ (genarally 1-h ≃1) so we get, $\Rightarrow h = \sqrt{\dfrac{K_h}{c}}$

$\Rightarrow$ $[H^+] = ch = \sqrt{K_h \times c} = \sqrt{\dfrac{K_w}{K_b} \times c}$

$\Rightarrow$ $pH = -\log [H^+] = -\dfrac{1}{2}\,[\log K_w - \log K_b + \log c] = \dfrac{1}{2}\,[pK_w - pK_b - \log c]$

## Solved Examples

***Ex-15.*** Calculate degree of hydrolysis, $K_h$, h and pH of 1M urea hydrochloride Solution in water, $K_b$(Urea) = 1.5 x $10^{-14}$.

***Sol.*** $NH_2CONHCl$ is a salt of (SA + WB)

So $h = \sqrt{\dfrac{Kw}{K_b.C}} = \sqrt{\dfrac{10^{-14}}{1.5 \ \ x \ \ 10^{-14} \ \ x \ \ 1}}$ or h = 81.65%

$K_h = \dfrac{K_w}{K_b} = \dfrac{10^{-14}}{1.5 \ \ x \ \ 10^{-14}} = 6.667 \text{ x } 10^{-1}$

$pH = 7 - \dfrac{1}{2}\,pK_b - \dfrac{1}{2}\log C = 7 - \dfrac{1}{2}\,(13.82) - \dfrac{1}{2}\log (1)$ or pH = 0.09 Ans.

***Ex-16.*** Equal vol. of 0.2 M $NH_4OH$ (or ammonia) of 0.1 M $H_2SO_4$ are mixed calculate pH of final Solution (given that)

***Sol.*** $K_b$ of $NH_3 = 1.8 \times 10^{-5}$

$pH = 1/2\,\{14 - 4.74 + 1\} = \dfrac{10.26}{2} = 5.13$

---

**(iii)** **Salt of weak acid and strong base :**

The ***Example***s can be $CH_3COONa$, KCN, $Na_2C_2O_4$, $K_3PO_4$

Similar to above analysis we will get

$k_h = \dfrac{ch\ .ch}{c(1-h)} = \dfrac{ch^2}{(1-h)}$ (genarally 1-h ≃1) so we get, $\Rightarrow h = \sqrt{\dfrac{k_h}{c}}$

$k_h \times k_a = k_w$

$[OH^-] = ch = \sqrt{k_h \times c} = \sqrt{\dfrac{k_w}{k_a} \times c}$

$$pH = -\log [H^+] = -\frac{1}{2}[\ \log k_w + \log k_a - \log c] = \frac{1}{2}[pk_w + pk_a + \log c]$$

## Solved Examples

***Ex-17.*** If the equilibrium constant for reaction of HCN with NaOH is $10^{10}$, then calculate pH of $10^{-3}$ M NaCN soulition.

***Sol.*** $HCN + NaOH \rightleftharpoons H_2O + NaCN$ $K = 10^{10}$

$\Rightarrow$ $CN^- + H_2O \rightleftharpoons HCN + OH^-$ $K_h = 10^{-10}$

t = $10^{-3}$ M  0  0

$10^{-3}(1 - h)$  $10^{-3}h$  $10^{-3}h$

$K_h = 10^{-10} = \dfrac{10^{-3}h \times 10^{-3}h}{10^{-3}(1-h)}$ $\Rightarrow$ $h = \sqrt{\dfrac{K_h}{c}} = \sqrt{10^{-7}}$ ,

$\Rightarrow$ $[H^+] = \dfrac{10^{-14}}{10^{-3}\sqrt{10^{-7}}}$

$pH = 7 + \dfrac{1}{2}\log 10 = 7.5$

***Ex-18.*** Calculate degree of hydrolysis(h) and pH of Solution obtanied by dissolving 0.1 mole of $CH_3$ COONa in water to get 100 ml of Solution( take $K_a$ of acetic acid = $2 \times 10^{-5}$ )

***Sol.*** $c = \dfrac{0.1}{100} = 1 \times 10^{-3}$ ml

$k_h = \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{2 \times 10^{-5}} = 5 \times 10^{-10}$ , $\Rightarrow$ $h = \sqrt{\dfrac{K_h}{c}} = \sqrt{\dfrac{5 \times 10^{-10}}{2 \times 10^{-5}}} = 5 \times 10^{-3} = 0.5\%$

$c = \dfrac{0.1}{0.1} = 1$

$pH\ \dfrac{1}{2} = [pK_w + pK_a + \log c] = \dfrac{1}{2}\ [14 + 5 - \log 2 + \log 1] = \dfrac{1}{2}\ [18.7] = 9.35$

