9

Ionic Equilibrium

TOPIC 1

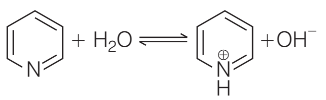
Ostwald's Dilution Law

01 The percentage of pyridine (C_5H_5N) that forms pyridinium ion $(C_5H_5N^+H)$ in a $0.10M$ aqueous pyridine solution (K_b for $C_5H_5N = 1.7 \times 10^{-9}$) is **[NEET 2016, Phase II]**

(a) 0.0060% (b) 0.013%
(c) 0.77% (d) 1.6%

Ans. *(b)*

The percentage of pyridine can be equal to the percentage of dissociation of pyridinium ion and pyridine solution as shown below:



As pyridinium is a weak base, so degree of dissociation is given as

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.7 \times 10^{-9}}{0.10}}$$

$$= \sqrt{1.7 \times 10^{-8}} = 1.3 \times 10^{-4}$$

or, percentage of dissociation

$$= (\alpha \times 100)\%$$

$$= (1.3 \times 10^{-4}) \times 100 = 0.013\%$$

02 The values of K_{p_1} and K_{p_2} for the reactions

$$X \rightleftharpoons Y + Z \quad \text{...(i)}$$

and $$A \rightleftharpoons 2B \quad \text{...(ii)}$$

are in ratio of 9:1. If degree of dissociation of X and A be equal, then total pressure at equilibrium (i) and (ii) are in the ratio **[CBSE AIPMT 2008]**

(a) 3 : 1 (b) 1 : 9
(c) 36 : 1 (d) 1 : 1

Ans. *(c)*

In equation,	X $\rightleftharpoons$	Y +	Z
Initial moles	1	0	0
At equil.	$(1-\alpha)$	α	α

where, α = degree of dissociation

Total number of moles

$$= 1 - \alpha + \alpha + \alpha = (1 + \alpha)$$

$$p_X = \left(\frac{1-\alpha}{1+\alpha}\right) p_1$$

$$p_Y = \left(\frac{\alpha}{1+\alpha}\right) p_1$$

$$p_Z = \frac{\alpha}{(1-\alpha)} p_1$$

$$K_{p_1} = \frac{[p_Y][p_Z]}{[p_X]} = \frac{\left(\frac{\alpha}{1+\alpha}\right) p_1 \times \left(\frac{\alpha}{1+\alpha}\right) p_1}{\left(\frac{1-\alpha}{1+\alpha}\right) p_1}$$

$$= \frac{\left(\frac{\alpha}{1+\alpha}\right)^2 p_1}{\left(\frac{1-\alpha}{1+\alpha}\right)} \quad \text{...(i)}$$

For equation,	A $\rightleftharpoons$	$2B$
Initial moles	1	0
At equil.	$(1-\alpha)$	2α

Total number of moles at equilibrium $= (1 + \alpha)$

$$p_B = \left(\frac{2\alpha}{1+\alpha}\right) p_2$$

$$p_A = \left(\frac{1-\alpha}{1+\alpha}\right) p_2$$

$$K_{p_2} = \frac{[p_B]^2}{[p_A]} = \frac{\left[\left(\frac{2\alpha}{1+\alpha}\right) p_2\right]^2}{\left(\frac{1-\alpha}{1+\alpha}\right) p_2}$$

$$K_{p_2} = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 p_2}{\left(\frac{1-\alpha}{1+\alpha}\right)} \quad \text{...(ii)}$$

Eq. (i) divide by Eq. (ii)

$$\frac{K_{p_1}}{K_{p_2}} = \frac{\alpha^2 \times p_1}{4\alpha^2 \times p_2}$$

$$\frac{9}{1} = \frac{p_1}{4p_2}$$

$$\frac{p_1}{p_2} = \frac{36}{1} = 36 : 1$$

03 The dissociation equilibrium of a gas AB_2 can be represented as

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

The degree of dissociation is x and is small compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure p is **[CBSE AIPMT 2008]**

(a) $(2K_p / p)$ (b) $(2K_p / p)^{1/3}$
(c) $(2K_p / p)^{1/2}$ (d) (K_p / p)

