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PHYSICAL
CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER

STUDY MATERIAL

Ionic Equilibrium

ENGLISH MEDIUM

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IONIC EQUILIBRIUM

4.0 INTRODUCTION

Formulae :

(i) $\ln x = \log_e x = 2.303 \log_{10} x = 2.303 \log x$

(ii) $\log (x \times y) = \log x + \log y$

(iii) $\log \left(\dfrac{x}{y} \right) = \log x - \log y$

(iv) $\log x^y = y \log x$

Ex.   (i) $\log 6$ $= \log (2 \times 3)$

                      $= \log 2 + \log 3$

                      $= 0.3010 + 0.4771 = 0.7781$

     (ii) $\log 30$ $= \log (3 \times 10)$

                      $= \log 3 + \log 10$

                      $= \log 0.4771 + 1 = 1.4771$

     (iii) $\log 1000 = \log 10^3$

                        $= 3 \log 10 = 3 \times 1 = 3$

A. Some values of Log :

$\log 1 = 0$
$\log 2 = 0.3010$
$\log 3 = 0.4771$
$\log 4 = 0.6020$
$\log 5 = 0.699$
$\log 6 = 0.7781$
$\log 7 = 0.8451$
$\log 8 = 0.9030$
$\log 9 = 0.9542$
$\log 10 = 1$
$\log 11 = 1.04$
$\log 100 = 2$
$\log 1000 = 3$

Some terms which are used in ionic equilibrium :   **Antilog :** Antilog $(x) = 10^x$

   Ex.   Antilog $(2) = 10^2 = 100$

        Antilog $(0.3010) = 10^{.3010} = 2$

        Antilog $[\log (2)] = $ Antilog $(0.3010) = 2$

pH - Scale : Given by – **Sorenson**

pH Scale is called Sorenson scale.

pH scale is a measuring scale used to measure strength of acid and base and its value is equal to $-\log[H^+]$

    i.e. $pH = -\log[H^+] = \log \dfrac{1}{\left[H^+ \right]}$

    Ex. $[H^+] = 10^{-3}$

               $pH = -\log 10^{-3} = +3 \log 10 = 3$

Conclusion :

      If $pH = x$ then $[H^+] = 10^{-x}$ or Vice versa

  i.e.   If $[H^+] = 10^{-x}$ then $pH = x$
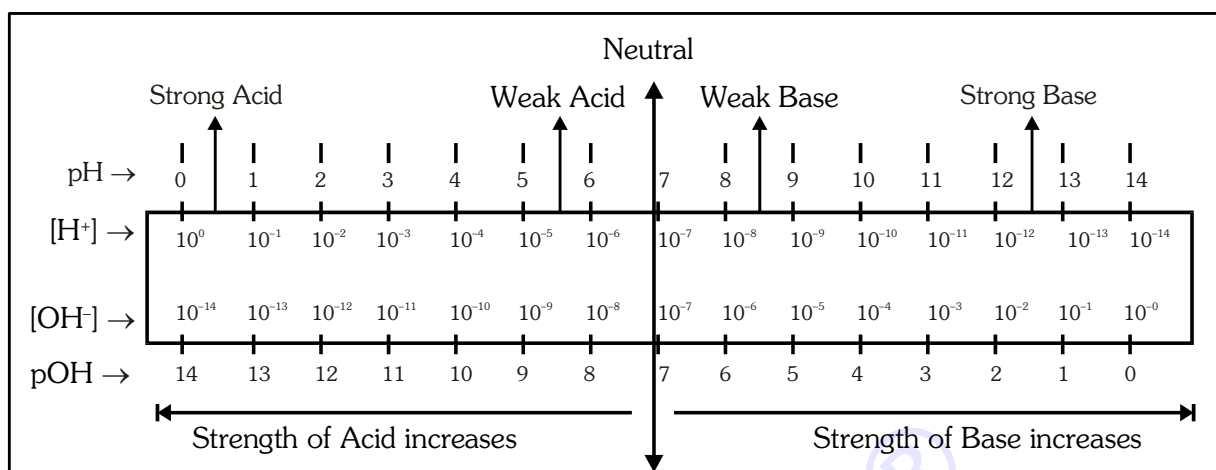
pOH $\rightarrow$ It is equal to $-\log [OH^-]$ i.e. $pOH = -\log [OH^-] = \log \dfrac{1}{[OH^-]}$

Ex.   If $X = \dfrac{a}{b} \times 10^{-c}$, then find pX ?

Sol. $pX = -\log X = -\log \left(\dfrac{a}{b} \times 10^{-c} \right)$

      $pX = - \left[\log \dfrac{a}{b} + \log 10^{-c} \right] = - [\log a - \log b - c]$

$\boxed{pX = c + \log b - \log a}$

pH scale at 25°C

According to conductivity substances are of two types :

(1) Non-Conductor - Those substances which do not show the flow of current or electricity.

Ex. Non - metals, plastic, rubber, wood etc.

**Exception** – Graphite is a non-metal but show conductivity due to motion of free electrons.

(2) Conductors – Those substances which show conductivity or flow of current are called conductors and these are of two types :

(a) Metallic conductor – Those conductor which show conductivity due to motion of free electrons.

Ex. All metals, Graphite

(b) Ionic conductors –

Those conductor which show conductivity due to movement of free ions. Ions are in free state in the solutions of ionic compounds. On passing electric current through the solution, ions move towards oppositely charged electrodes, i.e., the cation moves towards cathode (negative electrode) and the anion moves towards anode (positive electrode). Due to this reason, they are called cations and anions respectively. The current flows through the solution due to the movement of the ion Movement of ions through the solution of electrolyte ($AgNO_3$) towards oppositely charged electrodes.
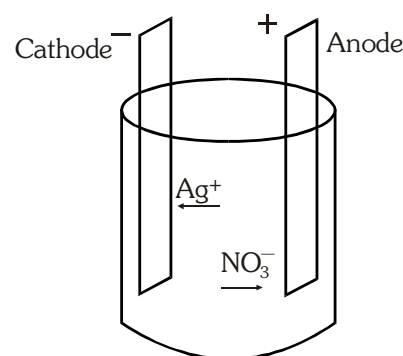
According to strength, ionic conductors are of two types –

(1) Strong electrolytes – Those ionic conductors which are **completely ionized in aqueous solution** are called as strong electrolytes.

For strong electrolyte the value of degree of ionisation is 100% i.e. $\alpha = 1$

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

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

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

(2) Weak electrolytes – Those electrolytes which are **partially ionized in aqueous solution** are called as weak electrolytes. For weak electrolytes the value of α is less than one.

Ex. (a) Weak acids → HCN, CH_3COOH, HCOOH, H_2CO_3, H_3PO_3, H_3PO_2, $B(OH)_3$, etc.

↓

H_3BO_3

(Boric acid)
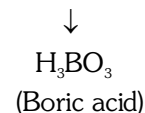
(b) Weak bases → NH_4OH, $Cu(OH)_2$, $Zn(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$ etc.

4.1 ARRHENIUS CONCEPT :

(a) According to Arrhenius when an electrolyte dissolves in water it splits up into two oppositely charged particles i.*e.* cation and anion.

(b) In an electrolytic solution (Aqueous solution of electrolyte), total +ve charge is equal to total –ve charge i.*e.* solution is electrically neutral.

⇒ In an electrolytic solution number of +ve ions may or may not be equal to the number of negative ions.

(c) Properties of an electrolytic solution are defined by its ions.

Ex. Blue colour of $CuSO_4$ aqueous solution is due to Cu^{+2} ion (dark blue colour)

(d) When electric current is pass in aqueous solution of electrolyte then cation shows migration towards cathode where as anion shows migration towards anode.

(e) When a weak electolyte is dissolved in water an equilibrium is set up between unionized moles and ionized moles.

This condition of the reversible ionic reaction is known as ionic equilibrium.

$$AB \, (Aq.) \rightleftharpoons A^+(Aq.) + B^-(Aq.)$$

According to law of mass action

Ionisation constant $\quad K = \dfrac{\left[A^+\right]\left[B^-\right]}{\left[AB\right]}$

──────────────── **Illustrations** ────────────────

Illustration 1   If $[H^+] = \dfrac{5}{3} \times 10^{-4}$ then find pH ?

Solution $pH = -\log [H^+] = -\log \left(\dfrac{5}{3} \times 10^{-4} \right)$

$= -\left[\log \dfrac{5}{3} + \log 10^{-4} \right] = -[\log 5 - \log 3 - 4]$

$= -[0.699 - 0.4771 - 4] = -[-3.778] = 3.778$

Illustration 2   *Assertion :* H_2SO_4 is a strong acid.

Reason : H_2SO_4 undergoes almost completely ionised in aqueous solution.

(1) Both (A) and (R) are true and (R) is the correct explanation of (A).
(2) Both (A) and (R) are true and (R) is NOT the correct explanation of (A).
(3) (A) is true but (R) is false.
(4) (A) is false but (R) is true.

Solution   **Ans. (1)**

4.2 OSTWALD'S DILUTION LAW

⇒   Ostwald dilution law is applicable only for weak electrolytes.

Statement : According to Ostwald when solution of weak electrolyte is diluted then degree of ionisation of solution is increased, is called dilution law.

Let $AB \, (Aq.) \rightleftharpoons A^+(Aq.) + B^-(Aq.)$
Initial concentration   C   0   0
Degree of ionisation (α) $(C - C\alpha)$ $(C\alpha)$ $(C\alpha)$

According to law of mass action

Ionisation constant $\quad K = \dfrac{\left[A^+\right]\left[B^-\right]}{\left[AB\right]} \; ; \; K = \dfrac{C\alpha \times C\alpha}{C(1-\alpha)} = \dfrac{C\alpha^2}{(1-\alpha)}$

If $\alpha <<<< 1$ then $\quad 1 - \alpha \simeq 1$

$K = C\alpha^2 \quad$ or $\quad \alpha = \sqrt{\dfrac{K}{C}}$ (K = constant, At constant temperature)

$\alpha \propto \dfrac{1}{\sqrt{C}} \quad (C \propto \dfrac{1}{V}) \qquad \alpha \propto \sqrt{V}$

volume ≡ dilution $\qquad \alpha \propto \sqrt{\text{dilution}} \qquad$ by dilution law

$$\text{dilution} \uparrow \quad \alpha \uparrow$$

At infinite dilution, $\alpha = 100 \%$

Thus for weak electrolytes the degree of ionisation is directly proportional to square root of dilution or inversely proportional to square root of concentration. This law is known as Ostwald Dilution Law.
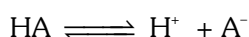
GOLDEN KEY POINTS

- At infinite dilution the value of α becomes equal to one.

Application of Ostwald's Dilution Law : $\boxed{K = C\alpha^2}$

(a) For mono basic weak acid (HA)

(i). Ionisation constant (K_a)

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

Initial concentration $\qquad$ C $\qquad$ 0 $\qquad$ 0

At equilibrium $\qquad$ C – Cα $\quad$ Cα $\quad$ Cα

If degree of ionisation is α

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

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

$\because \quad \alpha <<<< 1 \quad \therefore \quad (1-\alpha) \approx 1$

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

(b) For mono acidic weak base (BOH)

Ionisation constant (K_b)
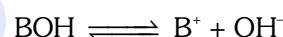
$$BOH \rightleftharpoons B^+ + OH^-$$

Initial concentration $\qquad$ C $\qquad$ 0 $\qquad$ 0

At equilibrium $\qquad$ C – Cα $\quad$ Cα $\quad$ Cα

If degree of ionisation is α

$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{C\alpha \times C\alpha}{C - C\alpha}$$

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

$\because \quad \alpha <<<< 1 \quad \therefore \quad (1-\alpha) \approx 1$

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

Where $\begin{array}{l} K_a \to \text{Ionisation constant of weak acid} \\ K_b \to \text{Ionisation constant of weak base} \end{array}$ $\left. \begin{array}{l} \\ \end{array} \right\}$ Both K_a and K_b depends only on temperature

(ii). $[H^+]$ (Concentration of H^+)

$[H^+] = C\alpha \qquad \qquad$ ....(1)

$K_a = C\alpha^2 \quad$ or $\quad \alpha = \sqrt{\dfrac{K_a}{C}} \quad$ ....(2)

from Eq. (1) and (2) $[H^+] = C \times \dfrac{\sqrt{K_a}}{\sqrt{C}}$

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

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

put the value of $[H^+]$

$pH = -\log(\sqrt{K_a \times C}) = -\log(K_a \times C)^{1/2}$

$pH = -\dfrac{1}{2}[\log K_a + \log C]$

$pH = -\dfrac{1}{2}\log K_a - \dfrac{1}{2}\log C$

$pH = \dfrac{1}{2}pK_a - \dfrac{1}{2}\log C$

$[OH^-]$ (Concentration of OH^-)

$[OH^-] = C\alpha \qquad \qquad$ ....(1)

$K_b = C\alpha^2 \quad$ or $\quad \alpha = \sqrt{\dfrac{K_b}{C}} \quad$ ....(2)

from Eq. (1) and (2) $[OH^-] = C \times \dfrac{\sqrt{K_b}}{\sqrt{C}}$

$[OH^-] = \sqrt{K_b \times C}$

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

put the value of $[OH^-]$

$pOH = -\log(\sqrt{K_b \times C}) = -\log(K_b \times C)^{1/2}$

$pOH = -\dfrac{1}{2}[\log K_b + \log C]$

$pOH = -\dfrac{1}{2}\log K_b - \dfrac{1}{2}\log C$

$pOH = \dfrac{1}{2}pK_b - \dfrac{1}{2}\log C$

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In summary :

1. $K_a = C\alpha^2$

2. $[H^+] = C\alpha = \sqrt{K_a \times C}$

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

or $pH = \dfrac{1}{2}pK_a - \dfrac{1}{2}\log C$

1. $K_b = C\alpha^2$

2. $[OH^-] = C\alpha = \sqrt{K_b \times C}$

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

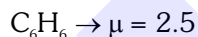or $pOH = \dfrac{1}{2}pK_b - \dfrac{1}{2}\log C$

Limitation of Ostwald Dilution Law :

It is not applicable for strong electrolytes.

Factors affecting the Value of Degree of ionisation :

(1) Temperature $\rightarrow$ On increasing temperature, ionization increases so α increases because dissociation is endothermic process.

(2) Dilution $\rightarrow$ $\alpha \propto \sqrt{V}$ so on dilution, α increases.

(3) Nature of electrolytes

    (i) Strong electrolytes   (ii) Weak electrolytes

        $\alpha = 100\%$ $\alpha < 100\%$

(4) Nature of solvent

    If Dielectric constant μ of solvent increases then the value of α increases.

$$H_2O \rightarrow \mu = 81$$
$$D_2O \rightarrow \mu = 79$$
$$C_6H_6 \rightarrow \mu = 2.5$$
$$CCl_4 \rightarrow \mu = 0$$
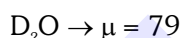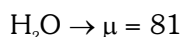
Mixing of ions :

(a) Common ion effect	(b) Odd ion effect
When an electrolyte having a common ion, is mixed with weak electrolyte then the degree of ionisation (α) of weak electrolyte is decreased. This effect is called common ion effect.	When an electrolyte having an odd ion, is mixed with weak electrolyte then the degree of ionisation (α) of weak electrolyte is increased. This effect is called odd ion effect.