---

**(iv)** **Salt of weak acid and weak base :**

***Example***s can include $CH_3COONH_4$, $NH_4CN$, $Ca(CH_3COO)_2$, $MgC_2O_4$

$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

t = 0  c  c  0  0

at eq.  c – ch  c – ch  ch  ch

$K_h = \dfrac{[CH_3COOH]\ [NH_4OH]}{[CH_3COO^-]\ [NH_4^+]}$ .....(i)

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$, $K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ .....(ii)

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ , $K_b = \dfrac{[NH_4^+][OH^-]}{[NH_4OH]}$ ......(iii)

$H_2O \rightleftharpoons H^+ + OH^-$, $K_w = [H^+]\ [OH^-]$ ......(iv)

So, $\mathbf{K_h \times K_a \times K_b = K_w}$,

$\Rightarrow$ $k_h = \dfrac{ch.ch}{c(1-h).c(1-h)} = \left(\dfrac{h}{1-h}\right)^2$ $\Rightarrow \left(\dfrac{h}{1-h}\right) = \sqrt{k_h}$

from (ii) equation

$[H^+] = k_a = K_a = K_a \times = K_a \times = K_a \times =$

$\mathbf{pH} = -\log [H^+] = \mathbf{[pK_w + pK_a - pK_b]}$

***Ex-19.*** Calcluate pH of $10^{-2}$ M $NH_4CN$ Solution given that $K_a$ of HCN = $5\times10^{-10}$ and $K_b$ of (aq .$NH_3$) =$2\times10^{-5}$.

***Sol.*** $pH = \dfrac{1}{2}[14 + pK_a - pK_b] = \dfrac{1}{2}[14 + 10 - \log 5 - 5 + \log 2] = \dfrac{1}{2}[18.6] = 9.3$

$$\frac{h}{1-h} = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{5\times10^{-10}\times2\times10^{-5}}} = 1$$

$\Rightarrow$ $2h = 1$

$\Rightarrow$ $h = \dfrac{1}{2} = 0.5$

---

## Section (G) : Buffer Solution and Buffer capacity

### (If the acids and bases are mixed in different amounts (equivalents))

Buffer Solutions are those, which resist a change in pH upon addition of small amount of acid or base. This does not mean that the pH will not change, and all it means is that the pH change would be less than the change that would have occurred, had it not been a buffer.

**There are various types of buffers :**

(i) Buffer of weak acid and its salt with a strong base ;

(ii) Buffer of a weak base and its salt with a strong acid.

(iii) The Solution of the salt of a weak acid and a weak base.

To calculate the pH of a buffer Solution made up of a weak acid and its salt with a strong base. We have

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ $K_a = \dfrac{[CH_3COO^-]\ [H^+]}{[CH_3CO_2H]} = \dfrac{[Salt][H^+]}{[Acid]} \Rightarrow [H^+] = K_a \times \dfrac{[Acid]}{[Salt]}$

Taking log of both sides. $\log [H^+] = \log K_a + \log \dfrac{[Acid]}{[Salt]}$

$\therefore$ $\mathbf{pH = pK_a + \log} \dfrac{[Salt]}{[Acid]}$

This is known as the **Henderson's equation of a buffer.**

For a buffer made up of weak base and its salt with a strong acid the Henderson's equation looks like this :

$\mathbf{pOH = pK_b + \log} \dfrac{[Salt]}{[Base]}$

**Buffer Capacity :** It is defined as the mole of a strong acid or strong base required to change the pH of a buffer by one unit, for 1 L Buffer solution.

**Maximum buffer capacity :** It can be proved that the maximum buffer capacity is achieved when the salt and acid or base concentration is equal.

## Solved Examples

***Ex-20.*** Calculate the amount of $(NH_4)_2SO_4$ in grams which must be added to 500ml of 0.2 M $NH_3$ to give a Solution of pH =9.3. Given $pk_b$ for $NH_3$ = 4.7

***Sol.*** $pOH = pk_b + \log \frac{[\text{Cojugate acid/salt}]}{[\text{Base}]}$

$4.7 = 4.7 + \log \frac{x}{0.2}$ ⇒ x = 0.2, so concentration of $(NH_4)_2SO_4$ required = 0.1 M

∴ moles of $SO_4^{2-}$ needed = 0.05

mol weight of $(NH_4)_2SO_4$ = 132 gm/mole

∴ weight of $(NH_4)_2SO_4$ needed = 132 × 0.05 = 6.6 gm

***Ex-21.*** The pH of a blood stream is maintained by a proper balance of $H_2CO_3$ and $NaHCO_3$. What volume of 5 M $NaHCO_3$ Solution should be mixed with 10ml of a sample of Solution which is 2.5 M in $H_2CO_3$ (assume no $NaHCO_3$), in order to maitain a pH = 7.4.($pK_a$ for $H_2CO_3$ = 6.7, log 2 = 0.3)