Ans. *(b)*

	$2AB_2(g)$ $\rightleftharpoons$	$2AB(g)$ +	$B_2(g)$
Initial moles	1	0	0
At equil.	$2(1-x)$	$2x$	x

where, x = degree of dissociation

Total moles at equilibrium

$$= 2 - 2x + 2x + x = (2 + x)$$

So, $p_{AB_2} = \frac{2(1-x)p}{(2+x)}$, $p_{AB} = \frac{2xp}{(2+x)}$

$$p_{B_2} = \frac{xp}{(2+x)}$$

$$K_p = \frac{(p_{AB})^2 (p_{B_2})}{(p_{AB_2})^2} = \frac{\left(\frac{2xp}{2+x}\right)^2 \left[\left(\frac{x}{2+x}\right) p\right]}{\left[\left(\frac{2(1-x)}{(2+x)}\right) p\right]^2}$$

$$= \frac{4x^3p^3}{(2+x)^3} \times \frac{(2+x)^2}{p^2 4(1-x)^2} = \frac{x^3 p}{(2+x)(1-x)^2}$$

$$= \frac{x^3 p}{2} \qquad [\because x <<< 1$$

and 2 $\quad x = \left(\frac{2K_p}{p}\right)^{1/3}$ $\qquad$ so, $(1-x) \approx 1$, $(2+x) \approx 2$

04 A weak acid, HA, has a K_a of 1.00×10^{-5}. If 0.100 mole of this acid is dissolved in one litre of water, the percentage of acid dissociated at equilibrium is closest to **[CBSE AIPMT 2007]**

(a) 99.0% (b) 1.00%
(c) 99.9% (d) 0.100%

Ans. *(b)*

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

At equilibrium $[H^+ = A^-]$

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

$$[H^+] = \sqrt{K_a[HA]} = \sqrt{1 \times 10^{-5} \times 0.1}$$

$$= \sqrt{1 \times 10^{-6}} = 1 \times 10^{-3}$$

$$\alpha = \frac{\text{Actual ionisation}}{\text{Molar concentration}}$$

$$= \frac{10^{-3}}{0.1} = 10^{-2}$$

% of acid dissociated $= 10^{-2} \times 1.00$
$= 1\% = 100\%$

05 At 25°C, the dissociation constant of a base, BOH is 1.0×10^{-12}. The concentration of hydroxyl ions in 0.01 M aqueous solution of the base would be **[CBSE AIPMT 2005]**

(a) 2.0×10^{-6} mol L^{-1}
(b) 1.0×10^{-5} mol L^{-1}
(c) 1.0×10^{-6} mol L^{-1}
(d) 1.0×10^{-7} mol L^{-1}

Ans. *(d)*

Base, BOH is dissociated as follows

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

So, the dissociation constant of BOH base

$$K_b = \frac{[B^+][OH^-]}{[OH]} \qquad \text{...(i)}$$

At equilibrium $[B^+] = [OH^-]$

$$\therefore \quad K_b = \frac{[OH^-]^2}{[BOH]}$$

Given that $K_b = 1.0 \times 10^{-12}$
and $[BOH] = 0.01$ M

Thus, $1.0 \times 10^{-12} = \frac{[OH^-]^2}{0.01}$

$$[OH^-]^2 = 1 \times 10^{-14}$$

$$[OH^-] = 1.0 \times 10^{-7} \text{mol L}^{-1}$$

06 Ionisation constant of CH_3COOH is 1.7×10^{-5} and concentration of H^+ ions is 3.4×10^{-4}. Then, find out initial concentration of CH_3COOH molecules. **[CBSE AIPMT 2001]**

(a) 3.4×10^{-4} (b) 3.4×10^{-3}
(c) 6.8×10^{-4} (d) 6.8×10^{-3}

Ans. *(a)*

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

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

Given that, $[CH_3COO^-] = [H^+] = 3.4 \times 10^{-4}$ M

K_a for $CH_3COOH = 1.7 \times 10^{-5}$

CH_3COOH is weak acid, so in it $[CH_3COOH]$ is equal to initial concentration. Hence,

$$1.7 \times 10^{-5} = \frac{(3.4 \times 10^{-4})(3.4 \times 10^{-4})}{[CH_3COOH]}$$

$$[CH_3COOH] = \frac{3.4 \times 10^{-4} \times 3.4 \times 10^{-4}}{1.7 \times 10^{-5}}$$

$$= 6.8 \times 10^{-3} \text{M}$$

TOPIC 2
Acid Base Concepts

07 Which of the following cannot act both as Bronsted acid and as Bronsted base? **[NEET (Odisha) 2019]**

(a) HCO_3^- (b) NH_3 (c) HCl (d) HSO_4^-

Ans. *(c)*

Key Idea Bronsted acid is a substance which has a tendency to donate proton. Bronsted base is a substance which has a tendency to accept proton.