Common ion : On mixing CH_3COONa with CH_3COOH solution

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

(On mixing $CH_3COONa \longrightarrow CH_3COO^- + Na^+$; $[CH_3COO^-]$ increases so $[H^+]$ decreases respectively.

Odd ion : On mixing, NaOH with CH_3COOH solution

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

(On mixing) $NaOH \longrightarrow Na^+ + OH^-$
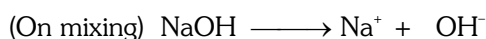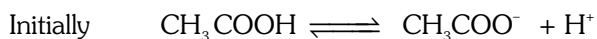
Due to odd ion effect $H^+ + OH^- \rightarrow$ Water

— **Illustrations** —

Illustration 3 For which, dilution law is applicable :

(1) NaCl (SASB salt)   (2) HCl (SA)

(3) CH_3COONa (WASB salt)   (4) None

Solution Ans. (4)

Illustration 4 Find out the value of α of 10^{-2} M HCN solution if $[H^+] = 10^{-3}$.

Solution $[H^+] = C\alpha$

$10^{-3} = 10^{-2}\alpha$ or $\alpha = \dfrac{10^{-3}}{10^{-2}} = 10^{-1}$ or $\alpha = 0.1$

$\%\alpha = 10\%$

Illustration 5 For 10 M CH_3COOH solution if $K_a = 10^{-5}$ then find out :

(i) α (ii) $[H^+]$ (iii) pH

Solution (i) α

(Degree of ionisation) :– $K_a = C\alpha^2$

$10^{-5} = 10\alpha^2$ or $= \alpha^2 = \dfrac{10^{-5}}{10} = 10^{-6}$ or $\alpha = 10^{-3}$

(ii) $[H^+] = C\alpha = 10 \times 10^{-3} = 10^{-2}$

(iii) pH $= -\log[H^+] = -\log 10^{-2} = 2$

4.3 EXPLANATION OF WATER

a. Nature of water is neutral. $[H^+] = [OH^-]$ $[=10^{-7}M$ (at 25°C)]

i.e.   at 25°C   pH = 7   and   pOH = 7

$\therefore$ pH = pOH

b. No. of H_2O moles in 1 litre water $= \dfrac{1000}{18} = 55.5$ moles

c. Molar concentration of H_2O = 55.5 mol L^{-1}

d. Number of H_2O molecules in 1 litre water = 55.5 N_A (N_A= Avogadro's number)

e. Concentration of H^+ and OH^- ions in 1 litre water

$[H^+] = 10^{-7}$ mol L^{-1} and $[OH^-] = 10^{-7}$ mol L^{-1}

f. No. of H^+ and OH^- ions in 1 litre water

No. of H^+ ions $= 10^{-7}N_A$ and No. of OH^- ions $= 10^{-7} N_A$

g. In water (Number of H_2O molecules : Number of H^+ ions)

$= 55.5 N_A : 10^{-7} N_A$

$= 55.5 \times 10^7 : 1$

i.e. one H^+ ion is obtained from $55.5 \times 10^7 H_2O$ molecules

h.   Degree of ionisation of water (α) :
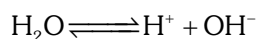
$$H_2O \rightleftharpoons H^+ + OH^-$$

According to Ostwald's dilution law

$[H^+] = C\alpha$

$$\alpha = \frac{10^{-7}}{55.5} = 1.8 \times 10^{-9}$$

$$\boxed{\alpha = 1.8 \times 10^{-7}\%}$$

Hence, water is a very weak electrolyte.

i.   K (Ionisation constant of water) :
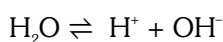
$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K = \frac{\left[H^+\right]\left[OH^-\right]}{\left[H_2O\right]}$$

$$K = \frac{10^{-7} \times 10^{-7}}{55.5} \quad \text{or} \quad \boxed{K = 1.8 \times 10^{-16}}$$

j.   Ionic product of water K_w :
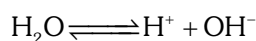
$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K = \frac{\left[H^+\right]\left[OH^-\right]}{\left[H_2O\right]}$$

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

Since, dissiociation takes place to a very small extent, $[H_2O]$ may be regarded as constant.

Thus, the product $K.\left[H_2O\right]$ gives another constant which designated as K_w. So,

$$\boxed{K_w = [H^+]\,[OH^-]}$$

At 25°C $K_w = 10^{-7} \times 10^{-7} = 10^{-14}$

$K\,[H_2O] = K_w \Rightarrow \boxed{K_w > K}$ (always)

Various forms of K_w

(a) $K_w = [H^+]\,[OH^-]$ for water $[H^+] = [OH^-]$

(b) $K_w = [H^+]^2$

(c) $K_w = [OH^-]^2$

(d) $K_w = [H_3O^+]\,[OH^-]$

(e) $K_w = [H_3O^+]^2$ $\{[H_3O^+] = [H^+]\}$

Hydronium ion   Proton

- **Relation in between pH and pOH :**

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

  taking $-\log$ on both sides

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

  $$\boxed{pK_w = pH + pOH}$$

- Nature of water is neutral so,

  $[pH = pOH]$

$pK_w = pH + pH$	$pK_w = pOH + pOH$
$2pH = pK_w$	$2pOH = pK_w$
$pH = \dfrac{pK_w}{2}$	$pOH = \dfrac{pK_w}{2}$

  $$\boxed{pH = pOH = \dfrac{pK_w}{2}}$$

  At 25℃, $K_w = 10^{-14}$ or $pK_w = 14$ $\therefore$ $pH + pOH = 14$ or $pH = pOH = 7$

k.   Effect of temperature :-

   $H_2O \rightleftharpoons H^+ + OH^-$
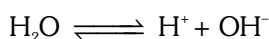
   Ionization of water is endothermic process so, on increasing temperature α increases or $[H^+]$ and $[OH^-]$ increases or $[H^+][OH^-]$ increases i.e. K_w increases means pH decreases or pOH decreases.

   $T \uparrow = \alpha \uparrow = [H^+][OH^-] \uparrow = K_w \uparrow \Rightarrow pK_w \downarrow$

   At 25° C, $K_w = 10^{-14}$

   At 90° C, $K_w = 10^{-12}$

Parameters	At 25℃	At 90℃
K_w	10^{-14}	10^{-12}
pK_w	14	12
$pH = \dfrac{pK_w}{2} = pOH$	7	6
$[H^+] = [OH^-] = \sqrt{K_w}$	10^{-7}	10^{-6}
$pH + pOH = pK_w$	14	12

GOLDEN KEY POINTS

- On increasing temperature, both $[H^+]$ and $[OH^-]$ increases equally so water remains neutral but neutral pH changes from 7 to 6 at 90℃.

——————————————— **Illustrations** ———————————————

Illustration 6   Dissociation constant of water at 25° C is

   (1) $10^{-14} \times (55.5)^{-1}$ (2) $10^{-7} \times (18)^{-1}$ (3) $10^{-14} \times (18)^{-1}$ (4) $10^{-7} \times (55.4)^{-1}$

Solution   **Ans. (1)**

Illustration 7   What should be the number of H^+ ions in 1 mL of distilled water, if the number of H^+ ions in 1 L is 6.023×10^{16}?

Solution   Number of H^+ ions in 1 mL distilled water $= \dfrac{6.023 \times 10^{16}}{1000} = 6.023 \times 10^{13}$

BEGINNER'S BOX-1

1. The pH of a 0.005 M H_2SO_4 solution is–

(1) 3.3　　　　　(2) 5.0　　　　　(3) 2.0　　　　　(4) 4.0

2. If pure water has $pK_w = 13.36$ at 50°C, the pH of pure water will be–

(1) 6.68　　　　　(2) 7.0　　　　　(3) 7.13　　　　　(4) 6.0

3. How many H^+ ions are present in 1 ml of a solution whose pH is 13 ?

(1) 10^{-16}　　　　　(2) 6.022×10^{13}　　　　　(3) 6.022×10^7　　　　　(4) 6.022×10^{23}

**4.** The pH of solutions A, B, C and D are 9.5, 2.5, 3.5 and 5.5 respectively. The most acidic solution is–

(1) D　　　　　(2) C　　　　　(3) A　　　　　(4) B

5. Calculate the concentration of the formate ion present in 0.100 M formic acid (HCOOH) solution at equilibrium ($K_a = 1.7 \times 10^{-4}$).

(1) 4.1×10^{-3} M　　　　　(2) 3.1×10^{-3} M　　　　　(3) 2.1×10^{-3} M　　　　　(4) 5.1×10^{-3} M

6. Which of the following is the weakest acid ?

(1) Phenol ($K_a = 1.3 \times 10^{-10}$)　　　　　(2) Hydrocyanic acid ($K_a = 4.9 \times 10^{-10}$)

(3) Acetic acid ($K_a = 1.8 \times 10^{-5}$)　　　　　(4) Benzoic acid ($K_a = 6.5 \times 10^{-5}$)

7. The pH of 0.1 M monobasic acid is 4.50. The acidity constant (K_a) of the monobasic acid is–

(1) 1.0×10^{-7}　　　　　(2) 1.0×10^{-5}　　　　　(3) 1.0×10^{-4}　　　　　(4) 1.0×10^{-8}

8. Which of the following is the strongest base ?

(1) $C_6H_5NH_2$ ($pK_b = 9.42$)　　　　　(2) $C_6H_5NHCH_3$ ($pK_b = 9.15$)

(3) $C_6H_5N(CH_3)_2$ ($pK_b = 8.94$)　　　　　(4) $C_6H_5NHC_2H_5$ ($pK_b = 8.89$)

9. Value of dissociation constant of acetic acid is 10^{-6}, where as dissociation constant of formic acid is 10^{-5}. Which of the following will be the value of pK_a (acetic acid) - pK_a (formic acid)

(1) 10　　　　　(2) +1　　　　　(3) 10^{-1}　　　　　(4)–1

10. A solution has pOH equal to 13 at 298 K. The solution will be

(1) highly acidic　　　(2) highly basic　　　(3) moderately basic　　　(4) unpredictable

11. What would be $[H^+]$ of 0.006 M benzoic acid ($K = 6 \times 10^{-5}$)

(1) 0.6×10^{-4}　　　　　(2) 6×10^{-4}　　　　　(3) 6×10^{-3}　　　　　(4) 3.6×10^{-4}

4.4　SALTS, TYPES OF SALT AND CONJUGATE THEORY

(A)　SALT : Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid. Salts are ionic compounds.

i.e. A compound formed by the combination of acid and base is known as salt.

Acid + Base $\rightarrow$ Salt + Water;　　$\Delta H = -ve$

HCl + NaOH $\rightarrow$ NaCl (Salt) + H_2O
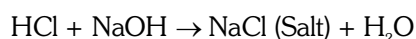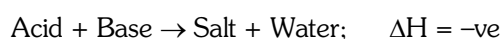
(B) TYPES OF SALT

(a) Normal/general salts :– The salts formed by the loss of all possible protons. (replaceable hydrogen ions as H⁺) are called normal salts. Such a salt does not contain either a replaceable hydrogen ion or a hydroxyl (OH⁻) group.

Ex. : $NaCl$, $NaNO_3$, K_2SO_4, $Ca_3(PO_4)_2$, Na_2HPO_3, NaH_2PO_2 etc.

(b) Acid salts :– Salts formed by incomplete neutralisation of poly basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen ions (H⁺).

Ex. : $NaHCO_3$, $NaHSO_4$, NaH_2PO_4, Na_2HPO_4 etc.

(c) Basic salts :– Salts are formed by incomplete neutralisation of poly acidic base are called basic salts. Such salts still contain one or more hydroxyl ion group.

Ex. : $Zn(OH)Cl$, $Mg(OH)Cl$, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$ etc.

(d) Double salts :– The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only i.e. when dissolved in water they break into simple ions.

Ex. : $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ etc.
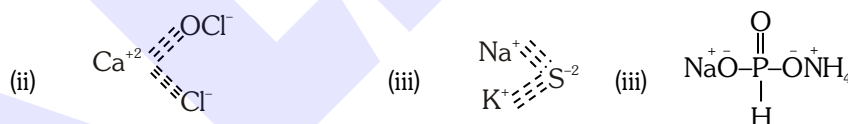
　　　(Ferrous ammonium sulphate)　　　　(Potash alum)

(e) Complex salts :– These salts when dissolved in water give complex ions. Complex ions are stable in solid state as well as in solutions.

Ex. : $K_4[Fe(CN)_6]$, $[Co(NH_3)_6]SO_4$, $[Ag(NH_3)_2]Cl$ etc.

(f) Mixed salts :– The salts which furnishes more than one type of cations or more than one type of anions when dissolved in water are called mixed salts.

These are formed by the neutralisation of more than one acids and bases.

Ex.　(i)　$\underset{\text{acid}}{H_2SO_4} + \underset{\text{base}}{NaOH} \longrightarrow \underset{\text{acidic salt}}{NaHSO_4} + H_2O$

$\underset{\text{acidic salt}}{NaHSO_4} + \underset{\text{base}}{KOH} \longrightarrow \underset{\text{(mixed salt)}}{NaKSO_4} \longrightarrow \underset{\text{(more than two radicals)}}{Na^+ K^+ SO_4^{-2}}$

(ii) $Ca^{+2} \begin{matrix} OCl^- \\ Cl^- \end{matrix}$　　(iii) $\begin{matrix} Na^+ \\ K^+ \end{matrix} S^{-2}$　(iii) $NaO\!-\!\overset{\displaystyle O}{\underset{\displaystyle H}{\overset{\|}{P}}}\!-\!ONH_4$
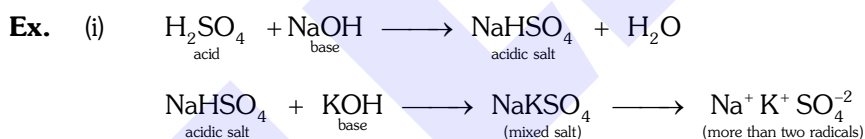
(a) Types of general salts :

(i) SASB　　(ii) SAWB　　　　(iii) WASB　　　　(iv) WAWB

(C) Conjugate acid-base pair :

(i) Conjugate acid-base pairs means difference between two species of only one H⁺ ion.

(ii) When an acid loses a proton, the residual part of it has a tendency to regain a proton. Therefore it behaves as a base.