***Sol.*** $pH = pk_a + \log \frac{\text{salt}}{\text{acid}}$ ⇒ $7.4 = 6.7 + \log \frac{\text{salt}}{\text{acid}}$ ⇒ $\frac{\text{salt}}{\text{acid}} = 5$

⇒ 5 × 2.5 × 10 = 5 × V ⇒ required volume = 25 ml

---

## Section (H) : Indicator and Acid base Titration

### Indicator :

Indicators are the substance, which indicates the end-point of a titration by changing their colour. They are in general, either weak organic acids or weak organic bases having characteristically different colours in the ionised and unionised forms. For ***Example***, methyl orange is a weak base (having red colour in ionised form and yellow colour in the unionised form) and phenolphthalein is a weak acid (having pink colour in the ionized form while its unionised form is colourless)

Let us consider the equilibrium between the ionised and unionsed form of an acid indicator (HIn)

$$HIn \rightleftharpoons H^+ + In^-$$

∴ $K_{HIn} = \frac{[H^+][In^-]}{[HIn]}$ [$K_{HIn}$ = indicator constant or dissociation constant of indicator]

or $[H^+] = K_{HIn} \times \frac{[HIn]}{[In^-]}$

Taking negative logarithm of both sides

$$-\log [H^+] = -\log K_{HIn} - \log \frac{[HIn]}{[In^-]}$$

∴ $pH = pK_{HIn} + \log \frac{[In^-]}{[HIn]}$ ⇒ $pH = pK_{HIn} + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$

In general, the intensity of a coloured Solution depends on the concentration of the colour imparting species. If the Solution contains two coloured species, then the colour of the Solution depends on the relative concentration of the colour imparting species. When the Solution contains two coloured species as HIn and $In^-$, then it is seen that the Solution acquires a distinct colour of $In^-$ only when the concentration of $In^-$ is approximately at least 10 times greater than the concentration of HIn and vice versa.

Let us consider two cases.

**Case-I :** In order for the Solution to show colour due to $In^-$ the minimum ratio of $\frac{[In^-]}{[HIn]}$ should be 10.

$\therefore$ $pH = pK_{HIn} + \log(10) = pK_{HIn} + 1$

At this stage, the percentage of the indicator in $In^-$ form would be given by

$$\frac{[In^-]}{[In^-]+[HIn]} \times 100 = \frac{10}{10+1} \times 100 \approx 91.$$

Thus, nearly 91% of the indicator has been present in the ionised form ($In^-$). In fact $pH = pK_{HIn} + 1$ is the minimum pH up to which the Solution has a distinct colour characteristic of $In^-$. At pH greater than this value, some more indicator will be present in the ionised form. Thus at $pH \geq pK_{Hin} + 1$, the Solution has a colour characteristic of $In^-$.

**Case-II :** In order for the Solution to show colour due to HIn, the maximum ratio of $\frac{[In^-]}{[HIn]}$ should be $\frac{1}{10}$.

$\therefore$ $pH = pK_{HIn} + \log\frac{1}{10} = pK_{HIn} - 1.$

At this stage, the percentage of the indicator in $In^-$ form would be given by

$$\frac{[In^-]}{[In^-]+[HIn]} \times 100 \frac{1}{10+1} \times 100 \approx 9.1$$

Thus, nearly 9.1% of the indicator has been present in the ionised from ($In^-$) and % of the indicator is present in the uionzed from (HIn). In fact $pH = pK_{HIn} - 1$ is the maximum pH up to which the Solution has a distinct colour characteristic of HIn. At pH smaller than this value, some more indicator will be present in the unionised form. Thus at $pH < pK_{HIn} - 1$, the Solution has a colour characteristic of HIn.

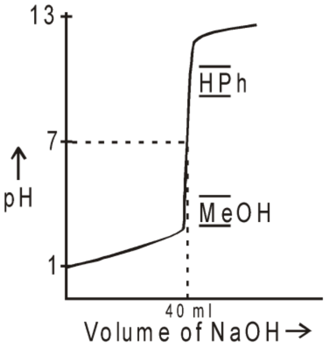
## Acid-Base Titration :

- Titration of SA vs SB :

40 ml 0.1 M HCl, NaOH 0.1 M

| **Volume of NaOH added** | **pH of** Solution |
|---|---|
| 0 ml | 1 |
| 10 ml | 1.22 |
| 20 ml | 1.48 |
| 30 ml | 1.84 |
| 39 ml | 2.90 |
| 39.9 ml | 3.90 |
| 40.0 ml | 7 |
| 40.1 ml | 10.1 |
| 41 ml | 11.1 |
| 50 ml | 12.05 |

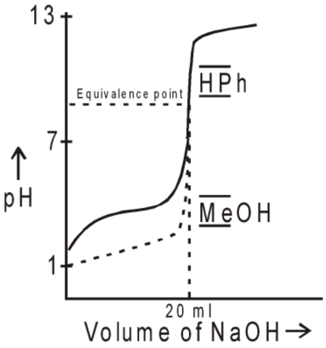
| | |
|---|---|
| 60 ml | 12.30 |



⇒ Indicator should change it colour sharply for indication of reaction to be complete so its pH - range should lie perfectly with in sharp change to avoid experimental error.