HCl can act as Bronsted acid becuase it can only donate proton.

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \rightleftharpoons H_3O^+ + Cl^-$$

The remaining options contains substances which act both as Bronsted acid and Bronsted base.

$$HCO_3^- + HCO_3^- \rightleftharpoons H_2CO_3 + CO_3^{2-}$$

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$HSO_4^- + HSO_4^- \rightleftharpoons H_2SO_4 + SO_4^{2-}$$

Thus, option (c) is correct.

08 Conjugate base for Bronsted acids H_2O and HF are **[NEET (National) 2019]**

(a) H_3O^+ and F^-, respectively
(b) OH^- and F^-, respectively
(c) H_3O^+ and H_2F^+, respectively
(d) OH^- and H_2F^+, respectively

Ans. *(b)*

An acid on losing a proton produces a species which has the tendency to accept H^+.

It is called conjugate base of that acid.

$$\underset{\text{Acid}}{H_2O} \rightleftharpoons \underset{\text{Conjugate base}}{\bar{O}H} + H^+,$$

$$\underset{\text{Acid}}{HF} \rightleftharpoons \underset{\text{Conjugate base}}{F^-} + H^+$$

Water (H_2O) is amphoteric in nature and thus act both as an acid and base. e.g.

$$\underset{\text{Acid}}{HF} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Conjugate base}}{F^-} + \underset{\text{Conjugate acid}}{H_3O^+}$$

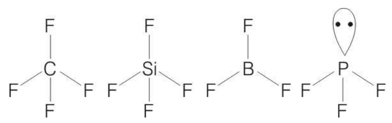
09 Which of the following fluoro-compounds is most likely to behave as a Lewis base? **[NEET 2016, Phase II]**

(a) BF_3 (b) PF_3
(c) CF_4 (d) SiF_4

Ans. *(b)*

Key Idea *The molecule with lone pair at centre atom, will behave as Lewis base.*

In the given molecules, only PF_3 has lone pair at P as shown below:



Thus, PF_3 acts as a Lewis base (electron-pair donor) due to presence of lone pair on P-atom.

10 Which is the strongest acid in the following? **[NEET 2013]**

(a) H_2SO_4 (b) $HClO_3$
(c) $HClO_4$ (d) H_2SO_3

Ans. *(c)*

The strength of oxyacids can also be decided with the help of the oxidation number of central atom. Higher the oxidation number of central atom, more acidic is the oxyacid.

$$H_2\overset{+6}{S}O_4, H\overset{+5}{Cl}O_3, H\overset{+7}{Cl}O_4, H_2\overset{+4}{S}O_3$$

Order of acidic nature

$$HClO_4 > H_2SO_4 > HClO_3 > H_2SO_3$$

Since, in $HClO_4$, oxidation number of Cl is highest, so, $HClO_4$ is the strongest acid among the given acids.

11 Which of these is least likely to act as a Lewis base? **[NEET 2013]**

(a) CO (b) F^-
(c) BF_3 (d) PF_3

Ans. *(c)*

Electron rich species are called **Lewis base**. Among the given, BF_3 is an electron deficient species, so have a capacity of electron accepting instead of donating. That's why it is least likely to act as a Lewis base. It is a Lewis acid.

12 Which of the following is electron deficient? **[NEET 2013]**

(a) $(CH_3)_2$ (b) $(SiH_3)_2$
(c) $(BH_3)_2$ (d) PH_3

Ans. *(c)*

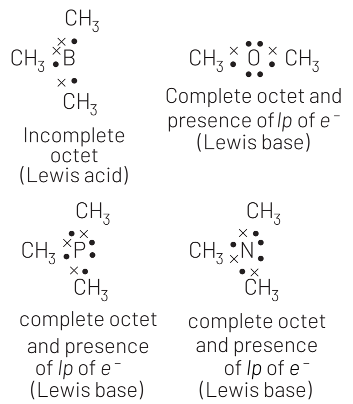
Boron is an element of 13 group and contains three electrons in its valence shell. When its compound BH_3 dimerises, each boron atom carry only 6 electrons that is their octet is incomplete. Hence, $(BH_3)_2$ is an electron deficient compound.

In all other given molecules octet of central atom is complete.