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

Weak acid　　　　　　　Conjugate strong base

$(K_a = 1.85 \times 10^{-5})$　　　　(acceptor ion)

$NH_4OH + H^+ \rightleftharpoons NH_4OH_2^+ \longrightarrow NH_4^+ + H_2O$

Weak base　　　　　　　　　　Conjugate strong acid

$(K_b = 1.85 \times 10^{-5})$　　　　　　　(acceptor ion)

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

Strong acid   Conjugate weak base (spectator ion)

Accepting tendency of $H^+ \simeq 0$

$$NaOH + H^+ \longrightarrow NaOH_2^+ \longrightarrow Na^+ + H_2O$$

Strong base   Conjugate weak acid

(spectator ion)
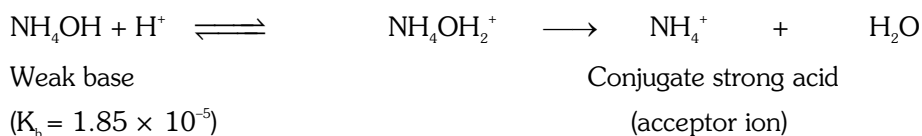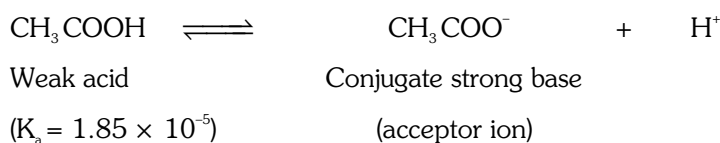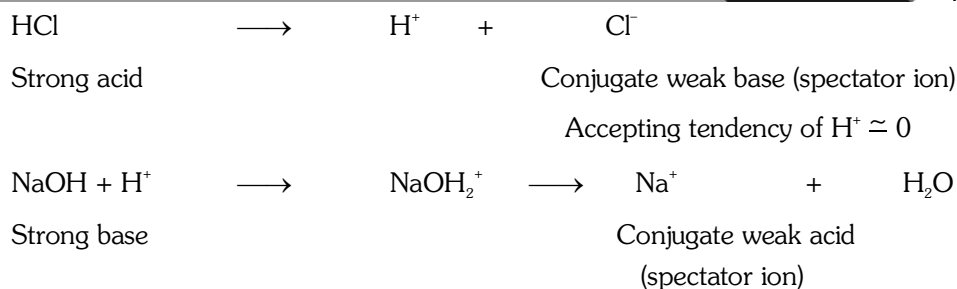
Note : Strong acids have weak conjugate bases while weak acids have strong conjugate bases. Similarly, strong bases have weak conjugate acids while weak bases have strong conjugate acids.

(D)   **Relation between conjugate acid-base pair :–**

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

       Acid   conjugate base

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

       Base   conjugate acid
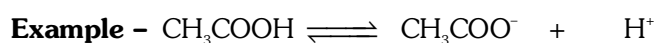
CH₃COOH	**CH₃COO⁻**
acid	**conjugate base**

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
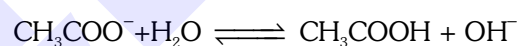
$K_a = \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$ ...... (i) $K_b = \dfrac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$ ..... (ii)

In both the reactions H₂O in excess quantity so active mass of H₂O is one.

Now multiply the equation (i) and (ii) $K_a \times K_b = [H^+][OH^-]$
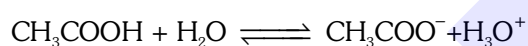
we know $[H^+] \times [OH^-] = K_W$ (Ionic product of water) $\boxed{K_a \times K_b = K_w}$

Taking –log on both sides $\boxed{pK_a + pK_b = pK_w}$

we know that for water at 25℃, $K_W = 10^{-14}$ or $pK_W = 14$

So $\boxed{K_a \times K_b = 10^{-14}}$ or $\boxed{pK_a + pK_b = 14}$

Above relation is applicable only for conjugate acid-base pairs.

───────────────── **Illustrations** ─────────────────

Illustration 8   Which salt is not an example of acidic salt :-

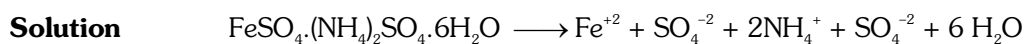(1) HCOONa   (2) NaH_2PO_2 (3) NaHS   (4) (1) and (2) both

Solution   **Ans. (4)**

Illustration 9   Calculate the no. of ions in Mohr's salt [FeSO₄.(NH₄)₂SO₄.6H₂O] or Ferrous Ammonium Sulphate

Solution $FeSO_4.(NH_4)_2SO_4.6H_2O \longrightarrow Fe^{+2} + SO_4^{-2} + 2NH_4^+ + SO_4^{-2} + 6H_2O$
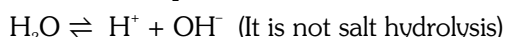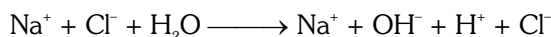
Total number of ions = 5

4.5. HYDROLYSIS OF SALTS

Salt hydrolysis is defined as the process in which water reacts with cation or anion or both of a salt to change the concentration of H^+ and OH^- ions of water.

Salt hydrolysis is reverse process of neutralization.

$$\text{Water + Salt} \rightleftharpoons \text{Acid + Base} ; \quad \Delta H = +ve$$

(A) Hydrolysis of strong acid and strong base [SA – SB] types of salt –

Ex. $NaCl$, $BaCl_2$, Na_2SO_4, $KClO_4$, $BaSO_4$, $NaNO_3$, KBr, KCl etc.

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

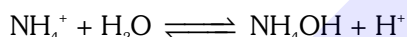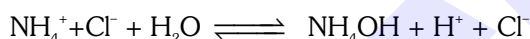$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(It is not salt hydrolysis)}$$

(i) Hydrolysis of salt of [SA – SB] is not possible as both cation and anion are not reactive.

(ii) Aqueous solution of these type of salt is neutral in nature. (pH = pOH = 7)

(iii) pH of the solution is 7.

(iv) No effect on litmus paper.

(B) Hydrolysis of strong acid and weak base [SA - WB] types of salt –

Ex. $CaSO_4$, NH_4Cl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$, $AgCl$, AgI, $AgNO_3$ etc

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$
$$\qquad\qquad\qquad\qquad WB \qquad SA$$

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

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$
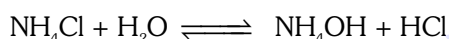
(i) In this type of salt hydrolysis, cation reacts with H_2O therefore called as cationic hydrolysis. The cation of the salt which has come from weak base is reactive.

(ii) Solution is acidic in nature as $[H^+]$ is increased.

(iii) pH of the solution is less than 7.

(iv) Solution turns blue litmus paper red.

K_h = Hydrolysis constant

K_w = Ionic product of water

K_a = Ionisation constant of acid

K_b = Ionisation constant of base

h = Degree of hydrolysis

C = Concentration of salt (concentration of ions)

(a) Relation between K_h , K_w and K_b

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$
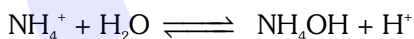
Hydrolysis constant $[K_h]$

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \qquad\qquad ....(1)$$

For weak Base $\qquad NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_4OH\right]} \qquad\qquad ....(2)$$

For water $\qquad H_2O \rightleftharpoons H^+ + OH^-$

$$K_w = [H^+][OH^-] \qquad\qquad ....(3)$$

Now mutiplying Eq. (1) and (2) = Eq. (3)

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

i.e. $K_h \times K_b = K_W$

$$\boxed{K_h = \frac{K_W}{K_b}}$$ ....(4)

(b)   Degree of hydrolysis – Represented by h

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

Initial concentration of salt   C   0   0
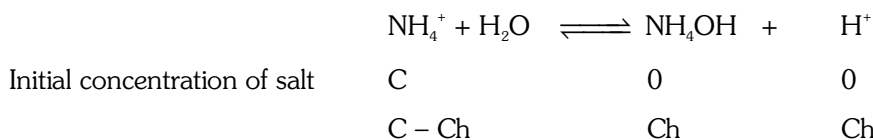
                                  C – Ch   Ch   Ch

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2h^2}{C(1-h)} = \frac{Ch^2}{(1-h)}$$

Since   h <<<< 1   then $(1 - h) \approx 1$

∴ $\boxed{K_h = Ch^2}$ ....(5)

$$h^2 = \frac{K_h}{C} \qquad \Rightarrow \qquad h = \sqrt{\frac{K_h}{C}}$$ ....(6)

∴ $K_h = \frac{K_W}{K_b} \qquad \Rightarrow \qquad h = \sqrt{\frac{\frac{K_W}{K_b}}{C}}$

$$h = \sqrt{\frac{K_W}{K_b \times C}}$$ ....(7)

(c)   pH of the solution : $pH = -\log[H^+]$

$$[H^+] = Ch = C\sqrt{\frac{K_W}{K_b \times C}} \qquad \Rightarrow \qquad [H^+] = \sqrt{\frac{K_W \times C}{K_b}}$$ ....(8)

taking – log on both sides
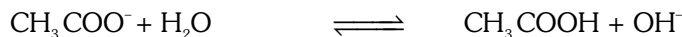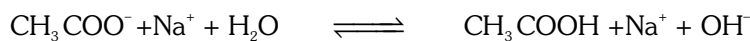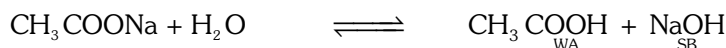
$$-\log[H^+] = -\log\sqrt{\frac{K_W \times C}{K_b}} \Rightarrow pH = -\log\left(\frac{K_W \times C}{K_b}\right)^{1/2}$$

$$pH = -\frac{1}{2}[\log K_W + \log C - \log K_b]$$

$$pH = -\frac{1}{2}\log K_W - \frac{1}{2}\log C - \frac{1}{2}(-\log K_b)$$

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

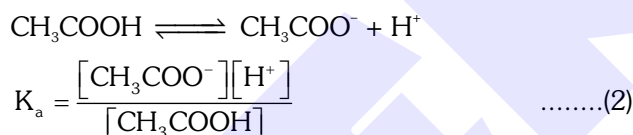$$\boxed{pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C}$$ ....(9)

(C) Hydrolysis of weak acid and strong base [WA – SB] types of salt –

Ex. CH_3COONa, $HCOONa$, KCN, $NaCN$, K_2CO_3, $BaCO_3$, K_3PO_4 etc.

$$CH_3COONa + H_2O \rightleftharpoons \underset{WA}{CH_3COOH} + \underset{SB}{NaOH}$$

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

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

(i) In this type of salt hydrolysis, anion reacts with water therefore called as anionic hydrolysis. The anion of the salt which has come from weak acid is reactive.

(ii) Solution is basic in nature as $[OH^-]$ increases.

(iii) pH of the solution is greater than 7.

(iv) Solution turns red litmus paper blue.

(a) Relation between K_h, K_W and K_a

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$
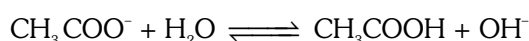
$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \qquad ....(1)$$

For weak acid

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

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad ....(2)$$

For water $\quad H_2O \rightleftharpoons H^+ + OH^-$

$$K_W = [H^+][OH^-] \qquad ....(3)$$

Now multiply eq. (1) × eq. (2) = eq. (3)

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

$$K_h \times K_a = K_W$$

$$\boxed{K_h = \frac{K_W}{K_a}} \qquad ....(4)$$

(b) Degree of hydrolysis (h) :

$$\begin{array}{ccccc} & CH_3COO^- & + & H_2O & \rightleftharpoons & CH_3COOH & + & OH^- \end{array}$$

Initial concentration of salt $\quad$ C $\qquad\qquad\qquad\qquad$ 0 $\qquad\qquad$ 0
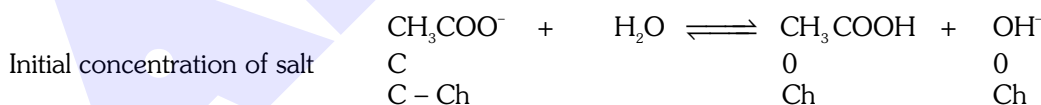
$\qquad\qquad\qquad\qquad\qquad$ C – Ch $\qquad\qquad\qquad\qquad$ Ch $\qquad\qquad$ Ch

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2h^2}{C(1-h)}$$

$$K_h = \frac{Ch^2}{(1-h)}$$

Since $\qquad$ h <<<< 1 $\qquad\qquad$ then $\qquad$ (1 – h) ≈ 1

∴ $\qquad \boxed{K_h = Ch^2} \qquad\qquad\qquad\qquad\qquad ....(5)$

$$h^2 = \frac{K_h}{C} \qquad or \qquad h = \sqrt{\frac{K_h}{C}} \qquad ....(6)$$

$$\boxed{h = \sqrt{\frac{K_W}{K_a \times C}}} \qquad ....(7)$$

(c) **pH of the solution**

$[OH^-] = Ch$

$[OH^-] = C \times \sqrt{\dfrac{K_W}{K_a \times C}}$ or $[OH^-] = \sqrt{\dfrac{K_W \times C}{K_a}}$ ....(8)

taking – log on both sides

$- \log [OH^+] = - \log \left(\dfrac{K_w.C}{K_a} \right)^{\frac{1}{2}}$

$pOH = -\dfrac{1}{2} [\log K_w + \log C - \log K_a]$

$pOH = \dfrac{1}{2} pK_w - \dfrac{1}{2} pK_a - \dfrac{1}{2} \log C$ or $pOH = 7 - \dfrac{1}{2} pK_a - \dfrac{1}{2} \log C$

$\because$ pH + pOH = 14

pH = 14 – pOH

$\therefore$ $pH = 7 + \dfrac{1}{2} pK_a + \dfrac{1}{2} \log C$ ....(9)

(D) **Hydrolysis of weak acid and weak base (WA - WB) type of salt :**

Ex. CH_3COONH_4 , AgCN, NH_4CN, $CaCO_3$, $[NH_4]_2CO_3$, $ZnHPO_3$ etc.

$CH_3COONH_4 + H_2O \rightleftharpoons \underset{WA}{CH_3COOH} + \underset{WB}{NH_4OH}$

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

(i) Maximum hydrolysis occurs of the salt of (WA – WB) as both the cation and anion are reactive.

(ii) Solution is almost neutral but it may be acidic or basic depending upon the nature of acid base

(iii) pH of the solution is near to 7.