⇒ MeOH and HpH both can be used for titration of SA and SB.

- Titration of WA vs SB :



WA = $CH_3COOH$ , $K_a = 2 \times 10^{-5}$ ,

0.5 , 20 ml, NaOH = 0.5 M

| Volume of NaOH | pH value |
|---|---|
| 0 | 2.5 |
| 5 ml | 4.23 |
| 10 ml | 4.7 |
| 15 ml | 4.7 + log 3 = 5.17 |
| 19 ml | 4.7 + log 19/1 = 6 |
| 20 ml | 7 + 1/2 (4.7) + 1/2 log (1/4) = 9.05 |
| 21 ml | 12.4 |
| 30 ml | 13.23 |

* In sharp change of pH HPh is suitable indicator.

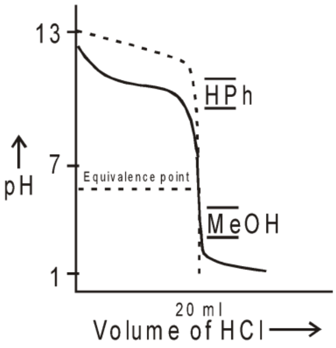
* Initially fast change in pH is due to free ions available fram weak acid.

* Slow down of pH change is due to Buffer formation, which is maximum at pH = pKa.

* Near equivalence point pH again increases fastly due to salt formation.

* After equiv. point pH changes very sharply due to presence of strong base.

- Titration of WB vs SA



Sharp change between 4 to 7

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## Section (I) : Solubility product and solubility calculation :

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

1. Simple Solution in $H_2O$
2. Effect of common ions on solubility
3. Simultaneous solubility
4. $\text{Precipitate}_1 + \text{electrolyte}_1 \rightarrow \text{Precipitate}_2 + \text{electrolyte}_2$
5. Condition for precipitation
6. Solubility in a buffer Solution
7. Solubilty due to complex formation

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

Following ***Example***s will illustrate the different type of solubilities and the effects of different factors or situations on solubility of a salt.

- **Simple Solubility**

  Let the salt is $A_xB_y$, in Solution in water, let the solubility in $H_2O$ = ‘s’ M, then

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

$$- \qquad xs \qquad ys \qquad\qquad \therefore \qquad \mathbf{K_{SP} = (xs)^x\,(ys)^y = x^x.y^y.(s)^{x+y}}$$

### Solved Examples

***Ex-22.*** Calculate $K_{SP}$ of $Li_3Na_3[AlF_6]_2$

***Sol.*** $K_{SP} = 3^3.3^3.2^2\,(s)^8 = 3^6.4.(s)^8 = 2916\,s^8$

---

- **Effect of common ions on solubility :**
  - Because of the presence of common ion, the solubility of the salt decreases.

### Solved Examples

***Ex-23.*** Calculate solubility of silver oxalate in $10^{-2}$ M Potassium oxlalate Solution given that $K_{SP}$ of silver oxalate ($Ag_2C_2O_4$) = $10^{-10}$.

***Sol.*** [oxalate] = $10^{-2} + 2x$, where x is the solubility of silver oxalate, this can be neglected in comparison to $10^{-2}$.So

$K_{sp} = 10^{-10} = 10^{-2} \times (2x)^2 \quad \Rightarrow \quad \frac{10^{-8}}{2\times 2} = x^2 \quad \Rightarrow \quad x = 5\times10^{-5}$

---

- **Calculation of simultaneous Solubility**
  - ○ When two sparingly soluble salts are added in water simultaneously, there will be two simultaneous equilibria in the Solution.

## Solved Examples

***Ex-24.*** Calculate simultaneous solubility of silverthiocyanate and sliver bromide in water given that $k_{SP}$ of silver thiocyanate = $10^{-12}$ and $k_{SP2}$ of silver bromide = $5\times10^{-13}$ respectively.