13 Which of the following molecules acts as a Lewis acid? **[CBSE AIPMT 2009]**

(a) $(CH_3)_3B$ (b) $(CH_3)_2O$
(c) $(CH_3)_3P$ (d) $(CH_3)_3N$

Ans. *(a)*



14 Which of the following statements about pH and H^+ ion concentration is incorrect? **[CBSE AIPMT 2000]**

(a) Addition of one drop of concentrated HCl in NH_4OH solution decreases pH of the solution
(b) A solution of the mixture of one equivalent of each of CH_3COOH and NaOH has a pH of 7
(c) pH of pure neutral water is not zero
(d) A cold and concentrated H_2SO_4 has lower H^+ ion concentration than a dilute solution of H_2SO_4

Ans. *(b)*

CH_3COOH is weak acid while NaOH is strong base, so one equivalent of NaOH cannot be neutralised with one equivalent of CH_3COOH. Hence, one equivalent of each does not have pH value 7. As the NaOH is a strong base, the solution will be basic having a pH more than 7.

15 The conjugate acid of NH_2^- is **[CBSE AIPMT 2000]**

(a) N_2H_4 (b) NH_4^+
(c) NH_2OH (d) NH_3

Ans. *(d)*

The species formed after adding a proton to the base is known as **conjugate acid of the base** and the species formed after losing a proton is known as **conjugate base of acid**. So,

$$\underset{\text{Base}}{NH_2^-} + H^+ \rightarrow \underset{\text{Conjugate acid}}{NH_3}$$

16 The strongest conjugate base is **[CBSE AIPMT 1999]**

(a) NO_3^- (b) Cl^-
(c) SO_4^{2-} (d) CH_3COO^-

Ans. *(d)*

Weak acid forms strong conjugate base. In HNO_3, HCl, H_2SO_4 and CH_3COOH, CH_3COOH is weakest acid, so its conjugate base is strongest.

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

17 The hydride ion H^- is stronger base than its hydroxide ion OH^-. Which of the following reactions will occur if sodium hydride (NaH) is dissolved in water? **[CBSE AIPMT 1997]**

(a) $2H^-(aq) + H_2O(l) \longrightarrow H_2O + H_2 + 2e^-$
(b) $H^-(aq) + H_2O(l) \longrightarrow OH^- + H_2$
(c) $H^- + H_2O(l) \longrightarrow$ No reaction
(d) None of the above

Ans. *(b)*

Sodium hydride dissolved in water as

$$NaH + H_2O \longrightarrow NaOH + H_2$$

or $\quad H^-(aq) + H_2O(l) \longrightarrow OH^- + H_2\uparrow$

In the above reaction hydride ion take proton from water molecule and hydrogen gas is evolved.

18 0.1M solution of which one of these substances will be basic? **[CBSE AIPMT 1992]**

(a) Sodium borate
(b) Calcium nitrate
(c) NH_4Cl
(d) Sodium sulphate

Ans. *(a)*

On hydrolysis sodium borate form sodium hydroxide and boric acid, so the solution will show basic character because sodium hydroxide is strong base and boric acid is weak acid. While solution of sodium sulphate is neutral and that of NH_4Cl and calcium nitrate is acidic.

19 Aqueous solution of acetic acid contains **[CBSE AIPMT 1991]**

(a) CH_3COO^- and H^+
(b) CH_3COO^-, H_3O^+ and CH_3COOH
(c) CH_3COO^-, H_3O^+ and H^+
(d) CH_3COOH, CH_3COO^- and H^+

Ans. *(b)*

The aqueous solution of acetic acid ionise as follows:

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

So, the aqueous solution of acetic acid contains CH_3COO^-, H_3O^+ and CH_3COOH.

TOPIC 3

Solubility Product and Common Ion Effect

20 Find out the solubility of $Ni(OH)_2$ in 0.1 M NaOH. Given, that the ionic product of $Ni(OH)_2$ is 2×10^{-15}. **[NEET (Sep.) 2020]**

(a) 2×10^{-8} M (b) 1×10^{-13} M
(c) 1×10^{8} M (d) 2×10^{-13} M

Ans. *(d)*

$$NaOH(aq) \longrightarrow \underset{(0.1M)}{Na^+(aq)} + \underset{(0.1M)}{OH^-(aq)}$$

$$Ni(OH)_2(s) \rightleftharpoons \underset{S'}{Ni^{2+}(aq)} + \underset{0.1+2S'}{2OH^-(aq)}$$