For WA - WB types of salt :

Terms	$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
1. Hydrolysis	Cationic-anionic	Anionic-cationic	Neutral hydrolysis
2. Nature	Acidic	Basic	Neutral
3. pH	pH < 7	pH > 7	pH = 7

(a) **Relation between K_h, K_w, K_a and K_b**

$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$
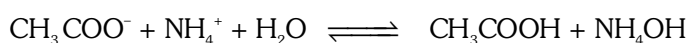
$K_h = \dfrac{\left[CH_3COOH \right] \left[NH_4OH \right]}{\left[CH_3COO^- \right] \left[NH_4^+ \right]}$ ....(1)

For weak base
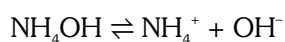
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_4OH\right]} \qquad\qquad ....(2)$$

For weak acid
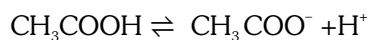
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{\left[CH_3COO^-\right]\left[H^+\right]}{\left[CH_3COOH\right]} \qquad\qquad ....(3)$$

For water

$$H_2O \rightleftharpoons H^+ + OH^-$$
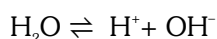
$$K_W = [H^+][OH^-] \qquad\qquad ....(4)$$

Multiply Eq. (1) × Eq. (2) × Eq. (3) = Eq. (4)

$$\frac{\left[CH_3COOH\right]\left[NH_4OH\right]}{\left[CH_3COO^-\right]\left[NH_4^+\right]} \times \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_4OH\right]} \times \frac{\left[CH_3COO^-\right]\left[H^+\right]}{\left[CH_3COOH\right]} = [H^+][OH^-]$$

$$K_h \times K_b \times K_a = K_W$$

$$\boxed{K_h = \frac{K_W}{K_a \times K_b}} \qquad\qquad ....(5)$$

(b) **Degree of hydrolysis (h) –**

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

Initial concentration of salt $\qquad$ C $\qquad\qquad$ C $\qquad\qquad\qquad\qquad$ 0 $\qquad\qquad$ 0
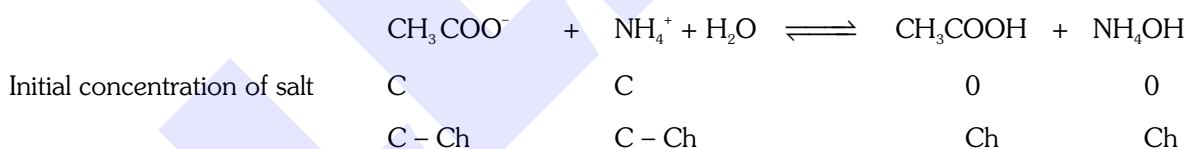
$\qquad\qquad\qquad\qquad\qquad\qquad$ C – Ch $\qquad\qquad$ C – Ch $\qquad\qquad\qquad$ Ch $\qquad\qquad$ Ch

$$K_h = \frac{\left[CH_3COOH\right]\left[NH_4OH\right]}{\left[CH_3COO^-\right]\left[NH_4^+\right]} = \frac{Ch \times Ch}{(C-Ch)(C-Ch)} = \frac{C^2h^2}{C(1-h) \times C(1-h)}$$

Since $\qquad$ h <<<< 1 $\qquad$ then $(1 - h) \approx 1$

∴ $\qquad \boxed{K_h = h^2} \qquad\qquad ....(6)$

or $\qquad h^2 = \dfrac{K_W}{K_a \times K_b} \qquad$ or $\qquad \boxed{h = \sqrt{\dfrac{K_W}{K_a \times K_b}}} \qquad ....(7)$

(c) **pH of the solution**

from equation (3)

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

$$\left[H^+\right] = \frac{K_a \times \left[CH_3COOH\right]}{\left[CH_3COO^-\right]} = \frac{K_a \times Ch}{C - Ch} = \frac{K_a \times h}{1 - h}$$

Since $h <<<< 1$ then $(1 - h) \approx 1$

$[H^+] = K_a \times h$ [Now put the value of h from eq. (5)]

$$= K_a \times \sqrt{\frac{K_W}{K_a \times K_b}}$$

$$\boxed{[H^+] = \sqrt{\frac{K_W \times K_a}{K_b}}}$$ ....(8)

taking $- \log$ on both sides $- \log [H^+] = - \log \left(\frac{K_W \times K_a}{K_b} \right)^{\frac{1}{2}}$

$$pH = - \frac{1}{2} [\log (K_w \times K_a) - \log K_b]$$

$$pH = - \frac{1}{2} [\log K_W + \log K_a - \log K_b]$$

$$pH = - \frac{1}{2} [\log K_W] - \frac{1}{2} [\log K_a] - \frac{1}{2} [- \log K_b]$$

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

$$\boxed{pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b}$$ ....(9)

GOLDEN KEY POINTS

- Degree of hydrolysis, pH of weak acid and weak base [WA – WB] type salts do not depend on the concentration of salt.

-

	SA SB salts	SA WB salts	WA SB salts	WA WB salts
1.	Neutral solution	Acidic solution	Basic solution	Almost neutral solution
2.	No hydrolysis	Cationic hydrolysis	Anionic hydrolysis	Hydrolysis by both cation and anion
3.	–	$K_h = \dfrac{K_W}{K_b}$	$K_h = \dfrac{K_W}{K_a}$	$K_h = \dfrac{K_W}{K_a \times K_b}$
4.	–	$h = \sqrt{\dfrac{K_W}{K_b C}}$	$h = \sqrt{\dfrac{K_W}{K_a C}}$	$h = \sqrt{\dfrac{K_W}{K_a K_b}}$
5.	–	$[H^+] = C \times h = \sqrt{\dfrac{K_W C}{K_b}}$	$[OH^-] = C \times h = \sqrt{\dfrac{K_W C}{K_a}}$	$[H^+] = K_a \times h = \sqrt{\dfrac{K_W K_a}{K_b}}$
6.	–	$pH = 7 - \dfrac{1}{2} pK_b - \dfrac{1}{2} \log C$	$pH = 7 + \dfrac{1}{2} pK_a + \dfrac{1}{2} \log C$	$pH = 7 + \dfrac{1}{2} pK_a - \dfrac{1}{2} pK_b$

─────────── **Illustrations** ───────────

Illustration 10 What is the pH of 1 M CH_3COONa solution? Ka of acetic acid = 1.8×10^{-5}, $K_w = 10^{-14}$ mol^2 L^{-2}

(1) 2.4   (2) 3.6   (3) 4.8   (4) 9.4

Solution   **Ans. (4)**

Illustration 11 Calculate the degree of hydrolysis of a mixture containing 0.1N NH_4OH and 0.1N HCN

If $K_a = 10^{-5}$ and $K_b = 10^{-5}$

Solution   Salt is [WA – WB]

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 10^{-5}}} = \sqrt{10^{-14} \times 10^{+10}} = \sqrt{10^{-4}} = 10^{-2}$$

BEGINNER'S BOX-2

1. When sodium acetate (CH_3COONa) is added to aqueous solution of acetic acid (CH_3COOH), the–

(1) the pH value becomes zero   (2) pH value remains unchanged

(3) pH value decreases   (4) pH value increases

2. Which of the following cations is not hydrolyzed in aqueous solution ?

(i) Mg^{2+} (ii) Ca^{2+} (iii) Na^+ (iv) K^+

(1) (i), (ii)   (2) (iii), (iv)   (3) (i), (ii), (iii), (iv)   (4) (i), (ii), (iii)

3. Which of the anions is not hydrolyzed in aqueous solution ?

(i) Cl^- (ii) NO_3^- (iii) Br^- (iv) ClO_4^-

(1) (i), (ii), (iii), (iv)   (2) (ii), (iii), (iv)   (3) (i), (ii), (iii)   (4) (ii), (iv)

4. Which of the following salts does not undergo hydrolysis ?

(1) KCN   (2) KCl   (3) NH_4NO_3 (4) $FeCl_3.6H_2O$

5. Which of the following salts undergoes anionic hydrolysis ?

(1) $AlCl_3$ (2) $CuSO_4$ (3) Na_2CO_3 (4) NH_4Cl

6. For cationic hydrolysis, pH is given by–

(1) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C$ (2) $pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log C$

(3) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$ (4) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_b + \frac{1}{2}\log C$

7. Which of the following salts is neutral in water ?

(1) KCl   (2) NH_4NO_3 (3) NH_4CN (4) NH_4OH

4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K_{sp})

(A) SOLUBILITY

(a) **Definition** At constant temperature the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of solution (i.e. saturated solution) is called solubility.

$$S(M) = \frac{\text{Number of moles of solute}}{\text{Volume of solution } (L)} \qquad S = \frac{x}{M_w \times V_L} \text{ mol L}^{-1}$$

$$S_{g/\ell} = S_M \times \text{molar mass}$$

### GOLDEN KEY POINTS

- Solubility does not depend on amount of substances and volume of solution where as depends on the following–

  (i) Temperature

  (ii) Presence of common ion

  (iii) Nature of solvent

- Solubility can be expressed in terms of molarity.

(B) SOLUBILITY PRODUCT(K_{sp}) :

When a sparingly soluble salt such as AgCl is put into water, a very small amount of AgCl dissolves in water and most of the salt remains undissolved in its saturated solution.

- The salt AgCl is an electrolyte, its dissociation occurs in solution. Hence, the quantity of AgCl that dissolves in water dissociates into Ag^+ and Cl^- ions. Thus, in the saturated solution of AgCl an equilibrium exists between undissolved solid AgCl and its ions, Ag^+ and Cl^- ions.

$$AgCl_{(s)} \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} Ag^+_{(aq)} + Cl^-_{(aq)}$$
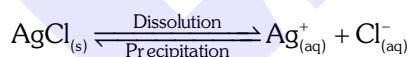
according to law of mass action $\quad K = \dfrac{\left[Ag^+\right]\left[Cl^-\right]}{\left[AgCl\right]}$

Since, the concentration of undissolved solid AgCl is constant. Thus, the product K.[AgCl] gives another constant which is designated as K_{sp}.

So, $\quad$ K.[AgCl] = [Ag$^+$] [Cl$^-$] $\qquad \therefore \qquad K_{sp}$ = [Ag$^+$] [Cl$^-$]

At constant temperature product of concentrations of ions in a saturated solution of substance is called solubility product of that substance. (Saturated solution is that solution in which solid solute and the ions in solution remain in equilibrium with each other.)

- **K_{sp} for CaCl$_2$** $\qquad$ $CaCl_2(s) \rightleftharpoons Ca^{+2}(aq) + 2Cl^-(aq)$

 Solubility product in terms of concentration of ions $\quad K_{sp} = [Ca^{+2}] [Cl^-]^2$

- **K_{sp} for AlCl$_3$** $\qquad$ $AlCl_3(s) \rightleftharpoons Al^{+3}(aq) + 3Cl^-(aq)$

 Solubility product in terms of concentration of ions $\quad K_{sp} = [Al^{+3}] [Cl^-]^3$

- **General form** $\qquad$ $A_xB_y(s) \rightleftharpoons xA^{+y}(aq) + yB^{-x}(aq)$

  $K_{sp} = [A^{+y}]^x [B^{-x}]^y$

4.7 APPLICATION OF SOLUBILITY PRODUCT (K_{sp})

(A) To find out the solubility (S) :

(i) K_{sp} of AB (Mono-mono, di-di, tri-tri valency) type salt –

Ex. NaCl, $BaSO_4$, CH_3COONa, $CaCO_3$, NaCN, KCN, NH_4CN, NH_4Cl etc.

$$AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$$

a	0	0
(a–s)	s	s
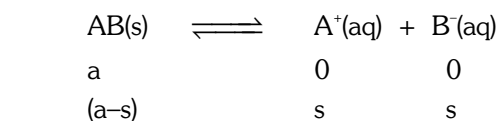
$K_{sp} = [A^+] [B^-]$

$K_{sp} = s^2$ or $s = \sqrt{K_{sp}}$

(ii) K_{sp} of AB_2 or A_2B (Mono-di or di-mono valency) type salt –

Ex. $CaCl_2$, $CaBr_2$, K_2S, $(NH_4)_2SO_4$, K_2SO_4, K_2CO_3 etc.

$$AB_2(s) \rightleftharpoons A^{+2}(aq) + 2B^-(aq)$$

a	0	0
a – s	s	2s
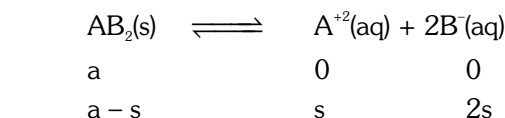
$K_{sp} = [A^{+2}] [B^-]^2$

$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$

$s = \left(\dfrac{K_{sp}}{4}\right)^{1/3}$

(iii) K_{sp} of AB_3 or A_3B (Mono-tri or tri-mono valency) type salt –

Ex. $FeCl_3$, $AlCl_3$, K_3PO_4 etc.

$$AB_3(s) \rightleftharpoons A^{+3}(aq) + 3B^-(aq)$$

a	0	0
a–s	s	3s
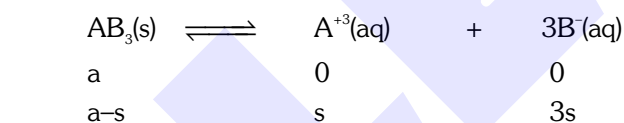
$K_{sp} = \left[A^{+3}\right]\left[B^-\right]^3 = s \times (3s)^3 = 27s^4$

$s = \left(\dfrac{K_{sp}}{27}\right)^{1/4}$

(iv) K_{sp} of A_2B_3 or A_3B_2 (Di-tri or tri-di valency) type salt

Ex. $Al_2(SO_4)_3$, $Ba_3(PO_4)_2$ etc.

$$A_2B_3(s) \rightleftharpoons 2A^{+3}(aq) + 3B^{-2}(aq)$$

a	0	0
a–s	2s	3s
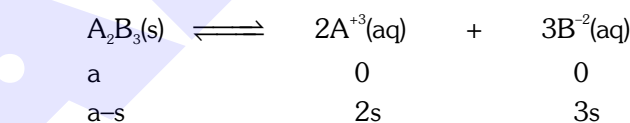
$K_{sp} = \left[A^{+3}\right]^2\left[B^{-2}\right]^3 = 2s \times 2s \times 3s \times 3s \times 3s = 108s^5$

$s = \left(\dfrac{K_{sp}}{108}\right)^{1/5}$

(v) General form :

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

a	0	0
a–s	xs	ys
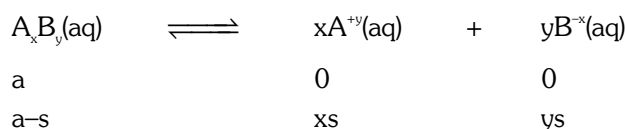
$K_{sp} = [A^{+y}]^x . [B^{-x}]^y$

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

—————————— Illustrations ——————————

Illustration 12 What will be the solubility product of following in terms of solubility (mol L^{-1})

(i) $Al_2(SO_4)_3(s)$ (ii) $Na_2KPO_4(s)$ (iii) $NaKRbPO_4(s)$

Solution (i) $Al_2(SO_4)_3(s) \rightleftharpoons 2Al^{+3}(aq) + 3SO_4^{-2}(aq)$

$Ksp = 2^2 \times 3^3 \times (S)^{2+3} = 4 \times 27 \times S^5 = 108\, S^5$
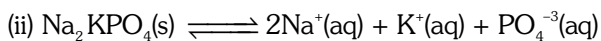
(ii) $Na_2KPO_4(s) \rightleftharpoons 2Na^+(aq) + K^+(aq) + PO_4^{-3}(aq)$

$Ksp = 2^2 \times 1^1 \times 1^1 (S)^{2+1+1} = 4S^4$

(iii) $NaKRbPO_4(s) \rightleftharpoons Na^+(aq) + K^+(aq) + Rb^+(aq) + PO_4^{-3}(aq)$
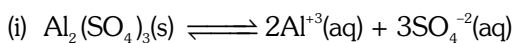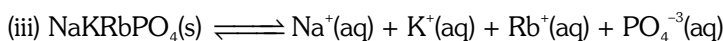
$Ksp = 1^1 \times 1^1 \times 1^1 \times 1^1 \times (S)^{1+1+1+1} = S^4$

Illustration 13 If solubility product of the base $M(OH)_3$ is 2.7×10^{-11}, the concentration of OH^{-1} will be
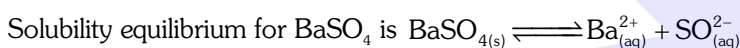
(1) 3×10^{-3} (2) 3×10^{-4} (3) 10^{-3} (4) 10^{-11}

Solution **Ans. (1)**

Illustration 14 The solubility of $BaSO_4$ in water is 1.07×10^{-5} mol dm^{-3}. Estimate its solubility product.