***Sol.*** Let the solubility of AgSCN be x and that of AgBr is y, then

$AgSCN \rightleftharpoons \underset{x+y}{Ag^+} + \underset{x}{SCN^-}$ $\qquad$ $AgBr \rightleftharpoons \underset{x+y}{Ag^+} + \underset{y}{Br^-}$

$10^{-12} = x(x + y)$ -------(i)

$5 \times 10^{-13} = y(x + y)$ -------(ii)

On solving we get, $x = 2y$

So $y = 4.08 \times10^{-7}$ and $x = 8.16 \times10^{-7}$

---

- **Condition of precipitation**
  - ○ **For precipitation ionic product ($K_{IP}$) should be greater than solubility product $K_{SP}$**

## Solved Examples

***Ex-25.*** You are given $10^{-5}$ M NaCl Solution and $10^{-8}$ M $AgNO_3$ Solution, they are mixed in 1:1 volume ratio, predict whether AgCl will be precipitated or not, if solubility product of AgCl in $10^{-2}$ M $AgNO_3$ is $= 10^{-10}$ mole per litre.

***Sol.*** Ionic product = $\frac{10^{-5}}{2} \times \frac{10^{-8}}{2} = 25\times10^{-15} < K_{sp}$

Hence no precipitation will take place.

---

- **Solubility in appropriate buffer** Solution**s.**

Appropriate buffer means that the components of buffer should not interfere with the salt or only $H^+$ or $OH^-$ ions should be interacting with the ions of the salt.

- **Selective Precipitation**

When the Ksp values differ then one of the salt can be selectively precipitated.

## Solved Examples

***Ex-26.*** What $[H^+]$ must be maintained in a saturated $H_2S$ (0.1 M) to precipitate CdS but not ZnS, if $[Cd^{2+}] = [Zn^{2+}] = 0.1$ initially ?

$K_{sp}$ (CdS) = $8 \times 10^{-27}$

$K_{sp}$ (ZnS) = $1 \times 10^{-21}$

$K_a$ ($H_2S$) = $1.1 \times 10^{-21}$

***Sol.*** In order to prevent precipitation of ZnS,

$[Zn^{2+}][S^{2-}] < K_{sp}(ZnS) = 1 \times 10^{-21}$

(Ionic product)

or $(0.1) . [S^{2-}] < 1 \times 10^{-21}$ or $[S^{2-}] < 1 \times 10^{-20}$

This is the maximum value of $[S^{2-}]$ before ZnS will precipitate. Let $[H^+]$ to maintain this $[S^{2-}]$ be x.

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

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{x^2(1 \times 10^{-20})}{0.1} = 1.1 \times 10^{-21} \quad \text{or} \quad x = [H^+] = 0.1\ M$$

∴ No ZnS will precipitate at a concentration of $H^+$ greater than 0.1 M.

## MISCELLANEOUS SOLVED PROBLEMS (MSPs)

**1.** Concentration of the anion will be 3c.h for the following weak electrolytes.

(1) $AB_2$ (2) AB (3) $AB_3$ (4) $A_3B_4$

**Sol.** $AB_3 \rightleftharpoons A^{3+} + 3B^-$

| | $AB_3$ | $A^{3+}$ | $3B^-$ |
|---|---|---|---|
| Initial mole | 1 | 0 | 0 |
| Mole at. Eq. | 1 – h | h | 3h |
| If volume is v, | $\frac{1-h}{v}$ | $\frac{h}{v}$ | $\frac{3h}{v}$ |

Therefore, 3c.h **Ans. (3)**

**2.** Dissociation constants of $CH_3COOH$ and HCN are $1.8 \times 10^{-5}$ and $7.2 \times 10^{-10}$ respectively, what will be the relation between the degree of hydrolysis of KCN ($h_1$) and $CH_3COOK$($h_2$) ?

(1) $h_1 > h_2$ (2) $h_1 < h_2$ (3) $h_1 = h_2$ (4) All of the above

**Sol.** The salt is formed from weak acid and strong base

Therefore, $h = \sqrt{K_h \times V}$ $K_h = \frac{K_w}{K_a}$

$h = \sqrt{\frac{K_w}{K_a} \times V}$ or $h \propto \sqrt{\frac{1}{K_a}}$

Therefore, its $K_a$ will be high and its h will be low. **Ans. (2)**

**3.** When $NH_4Cl$ solution is diluted, the pH

(1) decrease (2) Increases

(3) remains unchanged (4) First increases then decreases.

**Sol.** $NH_4Cl$ is formed from strong acid and weak base.

$[H^+] = \sqrt{\frac{K_w}{K_a} \times C}$

Therefore $[H^+] \propto \sqrt{C}$ **Ans. (2)**

Since concentration decreases on dilution , due to which $[H^+]$ decreases and the pH increases.