Ionic product $= (S')(0.1 + 2S')^2$ ($\because 2S'$ is very small)

$$2 \times 10^{-15} = S'(0.1)^2$$

$$S' = 2 \times 10^{-13}\ M$$

21 The molar solubility of CaF_2 ($K_{sp} = 5.3 \times 10^{-11}$) in 0.1 M solution of NaF will be **[NEET (Odisha) 2019]**

(a) 5.3×10^{11} mol L^{-1}
(b) 5.3×10^{-8} mol L^{-1}
(c) 5.3×10^{-9} mol L^{-1}
(d) 5.3×10^{-10} mol L^{-1}

Ans. *(c)*

Let the solubility of CaF_2 in 0.1 M NaF is 'S' mol L^{-1}

$$CaF_2(s) \rightleftharpoons \underset{S}{Ca^{2+}(aq)} + \underset{2S}{2F^-(aq)}$$

$$NaF(aq) \rightleftharpoons \underset{0.1\,M}{Na^+} + \underset{0.1M}{F^-(aq)}$$

$[F^-] = 2S + 0.1$

K_{sp} of $CaF_2 = [Ca^{2+}]\,[F^-]^2$

$= [S]\,[2S + 0.1]^2$

$= 5.3 \times 10^{-11} = [S]\,[2S + 0.1]^2$

$\Rightarrow \quad 5.3 \times 10^{-11} = [S]\,[0.1]^2$ [$\because 2S << 0.1$]

$$[S] = \frac{5.3 \times 10^{-11}}{(0.1)^2} = 5.3 \times 10^{-9}\ \text{mol L}^{-1}$$

22 pH of a saturated solution of $Ca(OH)_2$ is 9. The solubility product (K_{sp}) of $Ca(OH)_2$ is **[NEET (National) 2019]**

(a) 0.25×10^{-10} (b) 0.125×10^{-15}
(c) 0.5×10^{-10} (d) 0.5×10^{-15}

Ans. ***(d)***

For the reaction,

$$Ca(OH)_2(s) \rightleftharpoons \underset{S}{Ca^{2+}(aq)} + \underset{2S}{2\bar{O}H(aq)}$$

[where, S = solubility]

$K_{sp} = [Ca^{2+}][OH^-]^2 = S(2S)^2 \quad \ldots$(i)

Given, pH = 9

We know that, pH + pOH = 14

$\therefore \quad$ pOH = 14 − 9 = 5

pOH = $-\log[\bar{O}H]$

$5 = -\log[\bar{O}H]$

or, $[OH^-] = 10^{-5}$

From above equation,

$[\bar{O}H] = 2S = 10^{-5}$

$$\therefore \quad S = \frac{10^{-5}}{2}$$

On substituting the value of 'S' in eqn. (i), we get

$$K_{sp} = 4S^3 = 4\left(\frac{10^{-5}}{2}\right)^3 = 0.5 \times 10^{-15}$$

23 The solubility of $BaSO_4$ in water is 2.42×10^{-3} g L^{-1} at 298 K. The value of its solubility product (K_{sp}) will be

(Given molar mass of $BaSO_4$ = 233 g mol^{-1}) **[NEET 2018]**

(a) 1.08×10^{-14} mol^{2}L^{-2}
(b) 1.08×10^{-12} mol^{2}L^{-2}
(c) 1.08×10^{-10} mol^{2}L^{-2}
(d) 1.08×10^{-8} mol^{2}L^{-2}

Ans. ***(c)***

For a general reaction,

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

Solubility product $(K_{sp}) = [A^{y+}]^x\,[B^{x-}]^y$

For $BaSO_4$ (binary solute giving two ions)

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

$\therefore \quad K_{sp} = [\overset{S}{Ba^{2+}}][\overset{S}{SO_4^{2-}}] = (S)(S) = S^2 \quad \ldots$(i) [where, S = Solubility]

Given, $S = 2.42 \times 10^{-3}$ gL^{-1}

Molar mass of $BaSO_4$ = 233 g mol^{-1}

$\therefore$ Solubility of $BaSO_4$

$$(S) = \frac{2.42 \times 10^{-3}}{233}\ \text{mol L}^{-1}$$

$= 1.04 \times 10^{-5}$ mol L^{-1}

On substituting the value of S in Eq. (i), we get

$K_{sp} = (1.04 \times 10^{-5}\ \text{mol L}^{-1})^2$

$= 1.08 \times 10^{-10}$ mol^2 L^{-2}

24 Concentration of the Ag^+ ions in a saturated solution of $Ag_2C_2O_4$ is 2.2×10^{-4} mol^{-1} solubility product of $Ag_2C_2O_4$ is **[NEET 2017]**