Solution Solubility equilibrium for $BaSO_4$ is $BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{(aq)}$

The solubility product is, $K_{sp} = [Ba^{2+}][SO_4^{2-}]$

If S is the molar solubility of $BaSO_4$. then $K_{sp} = S^2$ because $x = 1 = y$.

Now, $S = 1.07 \times 10^{-5}$ M.

Hence, $K_{sp} = (1.07 \times 10^{-5})^2 = 1.145 \times 10^{-10}$

Illustration 15 The solubility product of AgBr is 5.2×10^{-13}. Calculate its solubility in mol dm^{-3} and g dm^{-3}. (Molar mass of AgBr. = 187.8 g mol^{-1})

Solution The solubility equilibrium of AgBr is $AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$

and $K_{sp} = [Ag^+][Br^-] = S^2$ because $x = 1 = y$.

The molar solubility S of AgBr is given by $S = \sqrt{K_{sp}} = \sqrt{5.2 \times 10^{-13}} = 7.2 \times 10^{-7}$ mol dm^{-3}

The solubility in g dm^{-3} = molar solubility (mol dm^{-3}) $\times$ molar mass (g mol^{-1})

Hence, solubility = 7.2×10^{-7} (mol dm^{-3}) $\times 187.8 = 1.35 \times 10^{-4}$ g dm^{-3}.

(B) **Condition of precipitation /Ionic product (IP or Q_{sp}) :**

- Ionic product (IP) of an electrolyte is defined in the same way as K_{sp}. The only difference is that ionic product expression contains the initial concentration of ions or the concentration at any time whereas the expression of K_{sp} contains only equilibrium concentration. Thus, for AgCl.

  $Q_{sp} = IP = [Ag^+]_i [Cl^-]_i$ and $K_{sp} = [Ag^+]_{eq}.[Cl^-]_{eq}$

- Ionic product changes with concentration but K_{sp} does not. K_{sp} is applicable for saturated solution of the sparingly soluble electrolyte.

- To decide whether an ionic compound will precipitate, its K_{sp} is compared with the value of ionic product. The following three cases arise :

  (i) $Q_{sp} < K_{sp}$:   The solution is unsaturated and precipitation will not occur.

  (ii) $Q_{sp} = K_{sp}$:   The solution is saturated and solubility equilibrium exists.

  (iii) $Q_{sp} > K_{sp}$:   The solution is supersaturated and hence precipitation of the compound will occur.

  Thus, a salt is precipitated when its ionic product exceeds the solubility product of the salt.

(C) **Common ion effect on solubility :**

Important point :- Solubility of substances always decreases in the presence of common ion. According to Le-Chatelier's principle on increasing common ion concentration equilibrium shifts in backward direction until the equilibrium is re-established so, the solubility of substances decreases but K_{sp} remains same because it is an equilibrium constant which depends only on temperature.

─── **Illustrations** ───

Illustration 16 Find out the solubility of AgCl in the presence of C molar NaCl solution ?
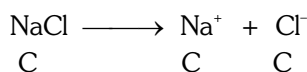
Solution.

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

S   S   S
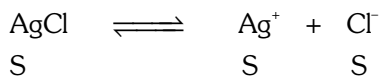
(Let solubility of AgCl is S mol L^{-1})

$$Ksp = [Ag^+][Cl^-]$$
$$Ksp = S^2$$

In NaCl solution

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

C   C   C

Let solubility of AgCl in the presence of NaCl solution is S' mol L^{-1}.

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

S'   S'   S'+C
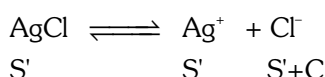
According to L.M.A.

$$K_{sp} = [Ag^+]'[Cl^-]'$$
$$K_{sp} = S'\ (S' + C) = S'^2 + S'C \quad \text{(Neglecting the higher power terms of S')}$$
$$K_{sp} = S'\ C \qquad \boxed{S' = \dfrac{K_{sp}}{C}}$$

Illustration 17 Find out the solubility of $CaCl_2$ solution in the presence of C NaCl solution ?

Solution

$$CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl^-$$
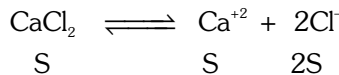
S   S   2S   [Let solubility of $CaCl_2$ is S mol L^{-1}]

$$K_{sp} = [Ca^{+2}][Cl^-]^2 = 4S^3$$

For NaCl solution

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

C   C   C
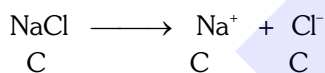
Let solubility of $CaCl_2$ in the presence of NaCl solution is S' mol L^{-1}.

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

S'   S'   2S'+C
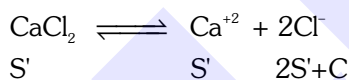
According to L.M.A.

$$K_{sp} = [Ca^{+2}]^1 [Cl^-]^2$$
$$K_{sp} = S'\ (2S' + C)^2 = S'(4S'^2 + 4S'C + C^2)$$
$$K_{sp} = 4S'^3 + 4S'^2C + S'C^2 \quad \text{(Neglecting the higher power terms of S')}$$
$$\boxed{S' = \dfrac{K_{sp}}{C^2}}$$

Illustration 18 Find out the solubility of NaCl in the presence of C $CaCl_2$ solution ?

Solution

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

C   C   2C
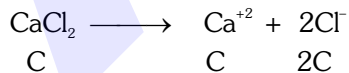
Let solubility of NaCl in the presence of $CaCl_2$ solution is S' mol L^{-1}.

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

S'   S'   S'+2C
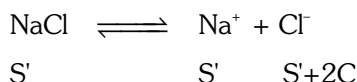
According to L.M.A.

$$K_{sp} = [Na^+]^1 [Cl^-]^1$$
$$K_{sp} = S'\ (S' + 2C) = S'^2 + 2S'C \text{ (Neglecting the higher power terms of S')}$$
$$\boxed{S' = \dfrac{K_{sp}}{2C}}$$

(D)   **Precipitation of soap and salt (NaCl)**

(i)   **Precipitation of NaCl (common salt) :**

For the precipitation of NaCl, HCl gas passed in saturated solution of NaCl to increase the concentration of Cl^- ion by common ion, so ionic product of concentration of Na^+ and Cl^- ion becomes more than K_{sp} of NaCl and NaCl easily precipitated.

Saturated solution of NaCl $NaCl \rightleftharpoons Na^+ + Cl^-$

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

By passing HCl gas $HCl \longrightarrow H^+ + Cl^-$
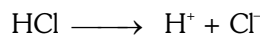
due to common ion $K_{sp} < [Na^+][Cl^-] \uparrow$

(ii)   **Precipitation of soap :**

For precipitation of soap, NaCl mixed in saturated solution of soap to increase the concentration of Na^+ ion by common ion. So ionic product of concentration of Na^+ and strearate ions is more than K_{sp} of soap and soap is easily precipitated.

Ex. $C_{17}H_{35}COONa$ (Sodium stearate)

Saturated solution of $C_{17}H_{35}COONa$ $\Rightarrow$ $C_{17}H_{35}COONa^+ \rightleftharpoons C_{17}H_{35}COO^- + Na^+$

$$K_{sp} = [C_{17}H_{35}COO^-][Na^+]$$

By mixing NaCl solution $NaCl \longrightarrow Na^+ + Cl^-$

due to common ion $K_{sp} < [C_{17}H_{35}COO^-][Na^+] \uparrow$

─────────────────── **Illustrations** ───────────────────

Illustration 19   Solubility products of $M(OH)_3$ and $M(OH)_2$ are 10^{-23} and 10^{-14} respectively. Which will be precipitated first on adding NH_4OH, if M^{+2} and M^{+3} both the ions are in solution ?

(1) M^{+2} (2) M^{+3}

(3) Both M^{+2} and M^{+3} together   (4) Precipitation will not take place.

Solution   **Ans. (2)**

Illustration 20   Solubility of $CaCl_2$ is 4×10^{-8}, then find out its K_{sp} and its new solubility in the presence of 10^{-2} M $Ca(OH)_2$.

Solution

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

     1   s   2s   (Initial solubility = s)

     $K_{sp} = 4s^3 = 4(4 \times 10^{-8})^3 = 256 \times 10^{-24}$ ....(i)

$$Ca(OH)_2 \longrightarrow Ca^{+2} + 2OH^-$$

     C   0   0

     0   C   2C

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

     1   s' +C   2s'   (New solubility = s')
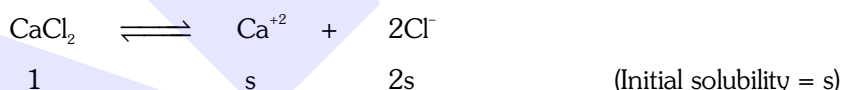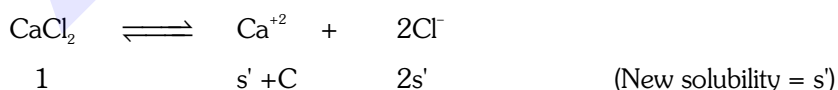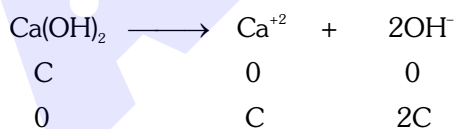
     $K_{sp} = [Ca^{+2}][Cl^-]^2$

         $= [s' + C][2s']^2 = 4s'^3 + 4s'^2C$ $(s'^3 = $ negligible$)$

     $K_{sp} = 4s'^2C$ ....(ii)

From equation (i) and (ii) $s'^2 = \dfrac{K_{sp}}{4C} = \dfrac{256 \times 10^{-24}}{4 \times 10^{-2}} = 64 \times 10^{-22}$

$$s' = 8 \times 10^{-11} \, mol \, L^{-1}$$

4.8 FEW IMPORTANT POINTS

(A) **Isohydric solution –** If different–different solution has same pH are called isohydric solution.

Sp. point :– Isohydric conditions for two given weak acids HA_1 and HA_2 which has concentration C_1 and C_2 and ionisation constants are K_{a_1} and K_{a_2} respectively.

$$\text{Then } [H^+]_1 = \sqrt{K_{a_1} C_1} \text{ and } [H^+]_2 = \sqrt{K_{a_2} C_2}$$

According to given condition for isohydric solution pH of different solution is same.

Hence $\qquad [H^+]_1 = [H^+]_2$

$$\sqrt{K_{a_1} C_1} = \sqrt{K_{a_2} C_2}$$

$$\boxed{K_{a_1} C_1 = K_{a_2} C_2} \text{ or } \text{If n = 1 mole then } \boxed{\frac{K_{a_1}}{V_1} = \frac{K_{a_2}}{V_2}} \because \boxed{C \propto \frac{1}{V}}$$

(B) **Relative strength of Acids :–** It indicates that how many times an acid is stronger than the other acid.

We know $\qquad \boxed{\text{Strength of acid} \propto [H^+]}$

If there are two weak acids HA_1 and HA_2 which has concentration C_1 and C_2, degree of ionisation α_1 and α_2 and ionisation constants Ka_1 and Ka_2 respectively then ratio of their strength of acids.

We know $\qquad [H^+] = C\alpha = \sqrt{K_a C}$

So $\dfrac{\text{Strength of weak acid} HA_1}{\text{Strength of weak acid} HA_2} = \dfrac{[H^+]_1}{[H^+]_2} = \dfrac{C_1 \alpha_1}{C_2 \alpha_2} = \dfrac{\sqrt{K_{a_1} C_1}}{\sqrt{K_{a_2} C_2}}$

If $\qquad C_1 = C_2$

$$\boxed{R.S. = \frac{\text{Strength of weak acid } HA_1}{\text{Strength of weak acid } HA_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} = \frac{\alpha_1}{\alpha_2}}$$

Thus the relative strength of two acids of equimolar concentration can be compared by taking square root of the ratio of their ionisation constants.

───────────── **Illustrations** ─────────────

Illustration 21 Which of the following solvents will undergo self-ionization ?

(1) H_2O (2) NH_3 (3) HF   (4) All of these

Solution **Ans. (4)**

Illustration 22 For two acids A and B, $pK_{a_1} = 1.2$, $pK_{a_2} = 2.8$ respectively in value, then which is true:-

(1) A & B both are equally acidic

(2) A is stronger than B

(3) B is stronger than A

(4) None of these

Solution **Ans. (2)**

Illustration 23 pH values of two acids A and B are 4 and 5. The strengths of these two acids are related as :-

(1) The strengths of the two acids cannot be compared.

(2) Acid B is 10 times stronger than acid A.

(3) Strength of acid A : Strength of acid B = 4 : 5

(4) Acid A is 10 times stronger than acid B.

Solution **Ans. (4)**

BEGINNER'S BOX-3

1. The units of solubility product of silver chromate (Ag_2CrO_4) will be–

(1) mol^2L^{-2} (2) mol^3L^{-3} (3) $mol\ L^{-1}$ (4) $mol^{-1}L$

2. At a certain temperature, the solubility of the salt A_xB_y is S moles per liter. The general expression for its solubility product will be–

(1) $K_{sp} = x^yy^xS^{x+y}$ (2) $K_{sp} = (xy)^{x+y}S^{x+y}$ (3) $K_{sp} = (x^xy^y)S^{x+y}$ (4) $K_{sp} = x^xy^yS^{xy}$

3. The molar solubility of silver sulphate is 1.5×10^{-2} mol L^{-1}. The solubility product of the salt will be–

(1) 2.25×10^{-4} (2) 1.35×10^{-5} (3) 1.7×10^{-6} (4) 3.0×10^{-3}

4. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed:

(1) 10^{-3} M Ca^{2+} + 10^{-5} M F^- (2) 10^{-5} M Ca^{2+} + 10^{-3} M F^-

(3) 10^{-2} M Ca^{2+} + 10^{-3} M F^- (4) 10^{-4} M Ca^{2+} + 10^{-4} M F^-

5. If S_0, S_1, S_2 and S_3 are the solubilities of AgCl in water, 0.01 M $CaCl_2$, 0.01 M NaCl and 0.5 M $AgNO_3$ solutions, respectively, then which of the following is true?