**4.** Decinormal solutio of acetic acid gets 1.3% ionised. What will be the ionisation constant of acetic acid ?

**Sol.** $K_a = \frac{C\alpha^2}{1-\alpha}$

$\alpha = \frac{1.3}{100} = 0.013$

C = 0.1 N

$\alpha < 0.1$ therefore $Ka = c\alpha^2$

$= 0.1 \times (0.013)^2 = 1.69 \times 10^{-5}$

**5.** If equal concentrations are mixed (of products & reactants) then which of the reaction will proceed to the right and which will proceed to the left.

(a) $H_2SO_4(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + HSO_4^-(aq)$

(b) $HCO_3^-(aq) + SO_4^{2-}(aq) \rightleftharpoons HSO_4^-(aq) + CO_3^{2-}(aq)$

**Sol.** (a) Right; (b) Left

**6.** (a) Write conjugate acids of $SO_4^{2-}$ , $RNH_2$ , $NH_2^-$ , $C_2H_5O\,C_2H_5$ , $F^-$

(b) Write conjugate base of $HNO_2$ , $OH^-$, $H_2CO_3$, $HClO_4$.

(c) Write conjugate acids and conjugate base of amphoteric species.

$HS^-$ , $NH_3$, $C_2H_5OH$, $H_2O$

**Sol.** (a) $HSO_4^-$, $RNH_3^{\oplus}$, $NH_3$, $(C_2H_5)_2OH^{\oplus}$, HF

(b) $NO_2^-$, $O^{2-}$, $HCO_3^-$, $ClO_4^-$

(c) Conjugate acids : $H_2S$ , $NH_4^+$, $C_2H_5OH_2^+$, $H_3O^+$

Conjugate base : $S^{2-}$, $NH_2^-$, $C_2H_5O^-$, $OH^-$

**7.** Which of the following is the strongest base-

(1) $C_2H_5^-$ (2) $C_2H_5COO^-$ (3) $C_2H_5O^-$ (4) $OH^-$

**Ans.** (1)

**8.** In the reaction, (a) $C_2H_5NH_2 + HI \rightleftharpoons (C_2H_5NH_3)^+ I^-$. Which reactant would be considered as Bronsted acid, is it also an arrhenius acid. Is it also a lewis acid ?

(b) What about the other species ($C_2H_5NH_2$) in the above reaction is it Arrhenius base, is it Bronsted base, is it lewis base ?

**Ans.** **(a) [HI, yes, no] (b) [No, yes, yes]**

**9.** Calculate the pH of solution obtained by mixing 10 mL of 0.1 M HCl and 40 mL of 0.2 M $H_2SO_4$.

**Sol.** Milli equivalent of $H^+$ from HCl = 10 × 0.1 = 1

Milli equivalent of $H^+$ from $H_2SO_4$ = 40 × 0.2 × 2 = 16

$\therefore$ Total Meq.of H+ in solution = 1 + 16 = 17

$\therefore$ $[H+] = \frac{17}{50} = 3.4 \times 10^{-1}$ $\left(\because [H^+] = \frac{\text{Meq.}}{V_{\text{in mL}}}\right)$

$\therefore$ $pH = -\log [H^+] = -\log 0.34$

pH = **0.4685**

**10.** Calculate pH of a KOH solution having :

**(a)** 5.6 g of KOH mixed in 50 water

**(b)** if it is further diluted to make 100 ml.

**Ans.** **(a)** 14.3 **(b)** 14

**11.** Calculate the pH of a solution which contains 100 mL of 0.1 M HCl and 9.9 mL of 1.0 M NaOH.

**Sol.**

| | HCl + | NaOH → | NaCl + | $H_2O$ |
|---|---|---|---|---|
| Meq. before reaction | 100 × 0.1<br>= 10 | 9.9 × 1<br>= 9.9 | 0 | 0 |
| Meq. after reaction | 0.1 | 0 | 9.9 | 9.9 |

∴ $[H^+]$ left from HCl $= \frac{0.1}{109.9} = 9.099 \times 10^{-4}$ M

∴ pH $= -\log H^+ = -\log 9.099 \times 10^{-4}$

pH = **3.0409**

**12.** Calculate the pH of 0.001 M HOCl having 25% dissociation. Also calculate dissociation constant of the acid.

**Sol.** $HOCl \rightleftharpoons H^+ + OCl^-$

$a - a\alpha \quad a\alpha \quad a\alpha$

So, $[H^+] = a\alpha = 10^{-3} \times \frac{25}{100} = 2.5 \times 10^{-5}$

So, pH = 4.86

Now, $K_a = \frac{(a\alpha)\ (a\alpha)}{a\ (1-\alpha)} = \frac{a\alpha^2}{1-\alpha} = \frac{1}{12} \times 10^{-3}$

**13.** A solution contains 0.1 M $H_2S$ and 0.3 M HCl. Calculate the conc. of $S^{2-}$ and $HS^-$ ions in solution. Given $K_{a1}$ and $K_{a2}$ for $H_2S$ are $10^{-7}$ and $1.3 \times 10^{-13}$ respectively.