(1) $S_0 > S_2 > S_1 > S_3$ (2) $S_0 = S_2 = S_1 > S_3$

(3) $S_3 > S_1 > S_2 > S_0$ (4) $S_0 > S_2 > S_3 > S_1$

6. Given K_{sp} (AgI) = 8.5×10^{-17}. The solubility of AgI in 0.1 M KI solution is–

(1) 0.1 M (2) 8.5×10^{-16} M

(3) 8.5×10^{-17} M (4) 8.5×10^{-18} M

4.9 pH

1. INTRODUCTION

pH of some important substances :-

(i)	Blood $\longrightarrow$	7.4
(ii)	Tear $\longrightarrow$	7.4
(iii)	Gastric Juice $\longrightarrow$	1 to 3
(iv)	Soft drink $\longrightarrow$	2 to 4
(v)	Acidic rain $\longrightarrow$	6
(vi)	Milk $\longrightarrow$	6.3 to 6.6
(vii)	Water $\longrightarrow$	7

2. TYPES OF pH

(i) pH of SA and SB. $[H^+]$ = C, $[OH^-]$ = C

(ii) pH of WA and WB. $[H^+]$ = Cα , $[OH^-]$ = Cα

(iii) pH of very dilute solution. (Consider H^+ & OH^- of H_2O also)

(iv) pH of salt solution.

(a) SA SB Type Salt (always 7)

(b) SA WB Type Salt (< 7)

(c) WA SB Type Salt (> 7)

(d) WA WB Type Salt (Almost 7)

3. pH of mixture of acid and base.

(a) pH of mixture of strong acids :

$N_1V_1 + N_2V_2 + N_3V_3 + \ldots\ldots\ldots\ldots = NV$

V = Volume of final solution = $V_1 + V_2 + V_3 + \ldots\ldots$

N = Normality of final solution = $[H^+]$ in final solution.

(b)   pH of mixture of strong base :

$N_1V_1 + N_2V_2 + N_3V_3 + ... = NV$

V = Volume of final solution = $V_1 + V_2 + V_3 + ...$

N = Normality of final solution = $[OH^-]$ in final solution.

(c)   pH of mixture of strong acids and strong bases :

For acid :

$\qquad N_1V_1 + N_2V_2 + N_3V_3 + ... = (NV)_{Acid}$

For base :

$\qquad N_1V_1 + N_2V_2 + N_3V_3 + ... = (NV)_{Base}$

(i)   If $(NV)_{Acid} > (NV)_{Base}$ then solution is acidic.

$\qquad NV = (NV)_{Acid} - (NV)_{Base}$ and

$\qquad [H^+] = N$

(ii)   If $(NV)_{Base} > (NV)_{Acid}$ then solution is basic.

$\qquad NV = (NV)_{Base} - (NV)_{Acid}$ and

$\qquad [OH^-] = N$

(iii)   If, $(NV)_{acid} = (NV)_{base}$ then solution is neutral.

(d)   pH of mixture of (WA + SB); when equivalent of WA > SB]

pH of mixture of (SA + WB); When equivalent of WB > SA]

$\qquad\qquad\qquad \Downarrow$

gives rise to concept of buffer solution

4.10 BUFFER SOLUTION

(A)   Definition : A solution which resist the change in pH and pH does not change significantly on addition of small amount of strong acid or strong base is called buffer solution.

(B)   Properties of buffer solution :

(i)   The pH of buffer solution does not change appreciably upon the addition of small amount of either strong acid or strong base.

(ii)   The pH of buffer solution does not depend on the volume of solution. Hence, solution can be diluted without change in pH.

(iii)   The pH of buffer solution remains constant even if it is kept for a long time.

(C)   Buffer solutions are used in

(a) Qualitative analysis of mixture

(b) Quantitative analysis of mixture

(c) Digestion of food

(d) Preservation of food and fruits.

(e) Agriculture and dairy product preservation.

(f) Industrial process such as manufacture of paper, dyes inks, paints, drugs etc.

TYPES OF BUFFER SOLUTION

(A).   Simple buffer solution

(B).   Mixed buffer solution :-   (i) Acidic buffer solution   (ii) Basic buffer solution

(A)   Simple buffer solution :- Aqueous solution of weak acid-weak base (WA – WB) types of salt.

Ex. CH_3COONH_4 , NH_4CN, $AgCN$ etc.

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

pH does not depend on concentration.

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

Buffer Action :

Case 1 **Case 2.**
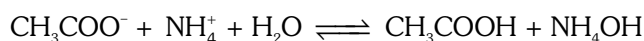
When mixing of acid [H$^+$] When mixing of base [OH$^-$]

$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$ $NH_4^+ + OH^- \rightleftharpoons NH_4OH$

$NH_4OH + H^+ \rightleftharpoons NH_4^+ + H_2O$ $CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$
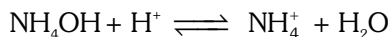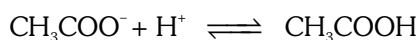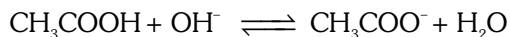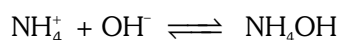
(B) **Mixed buffer solution :**

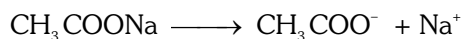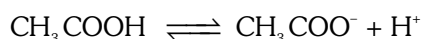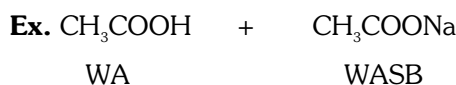**(i)** **Acidic buffer solution :-** The solution in which weak acid and its conjugate base are present.

OR

Aqueous solution of mixture of weak acid and salt of same weak acid with any strong base is called acidic buffer solution.

Ex. CH_3COOH + CH_3COONa

WA WASB

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

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

$\left[\underset{WA}{CH_3COOH} + \underset{CBase}{CH_3COO^-} \right] + Na^+$ (Spectator ion)

BUFFER ACTION :-

Case 1. If a small amount of acid is added to the buffer solution. The H$^+$ ions of the acid react with CH_3COO^- ions and produce CH_3COOH and most of the added H$^+$ ions are consumed so there is no appreciable change in pH.

$$CH_3COO^-_{(aq)} + H^+ \rightleftharpoons CH_3COOH_{(aq)}$$
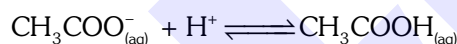
Case 2. If small amount of base is added to the buffer solution, the OH$^-$ ions are consumed by CH_3COOH.

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H_2O_{(\ell)}$$

So, there is no appreciable change in pH.

(a) **pH of acidic buffer solution :**

CH_3COOH + CH_3COONa

Acid + Salt

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

$CH_3COONa \longrightarrow CH_3COO^- + Na^+$
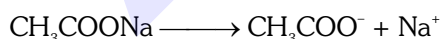
$$K_a = \frac{\left[CH_3COO^- \right]\left[H^+ \right]}{\left[CH_3COOH \right]}$$

or $\left[H^+ \right] = \dfrac{Ka[CH_3COOH]}{[CH_3COO^-]} = \dfrac{Ka[Acid]}{[Conjugate\,base]}$

taking –log on both sides

$pH = pK_a - \log \dfrac{[Acid]}{[Conjugate\,base]}$ or $pH = pK_a + \log \dfrac{[Conjugate\,base]}{[Acid]}$

Henderson's equation :

$$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} \text{ or } \frac{\left[\text{Conjugate base}\right]}{\left[\text{Acid}\right]}$$

- [Conjugate base]$_{eq} \simeq$ [Salt] because CH_3COO^- mainly comes from salt since dissociation of CH_3COOH in presence of CH_3COONa is appreciably decreased.

- [Acid]$_{aq}$ initial concentration of acid since it is almost unionised in presence of salt due to common ion effect.

(b) **pH range of acidic buffer solution :** It depends on pK$_a$ of acid and ratio of salt to acid concentrations.

$$[CH_3COOH] : \quad [CH_3COONa] \quad \Rightarrow \quad pH = pK_a + \log\frac{\left[CH_3COONa\right]}{\left[CH_3COOH\right]}$$

(i)   If,   1   :   10 $\Rightarrow$ $pH = pK_a + \log\frac{10}{1} = pK_a + 1$

(ii) If,   10   :   1 $\Rightarrow$ $pH = pK_a - 1$

So pH range

$$\boxed{pH = pK_a \pm 1}$$

(c) **Maximum buffer action condition of acidic buffer solution :**

$$[CH_3COOH] : \quad [CH_3COONa]$$

1   :   1 $\Rightarrow$ $pH = pK_a + \log\frac{1}{1}$

$$\boxed{pH = pK_a}$$

(ii) **Basic buffer solution :**

Definition : The solution in which weak base and its conjugate acid are present. OR

Aqueous solution of mixture of weak base and salt of same weak base with any strong acid is called basic buffer solution.

Ex. $NH_4OH + NH_4Cl$

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

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

$$\left[\underset{\text{W.B.}}{NH_4OH} + \underset{\text{C.acid}}{NH_4^+}\right] + Cl^- [\text{Spectator ion}]$$
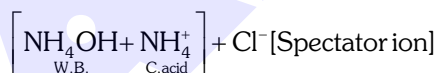
BUFFER ACTION :-

Case 1.   If a small amount of the acid is added to the buffer solution, the H^+ ions are consumed by NH_4OH.

$$NH_4OH_{(aq)} + H^+_{(aq)} \rightleftharpoons NH^+_{4(aq)} + H_2O_{(\ell)}$$
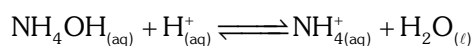
So there is no appreciable change in pH.

Case 2.   If small amount of base is added to the buffer solution, the OH^- ions react with NH_4^+ ions to produce NH_4OH.

$$NH^+_{4(aq)} + OH^-_{(aq)} \rightleftharpoons NH_4OH_{(aq)}$$
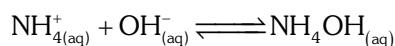
Hence most of the added OH^- ions are consumed. so there is no appreciable change in pH.

(a)   **pOH of basic buffer solution :**

$$[\underset{\text{Base}}{NH_4OH} \; + \; \underset{\text{Salt}}{NH_4Cl}]$$

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

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

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_4OH\right]} \quad \text{or} \quad [OH^-] = \frac{K_b\left[NH_4OH\right]}{\left[NH_4^+\right]}$$

taking –log on both sides $\qquad pOH = pK_b + \log\dfrac{\left[NH_4^+\right]}{\left[NH_4OH\right]}$

Henderson's equation :

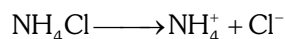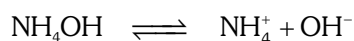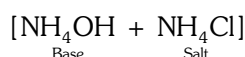$$\boxed{pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]} \text{ or } \frac{\left[\text{Conjugate acid}\right]}{\left[\text{Base}\right]}}$$

(b)   **pOH range of basic buffer solution :** It depends on pK_b of base and ratio of salt to base concentrations.

$$[NH_4OH] \quad : \quad [NH_4Cl] \quad \Rightarrow \quad pOH = pK_b + \log\frac{\left[NH_4Cl\right]}{\left[NH_4OH\right]}$$

(i)   If,   1   :   10 $\Rightarrow$ $pOH = pK_b + 1$

(ii)   If,   10   :   1 $\Rightarrow$ $pOH = pK_b - 1$

So, pOH range   : $\boxed{pOH = pK_b \pm 1}$

(c)   **Maximum buffer action condition of basic buffer solution :**
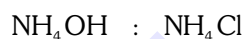
$$NH_4OH \quad : \quad NH_4Cl$$
$$1 \quad : \quad 1$$
$$\boxed{pOH = pK_b}$$

3.   **BUFFER CAPACITY**

Definition :-

(i)   It is defined as the number of moles of strong acid (or strong base) added to one litre of a buffer solution to change its pH by one unit.

(ii)   It measures the effectiveness of a buffer.

(iii)   Larger the value of buffer capacity more resistant is the solution to pH change.

$$\text{Buffer capacity} = \frac{\text{Number of moles of } H^+ \text{ or } OH^- \text{ added per litre}}{\text{Change in pH of buffer solution}}$$

———————————————— **Illustrations** ————————————————

Illustration 24   When 2 moles of HCl is added to 1 L. of an acidic buffer solution, its pH changes from 3.9 to 3.4. Find its buffer capacity.

Solution   B.C. $= \dfrac{2}{0.5} = 4$

BEGINNER'S BOX-4

1. A buffer solution is one which has–

(1) reserved acid   (2) reserved base   (3) constant pH   (4) pH equal to 7

2. Which of the following solutions cannot act as a buffer system ?

(1) KH_2PO_4/H_3PO_4 (2) $NaClO_4/HClO_4$ (3) $C_5H_5N/C_5H_5N^+HCl^-$ (4) $Na_2CO_3/NaHCO_3$

3. A buffer solution can not be prepared by mixing equimolar amounts of–

(1) $B(OH)_3$ and $Na_2B_4O_7.10H_2O$ (2) NH_3 and NH_4Cl

(3) HCl and NaCl   (4) CH_3COOH and CH_3COONa

4. Which of the following salt solution will act as a buffer ?

(1) CH_3COONH_4 (aq.)   (2) NH_4Cl (aq.)   (3) CH_3COONa (aq.)   (4) NaCl (aq.)

5. Which of the following combinations will make a buffer solutions ?

(i) CH_3COONa (2 mol) + HCl (1 mol)   (ii) CH_3COOH (2 mol) + NaOH (1 mol)

(iii) CH_3COOH (1 mol) + CH_3COONa (1 mol)

(1) (iii)   (2) (i), (ii)   (3) (ii), (iii)   (4) (i), (ii), (iii)

6. The pH of blood circulating in a human body is maintained around 7.4 by the action of the buffer system–

(1) CH_3COOH/CH_3COONa (2) NH_4Cl/NH_3

(3) $H_2PO_4^{2-}$ (4) H_2CO_3/HCO_3^-

4.11 INDICATOR

(A) **Definition :-** An indicator is a substance that undergoes change in its colour to show end point of an acid-base titration.

• Titration involves neutralization of an acid and base.

(B) **Types of indicators :**

(a) **Acidic indicator (HIn)**

Ex. Phenolphthalein (HPh)

HPh $\rightleftharpoons$ H^+ + Ph^-

colourless   pink
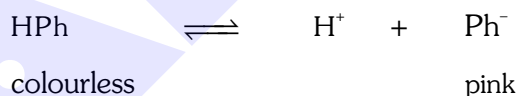
(b) **Basic indicator (InOH)**

Ex. Methyl orange (MeOH)

MeOH $\rightleftharpoons$ Me^+ + OH^-

yellow   orange red
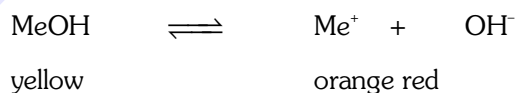
OSTWALD THEORY OF INDICATORS

(i) According to this theory, all the indicators are weak organic acid or base.

(ii) Every indicator has light colour in its unionised form and dark colour in ionised form.

(iii) Every indicator has one colour in acidic medium and an altogether different colour in basic medium due to common ion effect and odd ion effect.

Ex.   Acidic indicator [HPh]

Case 1. $HPh \rightleftharpoons H^+ + Ph^-$ [HPh] > [Ph⁻]

In acidic medium [H⁺]   Colourless due to common ion effect.

Case 2. $HPh \rightleftharpoons H^+ + Ph^-$ [Ph⁻] > [HPh]

In basic medium [OH⁻]   Pink colour due to odd ion effect.
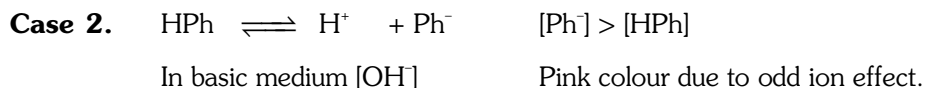
(a)   pH of acidic indicator -

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

$$K_a \text{ or } K_I = \frac{[H^+][In^-]}{[HIn]}$$

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

Taking – log on both sides

pH = pK$_I$ – log [HIn] + log [In⁻]

$$pH = pK_I + \log \frac{[In^-]}{[HIn]}$$ $\boxed{pH = pK_I + \log \frac{[Ionised\ form]}{[Unionised\ form]}}$

(b)   pOH of basic indicator -
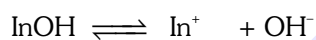
$$InOH \rightleftharpoons In^+ + OH^-$$

$$K_b \text{ or } K_I = \frac{[In^+][OH^-]}{[InOH]}$$ $\boxed{pH = pK_I + \log \frac{[Ionised\ form]}{[Unionised\ form]}}$

(c)   pH range of indicators :

Indicators show colour change for a certain pH range not at a definite pH which is called pH range of indicator.
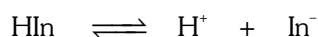
(i)   pH range of acidic indicator :

[HIn]	:	[In⁻]
1	:	10
10	:	1

$\boxed{pH = pK_I \pm 1}$

(ii)   pOH range of basic indicator :

[InOH]	:	[In⁺]
1	:	10
10	:	1

$\boxed{pOH = pK_I \pm 1}$

(iii)   Neutral condition for indicators (No working condition)

For acidic indicator

[HIn]	:	[In⁻]
1	:	1

$\boxed{pH = pK_I}$

For basic indicators

[InOH]	:	[In⁺]
1	:	1

$\boxed{pOH = pK_I}$

S.No.	Name of indicator	Colour in acidic medium	Colour in basic medium	Working pH range of indicators
1.	Methyl orange (MeOH)	Orange red	Yellow	3.1 to 4.5
2.	Methyl red	Red	Yellow	4.2 to 6.2
3.	Phenol red	Yellow	Red	6.2 to 8.2
4.	Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

3. ACID-BASE TITRATION

S.No.	Type of titration	pH range of titration	Suitable indicators
1.	SA/SB.	3 – 11	All indicators (MeOH, HPh etc.)
2.	SA/WB	3 – 7	Methyl orange (MeOH) and methyl red
3.	WA/SB	7 – 11	Phenolphthalein (HPh)

Important points of titration :

(i). Titration is always possible in two opposite solution. (i.e. one is acidic and other is basic).

(ii). For any titration only that indicator is suitable if their working pH range is in pH range of titration.

(iii). At the end point of titration equivalents of acids and bases are always same.

(iv). At the euivalence point, nature of solution depends on the type of titration.

SA/SB	-	Neutral (pH = 7)
SA/WB	-	Acidic
WA/SB	-	Basic
WA/WB	-	Any one possible

4.12   ACID AND BASE

(1)   INTRODUCTION

The earliest classification of substances into acids and bases was bases upon the characteristic properties possessed by each one of them. For example,

Acid was defined as a substance whose aqueous solution possesses the following characteristic properties:

(i) conducts electricity,

(ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,

(iii) turns blue litmus red.

(iv) has a sour taste.

(v) whose acidic properties disappear on reaction with a base.

Base was defined as a substance whose aqueous solution possessed the following characteristic properties:
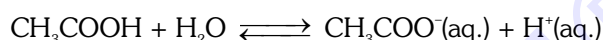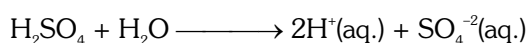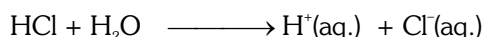
(i) conducts electricity,

(ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,

(iii) turns red litmus blue,

(iv) has a bitter taste

(v) whose basic properties are destroyed on reaction with an acid.

The above definitions of acids and bases are called operational definitions as they are based certain operations (i.e. tests) to be performed on the substances. However, these have been replaced by conceptual definitions (put forward by Arrhenius, Bronsted-Lowry and Lewis) which go into the causes of the observed behavior, based upon structure and composition of the substances.
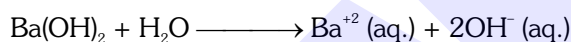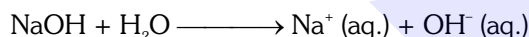
(2)   Arrhenius Concept (1884)

(a)   Acid:- According to this concept, those substances which produce free H^+ ions in aqueous solution are called acid.

Example HCl, HNO_3, H_2SO_4, H_3PO_4, H_2CO_3, H_2S, CH_3COOH etc.

$$HCl + H_2O \longrightarrow H^+(aq.) + Cl^-(aq.)$$

$$H_2SO_4 + H_2O \longrightarrow 2H^+(aq.) + SO_4^{-2}(aq.)$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^-(aq.) + H^+(aq.)$$

(b)   Base :- Those substances which produce free OH^- ions in aqueous solution are called base.

Example $NaOH$, KOH, $Cs(OH)$, $Rb(OH)$, NH_4OH, $Ba(OH)_2$, $Ca(OH)_2$, $Al(OH)_3$ etc.

$$NaOH + H_2O \longrightarrow Na^+ (aq.) + OH^- (aq.)$$

$$Ba(OH)_2 + H_2O \longrightarrow Ba^{+2} (aq.) + 2OH^- (aq.)$$

(c)   Nature of water :- According to this concept nature of water is neutral and act as a solvent.

(d)   Neutralisation Reaction :- Those reactions in which acid and base react together to form water molecule are called neutralisation reactions.

i.e. $Na^+ + OH^- + H^+ + Cl^- \longrightarrow NaCl + H_2O$

$H^+ + OH^- \longrightarrow H_2O$
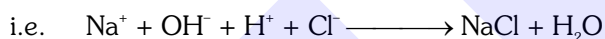
(e)   Strength of acids and bases :- This concept explains the strength of acids and bases depending upon the basis of degree of ionisation.

Example   For strong electrolytes $\alpha \simeq 100\%$

For weak electrolytes $\alpha < 100\%$

(f)   Advantage :- This concept explains the acids and bases practically. i.e. To find out the pH, ionisation constant, hydrolysis constants, heat of neutralisation etc.

(g)   Disadvantage :- It explains the behaviour of acids and bases only in aqueous (water) solvents.

——————————————— **Illustrations** ———————————————

**Illustration 25**   Gaseous hydrogen chloride is a very poor conductor of electricity but a solution of hydrogen chloride in water is a good conductor. This is due to the fact that :-

(1) Water is a good conductor of electricity

(2) Hydrogen chloride ionises in water

(3) A gas cannot conduct electricity but a liquid can

(4) HCl does not obey Ohm's law where as the solution does

Solution   (2)

Illustration 26   Which is acid in the following pairs according to Arrhenius concept ?

(1) HCl(g) and HCl (aq)   (2) $CH_3COOH(l)$ and $CH_3COOH(aq)$

Solution   (1) HCl(aq.)   (2) $CH_3COOH(aq.)$
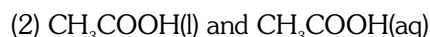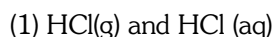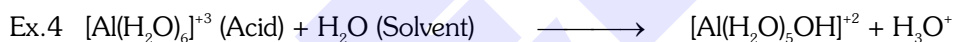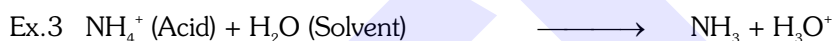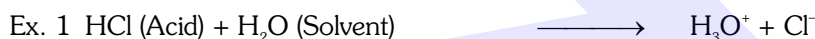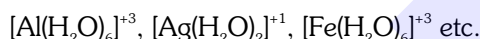
(3)   Bronsted-Lowry Concept (1923)

It is based upon the exchange of proton.

(a) Acid :- According to this concept those substances which have tendency to donate the proton (H^+) by any method in any solvent are called acids.

Example   (i) Neutral molecules - HCl, HNO_3, H_2SO_4, H_2CO_3, H_2S, CH_3COOH, H_3PO_3 etc.

(ii) Anions - HS^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, HPO_4^{-2}, H_2O etc.

(iii) Cations - NH_4^+, H_3O^+, PH_4^+, $CH_3COOH_2^+$ etc.

$[Al(H_2O)_6]^{+3}$, $[Ag(H_2O)_2]^{+1}$, $[Fe(H_2O)_6]^{+3}$ etc.

Ex. 1 HCl (Acid) + H_2O (Solvent) $\longrightarrow$ $H_3O^+ + Cl^-$

Ex.2 HS^- (Acid) + H_2O (Solvent) $\longrightarrow$ $H_3O^+ + S^{-2}$

Ex.3 NH_4^+ (Acid) + H_2O (Solvent) $\longrightarrow$ $NH_3 + H_3O^+$

Ex.4 $[Al(H_2O)_6]^{+3}$ (Acid) + H_2O (Solvent) $\longrightarrow$ $[Al(H_2O)_5OH]^{+2} + H_3O^+$

(b) Base :- Those substances which have tendency to accept the proton by any method in any solvent are called the bases.

(1) HS^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, HPO_4^{-2}, O^{-2}, SO_4^{-2}, CO_3^{-2}, Cl^-, Br^-, I^-, CN^- etc.

(2) NH_3, RNH_2, R_2NH, R_3N, $C_6H_5NH_2$, C_5H_5N, H_2N-NH_2 etc.

Example   (i) HS^- (Base) + H_2O (Solvent) $\longrightarrow$ $H_2S + OH^-$

(ii) NH_3 (Base) + H_2O (Solvent) $\longrightarrow$ $NH_4^+ + OH^-$

(iii) CO_3^{-2}(Base) + H_2O (Solvent) $\longrightarrow$ $HCO_3^- + OH^-$
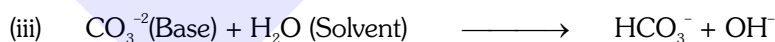
(c) Nature of water :- According to this concept nature of water is amphoteric or amphiprotic i.e. water can act as both acid and base.

(i) HCl (Acid) + H_2O (Base) $\longrightarrow$ $Cl^- + H_3O^+$

(ii) NH_3 (Base) + H_2O (Acid) $\longrightarrow$ $NH_4^+ + OH^-$
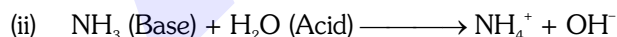
(d) Neutralisation Reaction :- According to this concept those reaction in which acid and base react together and convert into their respective conjugate acid and base are called neutralisation reactions.

Example

$$\begin{array}{ccccccc}
HCl & + & NH_3 & \rightleftharpoons & Cl^- & + & NH_4^+ \\
Acid & & Base & & Conjugate & & Conjugate \\
& & & & Base & & Acid
\end{array}$$
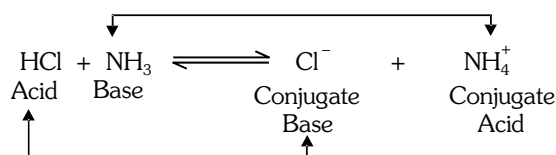
(e) Strength of acids and bases :- This concept explain the strength of acid and base depending upon the basis of relative tendency to accept or donate the proton.

(i)	$HClO_4$	(ix)	H_3PO_4	(xvii)	H – OH
(ii)	HI	(x)	HF	(xviii)	C_2H_5–OH
(iii)	HBr	(xi)	CH_3COOH	(xix)	$C_6H_5NH_2$
(iv)	H_2SO_4	(xii)	H_2CO_3	(xx)	NH_3
(v)	HCl	(xiii)	H_2S	(xxi)	$R–NH_2$
(vi)	HNO_3	(xiv)	NH_4^+	(xxii)	CH_4
(vii)	H_3O^+	(xv)	HCN	(xxiii)	H_2
(viii)	HSO_4^-	(xvi)	C_6H_5OH		

Example

(i) HCl   + H_2O $\rightleftharpoons$ Cl^- + H_3O^+

Strong acid   Strong base   Weak base   Weak acid

(ii) CH_3COOH + H_2O $\rightleftharpoons$ CH_3COO^- + H_3O^+

Weak acid   Weak base   Strong base   Strong acid

(iii) NH_3 + H_2O $\rightleftharpoons$ NH_4^+ + OH^-

Weak base   Weak acid   Strong acid   Strong base

(iv) HCl   + CH_3COOH $\rightleftharpoons$ Cl^- + $CH_3COOH_2^+$

Weak acid   Weak base   Strong base   Strong acid

(v) HCl   + NH_3 $\rightleftharpoons$ Cl^- + NH_4^+

Strong acid   Strong base   Weak base   Weak acid

(vi) CH_3COOH + NH_3 $\rightleftharpoons$ CH_3COO^- + NH_4^+

Strong acid   Strong base   Weak base   Weak acid

GOLDEN KEY POINTS

Types of Solvent

(a) Protogenic or acidic solvent :- They have a tendency to generate or donate the protons.

Example CH_3COOH, HCl, HNO_3, H_2SO_4 etc.

(b) Protophilic or basic solvent :- They have a tendency to accept the protons.

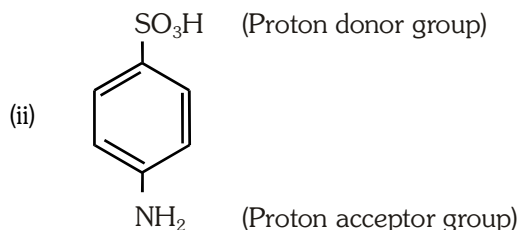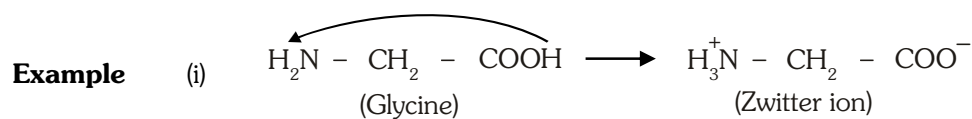**Example** NH_3, CH_3OH, RNH_2 etc.

(c) Amphiprotic or amphoteric solvents :- They have the tendency to accept or donate the protons or they are either protophilic or protogenic.

Example H_2O, HS^-, HSO_4^-, HCO_3^- etc.

(d) Aprotic solvents :- They neither donate nor accept the protons.

Example C_6H_6, CCl_4, $CHCl_3$, BrF_3, NO_2, $COCl_2$ etc.

(e) Ampholyte solvents-Those solvents in which the same molecule acts as proton donor and proton acceptor.