**Sol.** $H_2S \rightleftharpoons H^+ + HS^-$; $K_{a1} = 10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-}$; $K_{a2} = 1.3 \times 10^{-13}$

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

Due to common ion effect the dissociation of $H_2S$ is suppressed and the $[H^+]$ in solution is due to HCl.

∴ $K_{a1} = \frac{[H^+][HS^-]}{[H_2S]}$ $\quad 10^{-7} = \frac{[0.3][HS^-]}{[0.1]}$ [▯ $[H^+]$ from HCl = 0.3]

∴ $[HS^-] = \frac{10^{-7} \times 0.1}{0.3}$ = **$3.3 \times 10^{-8}$ M**

Further $K_{a2} = \frac{[H^+][S^{2-}]}{[HS^-]}$ $\quad 1.3 \times 10^{-13} = \frac{[0.3][S^{2-}]}{3.3 \times 10^{-8}}$

∴ $[S^{2-}] = \frac{1.3 \times 10^{-13} \times 3.3 \times 10^{-8}}{0.03}$ = **$1.43 \times 10^{-20}$ M**

**14.** Calculate the ratio of pH of a Solution containing 1 mole of $CH_3COONa$ + 1 mole of HCl per litre and of other Solution containing 1 mole $CH_3COONa$ + 1 mole of acetic acid per litre.

**Sol.** Case I: pH when 1 mole $CH_3COONa$ and 1 mole HCl are present.

| | $CH_3COONa$ | + | HCl | → | CHCOOH | + | NaCl |
|---|---|---|---|---|---|---|---|
| Before reaction | 1 | | 1 | | 0 | | 0 |
| After reaction | 0 | | 0 | | 1 | | 1 |

∴ $[CH_3COOH] = 1$ M

∴ $[H^+] = C.\ \alpha = C\sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{(K_a.C)} = \sqrt{(K_a)}$ ∴ C = 1

∴ $pH_1 = -\frac{1}{2}\log K_a$

Case II : pH when 1 mole $CH_3COONa$ and 1 mole of $CH_3COOH$; a buffer Solution.

∴ $pH_2 = -\log K_a + \log \frac{[Salt]}{[Acid]}$ ∴ $[Salt] = 1\ M$

$pH_2 = -\log K_a$ ∴ $[Acid] = 1\ M$

∴ $\frac{pH_1}{pH_2} = \frac{1}{2}$

**15.** Calculate the amount of $NH_3$ and $NH_4Cl$ required to prepare a buffer Solution of pH 9, when total concentration of buffering reagents is 0.6 mol litre$^{-1}$. $pK_b$ for $NH_3 = 4.7$, log 2 = 0.30

**Sol.** $pOH = -\log K_b + \log \frac{[Salt]}{[Base]}$

$5 = 4.7 + \log \frac{a}{b}$

$\frac{a}{b} = 2$ ∴ $a = 2b$

Given $a + b = 0.6$

$2b + b = 0.6$

∴ $3b = 0.6$

or $b = 0.2$ mole or $0.2 \times 17 =$ **3.4 g/L** 3.4 g/L

∴ $a = 0.4$ mole or $0.4 \times 53.5 =$ **21.4 g/L**

Thus, $[Salt] =$ **0.4 M** and $[Base] =$ **0.2 M**

**16.** The solubility product of $SrF_2$ in water is $8 \times 10^{-10}$. Calculate its solubility in 0.1 M NaF aqueous Solution.

**Sol.** $K_{sp} = [Sr^{2+}]\,[F^-]^2$

$8 \times 10^{-10} = s[2s + 0.1]^2$

∴ $s = \frac{8\times10^{-10}}{(0.1)^2} = 8 \times 10^{-8}\ M$

**17.** Calculate $K_{SP}$ of $Mg_3(PO_4)_2$ in terms of solubility in water.

**Ans.** $108\ S^5$

**18.** Calculate solubility of $BaSO_4$ when $CaSO_4$ and $BaSO_4$ are dissolved in water simultaneously $K_{sp}$ $CaSO_4 = p$, $K_{sp}$ $BaSO_4 = q$ and solubility of $CaSO_4$ is 'b' mol/litre.

**Ans.** bq / p

**19.** A solution of HCl has a pH = 5. If one mL of it is diluted to 1 litre, what will be pH of resulting solution.

**Sol.** $HCl_I = 10^{-5}$ M since pH = 5

Meq. of $HCl_I$ in 1 mL = $10^{-5} \times 1$

Meq. of $HCl_{II}$ in 1000 mL = $N \times 1000$

Since II is prepared by diluting I and Meq. does not change on dilution.

i.e., Meq. of HCl (concentrated) = Meq. of HCl (dilute)

∴ $10^{-5} \times 1 = N \times 1000$

∴ $N_{HCl_{II}} = 10^{-8}$

∴ pH = **6.9788**

**20.** How much will be the solubility of AgCl in 0.001 M NaCl, If solubility product of AgCl is $10^{-10}$ ?

**Sol.** $AgCl \rightleftharpoons Ag^{+1} + Cl^{-}$

$s \quad s \quad s + 0.001$

$NaCl \rightleftharpoons Na^{+} + Cl^{-}$

$0.001 \quad 0.001 \quad 0.001 + s$

Therefore, $[Ag^{+}] = s$

$K_{sp} = [Ag^{+}] \quad [Cl^{-}] \qquad [Cl^{-}] = s + 0.001$

$(s) \quad (s + 0.001) = s^2 + 0.001\,s = 10^{-10}$

$s^2 <<< 1$

$\therefore 0.001\,s = 10^{-10} \qquad s = \frac{10^{-10}}{10^{-3}} = 10^{-7}$

**21.** 0.002 M solid $Ca(NO_3)_2$ is added to 0.004 M $H_2SO_4$ solution. Find out, whether $CaSO_4$ will be precipitated or not, if $K_{sp}$ of $CaSO_4 = 2.5 \times 10^{-5}$ .

**Sol.** $[SO_4^{2-}]$ given by 0.004 M($H_2SO_4$) = 0.004 M $\qquad$ $[Ca^{+}]$ given by solid $Ca(NO_3)_2$ = 0.002 M

$K_{IP} = [Ca^{2+}]\,[SO_4^{-2}] \qquad 0.002 \times 0.004 = 8 \times 10^{-6}$

Here, ionic product of $CaSO_4$ is $8 \times 10^{-6}$, which is less than its solubility product $2.5 \times 10^{-6}$. Therefore precipitation will not take place.

**22.** Equal volume of 0.004 M $CaCl_2$ and 0.002 M $Na_2SO_4$ are mixed. Find out, whether $CaSO_4$ will be precipitated or not, if $K_{sp}$ of $CaSO_4$ $K_{sp} = 2.5 \times 10^{-5}$ ?

**Sol.** When equal amounts of $CaCl_2$ and $Na_2SO_4$ are mixed, the concentration becomes half.

$[Ca^{+}] = \frac{[CaCl_2]}{2} = \frac{0.004}{2} = 0.002\text{ M} \qquad [SO_4^{-2}] = \frac{0.002}{2} = 0.001\text{ M}$

Ionic products = $[Ca^{+2}] \times [SO_4^{-2}] = (0.002) \times (0.001) = 2 \times 10^{-6}$

Here ionic product of $CaSO_4$ is $2 \times 10^{-6}$, which its less than its solubility product. Therefore precipitation will not take place.

**23.** What should be the ionic product of $CaSO_4$, whose $K_{sp} = 2.4 \times 10^{-5}$, when 150 ml of 0.0008 M ammonium sulphate solution is mixed with 50 ml of 0.04 M calcium nitrate solution ?

(1) $< K_{sp}$ $\qquad$ (2) $> K_{sp}$ $\qquad$ (3) $K_{sp}$ $\qquad$ (4) None of the above

**Sol.** $M_1V_1 = M_2V_2$ for $Ca^{2+}$ ion

$50 \times 0.04 = M_2 \times 200$ ( total volume 50 + 150 = 200)

$M_2 = \frac{50 \times 0.04}{200} = 0.01$

Therefore, $[Ca^{2+}] = 0.01$

$[SO_4^{-2}] = M_1V_1 = M_2V_2$

$150 \times 0.0008 = M_2 \times 200$

$M_2 = \frac{150 \times 0.0008}{200} = 0.0006$

$[SO_4^{-2}] = 0.0006$

$K_{IP} = [Ca^{2+}] \times [SO_4^{-2}] = (0.01) \times (0.0006) = 6 \times 10^{-6}$ **Ans.** **1**

Therefore, $K_{sp} > K_{IP}$

**24.** The solubility of AgCl $4 \times 10^{-6}$ (s) then findout its $K_{sp}$ and its new solubility in the presence of $2 \times 10^{-3}$ M $CaCl_2$.

**Sol.** $K_{sp} = s^2 = (4 \times 10^{-6}) = 1.6 \times 10^{-11}$

$CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl^-$

$c \qquad c \qquad 2c + s$

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

$s \qquad s \qquad s + 2c$

$K_{sp} = [S]\,[S+2C]$

s can be neglected hence s + 2c 2c

$S = \dfrac{16\times10^{-12}}{2\times2\times10^{-3}}$ $\qquad s = 4 \times 10^{-9}$