Example   (i) $H_2N - CH_2 - COOH \longrightarrow H_3^+N - CH_2 - COO^-$

(Glycine)   (Zwitter ion)

(ii)

SO_3H (Proton donor group)

NH_2 (Proton acceptor group)

(f) Advantage :-

(i)   It explain the behaviour of acids and bases in any type of solvent.

(ii)   It explain the stability of proton (H^+).

(g) Disadvantage :-

(i)   It does not explain the acid and base practically.

(ii)   It does not explain acidic behaviour of aprotic acid. (SO_2, SO_3, CO_2, $AlCl_3$, $SiCl_4$ etc.)

Illustrations

Illustration 27   In the process : $NH_3 + NH_3 \rightleftharpoons NH_2^- + NH_4^+$, The nature of ammonia is:-

(1) Acidic   (2) Basic   (3) Amphoteric   (4) None

Solution.   **Ans.(3)**

Illustration 28   Which of the following behave both as Bronsted acid as well as Bronsted bases ?

H_2O, HCO_3^-, H_2SO_4, H_3PO_4, HS^-, NH_3

Solution. H_2O, HCO_3^-, HS^-, NH_3

(4)   Lewis Concept (1939)

(a) Lewis Acid :- According to this concept those species which have self tendency to accept the lone pair of electrons are called acids. i.e. Lewis acid is an electron pair acceptor (electrophilic).

$H^+ + :\ddot{O}_x H^- \longrightarrow H:\ddot{O}_x H$

Acid   Base
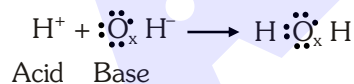
Classification of Lewis Acids :-

(i)   Compounds whose central atom have an incomplete octet (electron deficient)

Example BF_3, BBr_3, BCl_3, BI_3, $B(CH_3)_3$, $B(OH)_3$, $AlCl_3$, $GeCl_3$ etc.

$$\overset{-\delta}{F} \longleftarrow \overset{+\delta}{B} \longrightarrow \overset{-\delta}{F}$$
$$\downarrow$$
$$\overset{}{F}^{-\delta}$$
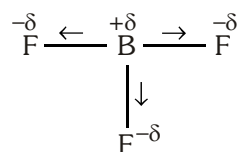
(ii)   Compounds whose central atom have vacant d-orbitals and can accept one or more pair of lone electrons.

Example SF_4, SF_6, $SnCl_2$, $SnCl_4$, PX_3, PX_5, GeX_4, TeX_4, IF_5, IF_7, etc.
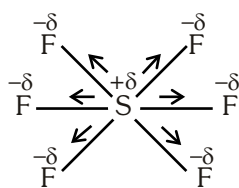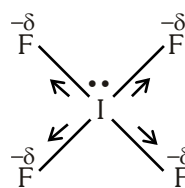
SF_6 IF_5

(iii)   Molecules with a multiple bond between atoms of different electronegativities.

Example CO_2, SO_2, SO_3 etc.

$$\overset{-\delta}{O} = \overset{+\delta}{O} = \overset{-\delta}{O} \qquad \overset{-\delta}{O} = \overset{+\delta}{S} = \overset{-\delta}{O} \qquad \overset{-\delta}{O} = \overset{+\delta}{S} = \overset{-\delta}{O}$$
$$\underset{O^{-\delta}}{\overset{||}{}}$$

$$\overset{\frown}{O} = C = O \quad + \quad OH^- \longrightarrow \ ^-O - C = O \longrightarrow HCO_3^-$$

Lewis acid   Lewis base |
                                            OH

$$SO_3 \qquad + \qquad H_2O \longrightarrow H_2SO_4$$

Lewis acid   Lewis base

(iv)   **Cations :-**

Example Ag^+, Na^+, Li^+, Al^{+3}, Be^{+2}, Mg^{+2}, I^+, Cl^+, H^+ etc.

False cations :-   Example NH_4^+, H_3O^+, $CH_3COOH_2^+$, PH_4^+ etc.

Example $Ag^+ + 2\,(:NH_3) \rightleftharpoons [Ag\,(:NH_3)_2]^+$

$Cu^{+2} + 2\,(:H_2O)_2 \longrightarrow [Cu\,(:H_2O)_4]^{+2}$

(v)   Elements which have six electrons in their outermost shell or valence shell.

O–Family (O, S, Se, Te)   Po – Radioactive element

$$SO_3^{-2} + \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}: \longrightarrow [SO_3 \longrightarrow O]^{-2}$$

Base   Acid

(b) Lewis Base :- Those species which have self tendency to donate the lone pair of electrons are called bases. i.e. a base is an electron pair (lone pair) donor (nucleophile).
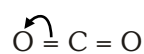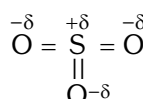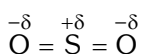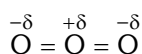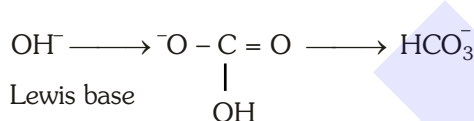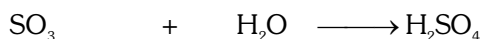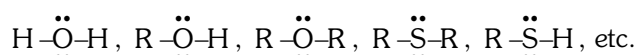
Classification of Lewis Bases

(i)   Those species whose central atom have lone pair of electrons and have self tendency to donate them –

Example $\overset{\bullet\bullet}{N}H_3$, $R - \overset{\bullet\bullet}{N}H_2$, $R_2 - \overset{\bullet\bullet}{N}H$, $C_6H_5 - \overset{\bullet\bullet}{N}H_2$, $C_5H_5 - \overset{\bullet\bullet}{N}$, $H_2\overset{\bullet\bullet}{N} - \overset{\bullet\bullet}{N}H_2$,

$H - \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} - H$, $R - \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} - H$, $R - \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} - R$, $R - \overset{\bullet\bullet}{\underset{\bullet\bullet}{S}} - R$, $R - \overset{\bullet\bullet}{\underset{\bullet\bullet}{S}} - H$, etc.

Explain :- $R \underset{+I}{\overset{\longrightarrow}{}} \overset{-\delta}{O} \underset{+I}{\overset{\longleftarrow}{}} R$ (Electron density on O, increases due to +I effect)
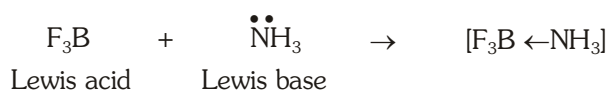
(ii)   **Anions** –

Example O^{-2}, SO_4^{-2}, CO_3^{-2}, Cl^-, Br^-, F^-, I^-, N^{-3}, P^{-3}, NO_3^-, S^{-2}, CN^-, etc.

(c) **Nature of water :-** According to this concept nature of water is basic i.e. water is a base.

(d) **Neutralisation Reaction :-** According to this concept those reactions in which acid and base react together to form a co-ordinate bond between them are called neutralisation reactions.
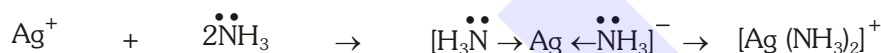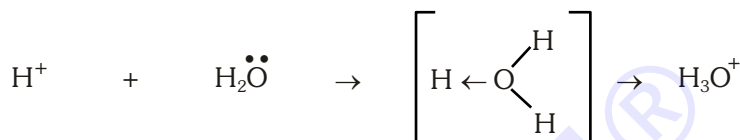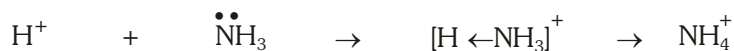
Example

$$F_3B \quad + \quad \overset{\bullet\bullet}{N}H_3 \quad \rightarrow \quad [F_3B \leftarrow NH_3]$$
Lewis acid   Lewis base

$$H^+ \quad + \quad \overset{\bullet\bullet}{N}H_3 \quad \rightarrow \quad [H \leftarrow NH_3]^+ \quad \rightarrow \quad NH_4^+$$

$$H^+ \quad + \quad H_2\overset{\bullet\bullet}{O} \quad \rightarrow \quad \left[H \leftarrow O \overset{H}{\underset{H}{<}} \right] \quad \rightarrow \quad H_3O^+$$

$$Ag^+ \quad + \quad 2\overset{\bullet\bullet}{N}H_3 \quad \rightarrow \quad [H_3\overset{\bullet\bullet}{N} \rightarrow Ag \leftarrow \overset{\bullet\bullet}{N}H_3]^- \rightarrow \quad [Ag\,(NH_3)_2]^+$$

(e) **Strength of acids and bases :-** This concept explain the strength of acids and bases depending upon the basis of self tendency. To accept or donate the lone pair of electrons (e^-).

Example $SO_2 < SO_3$ (Strong acid)

(f) **Advantage :-**
   (a)   This concept explains the acid and base without any solvent.
   (b)   This concept explains those acids and bases which are not explained by other concepts.
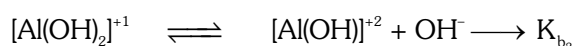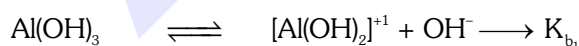
(g) **Disadvantage :-**
   (a)   This concept fails to explain the acid and base practically.
   (b)   According to this concept forming of co-ordinate bond in neutralisation reaction of acid and base is a slow process, whereas neutralisation reaction of acids and bases is actually fast process.
   (c)   This concept fails to explain the real acids and bases
        Example   HCl, HNO_3, H_2SO_4, NaOH, KOH, etc.

• All the lewis bases are bronsted bases but all the lewis acids are not bronsted acids.

• All Arrhenius acids are Bronsted acids but it is not so for bases.

(6) **POLYACIDIC BASE AND POLYBASIC ACIDS**

   (a) **Polyacidic Base**

$$Al(OH)_3 \quad \rightleftharpoons \quad Al^{+3} + 3OH^- \longrightarrow K_b$$

$$Al(OH)_3 \quad \rightleftharpoons \quad [Al(OH)_2]^{+1} + OH^- \longrightarrow K_{b_1}$$

$$[Al(OH)_2]^{+1} \quad \rightleftharpoons \quad [Al(OH)]^{+2} + OH^- \longrightarrow K_{b_2}$$

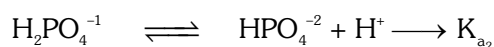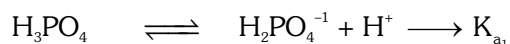$$[Al(OH)]^{+2} \quad \rightleftharpoons \quad Al^{+3} + OH^- \longrightarrow K_{b_3}$$

$$K_b = K_{b_1} \times K_{b_2} \times K_{b_3}$$

taking –log on both sides

$$pK_b = pK_{b_1} + pK_{b_2} + pK_{b_3}$$

i.e. $\boxed{K_{b_1} > K_{b_2} > K_{b_3}}$ $\Rightarrow$ $\boxed{pK_{b_1} < pK_{b_2} < pK_{b_3}}$

(b)   Polybasic Acid

$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{-3} \longrightarrow K_a$

$H_3PO_4 \rightleftharpoons H_2PO_4^{-1} + H^+ \longrightarrow K_{a_1}$

$H_2PO_4^{-1} \rightleftharpoons HPO_4^{-2} + H^+ \longrightarrow K_{a_2}$

$HPO_4^{-2} \rightleftharpoons PO_4^{-3} + H^+ \longrightarrow K_{a_3}$

$K_a = K_{a_1} \times K_{a_2} \times K_{a_3}$

taking –log on both sides

$pK_a = pK_{a_1} + pK_{a_2} + pK_{a_3}$

$\boxed{K_{a_1} > K_{a_2} > K_{a_3}} \quad \Rightarrow \quad \boxed{pK_{a_1} < pK_{a_2} < pK_{a_3}}$

─────────────────── **Illustrations** ───────────────────

Illustration 29   In the dissociation , $H_2A \xrightleftharpoons{K_1} H^+ + HA^-$; $HA^- \xrightleftharpoons{K_2} H^+ + A^{-2}$

(1) K_1 is equal to K_2 (2) K_1 is smaller than K_2
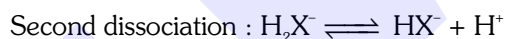
(3) K_1 is greater than K_2 (4) K_1 is negligible

Solution.   **Ans. (3)**

Illustration 30   Calculate the pH of 2.0×10^{-4} M H_3X Solution assuming first dissociation to be 100%, second to be 50% and third to be negligible :

Solution.   First dissociation : $H_3X \rightleftharpoons H_2X^- + H^+$

∴ H^+ ion concentration = 2×10^{-4} M

Second dissociation : $H_2X^- \rightleftharpoons HX^- + H^+$

H^+ ion concentration = $C\alpha = 2 \times 10^{-4} \times 0.5$

∵   Third dissociation is negligible

∴ $[H^+] = 2 \times 10^{-4} + 10^{-4} = 3 \times 10^{-4}$

pH = $4 - \log 3 = 3.52$

─────────────────────── **BEGINNER'S BOX-5** ───────────────────────

1.   Which of the following is a Bronsted acid ?

(i) HCN   (ii) $H_2PO_4^-$ (iii) NH_4^+ (iv) HCl

(1) (i), (iii)   (2) (i), (ii), (iii), (iv)   (3) (ii), (iii)   (4) (i), (iii),(iv)

2.   Which of the following is a Bronsted base ?

(i) NH_3 (ii) CH_3NH_2 (iii) HCO_3^- (iv) SO_4^{2-}

(1) (i), (ii), (iii), (iv)   (2) (i), (ii)   (3) (i), (ii), (iii)   (4) (i), (iii),(iv)

3.   The conjugate base of hydroxide ion is–

(1) H_2O (2) H_3O^+ (3) O^{2-} (4) O_2

4.   The conugate acid of amide ion (NH_2^-) is–

(1) N_2H_4 (2) NH_2OH (3) NH_4^+ (4) NH_3

5. Which of the following can act both as a Bronsted acid as well as a Bronsted base ?

(1) H_2SO_4 (2) HCO_3^- (3) O^{2-} (4) NH_4^+

6. Which of the following acid-base reactions cannot be explained by the Bronsted theory ?

(1) $CO_2 + CaO \longrightarrow CaCO_3$ (2) $BF_3 + NH_3 \longrightarrow \bar{B}F_3 \overset{+}{N}H_3$

(3) $Ni + 4CO \longrightarrow Ni(CO)_4$ (4) All of these

7. Which of the following Bronsted acid has the weakest conjugate base ?

(1) H_2O (2) HCN   (3) HCOOH   (4) HF

ANSWER KEY

	Que.	1	2	3	4	5	6	7	8	9	10
BEGINNER'S BOX-1	Ans.	3	1	3	4	1	1	4	4	2	1
	Que.	11									
	Ans.	2									

	Que.	1	2	3	4	5	6	7
BEGINNER'S BOX-2	Ans.	4	2	1	2	3	2	1

	Que.	1	2	3	4	5	6
BEGINNER'S BOX-3	Ans.	2	3	2	3	1	2

	Que.	1	2	3	4	5	6
BEGINNER'S BOX-4	Ans.	3	2	3	1	4	4

	Que.	1	2	3	4	5	6	7
BEGINNER'S BOX-5	Ans.	2	1	3	4	2	4	4