(a) 2.42×10^{-8} (b) 2.66×10^{-12}
(c) 4.5×10^{-11} (d) 5.3×10^{-12}

Ans. ***(d)***

Key concept *For a sparingly soluble salt, if S is the molar solubility,*

$$A_xB_y(s) + H_2O \rightleftharpoons xA^{y+} + yB^{x-}$$

At saturation,

$K[A_xB_y] = [A^{y+}]^x \times [B^{x-}]^y = [xS]^x\,[yS]^y$

or $\quad K_{sp} = x^y \cdot y^y\, S^{x+y}$

Where, the constant K_{sp} is called solubility product.

$$Ag_2C_2O_4(s) \rightleftharpoons \underset{2S}{2Ag^+} + \underset{S}{C_2O_4^{2-}}$$

$K_{sp} = [Ag^+]^2\,[C_2O_4^{2-}] = [2S]^2\,[S]$

Given, $2S = 2.2 \times 10^{-4}$ or $S = 1.1 \times 10^{-4}$ M

$\therefore \quad K_{sp} = [2.2 \times 10^{-4}]^2\,[1.1 \times 10^{-4}]$

$= 5.3 \times 10^{-12}$

25 The solubility of AgCl(s) with solubility product 1.6×10^{-10} in 0.1 M NaCl solution would be **[NEET 2016, Phase II]**

(a) 1.26×10^{-5} M (b) 1.6×10^{-9} M
(c) 1.6×10^{-11} M (d) zero

Ans. ***(b)***

Key Idea *As solubility of* AgCl*(s) is asked in* 0.1 M NaCl *solution, so in the calculation, solubility of* Cl^- *(from* NaCl*) must be added to the solubility of* Cl^- *(from* AgCl*).*

Let s be the solubility of Ag^+ *and* Cl^- *in* AgCl *before the addition of* NaCl.

	$NaCl(aq)$	$\longrightarrow$	$Na^+(aq)$	+	$Cl^-(aq)$
	0.1 M		0		0
	0		0.1M		0.1+s

$$AgCl(s) \rightleftharpoons \underset{s}{Ag^+(aq)} + \underset{s+0.1}{Cl^-(aq)}$$

Given, $\quad K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-]$

or $\quad 1.6 \times 10^{-10} = s(0.1 + s) = 0.1s + s^2$

$\because K_{sp}$ is small, so s is very less in comparison with 0.1. Hence, s^2 can be neglected.

Thus, $1.6 \times 10^{-10} = 0.1s$

or $\quad s = 1.6 \times 10^{-9}$ M

26 MY and NY_3, two nearly insoluble salts, have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be true in regard to MY and NY_3? **[NEET 2016, Phase I]**

(a) The molar solubility of MY in water is less than that of NY_3.
(b) The salts MY and NY_3 are more soluble in 0.5M KY than in pure water
(c) The addition of the salt of KY to solution of MY and NY_3 will have no effect on their solubilities
(d) The molar solubilities of MY and NY_3 in water are identical.

Ans. ***(a)***

For MY, $\quad \underset{0}{MY} \rightleftharpoons \underset{S}{M^+} + \underset{S}{Y^-}$

where, s = solubility and K_{sp} = solubility product.

$\therefore \quad K_{sp} = [M^+][Y^-] = S^2$

$$S = \sqrt{K_{sp}} = \sqrt{6.2 \times 10^{-13}} = 7.874 \times 10^{-7}$$

Similarly, for NY_3,

$$\underset{0}{NY_3} \rightleftharpoons \underset{S}{N^+} + \underset{3S}{3Y^-}$$

$\therefore \quad K_{sp} = [N^+]\,[Y^-]^3 = s \times (3s)^3$

$K_{sp} = 27S^4$

$$\therefore \quad s = \sqrt[4]{\frac{K_{sp}}{27}} = \sqrt[4]{\frac{6.2 \times 10^{-13}}{27}} = 3.89 \times 10^{-4}$$

Therefore, molar solubility of MY in water is less than that of NY_3.

27 The K_{sp} of Ag_2CrO_4, AgCl, AgBr and AgI are respectively, 1.1×10^{-12}, 1.8×10^{-10}, 5.0×10^{-13}, 8.3×10^{-17}. Which one of the following salts will precipitate last if $AgNO_3$ solution is added to the solution containing equal moles of NaCl, NaBr, NaI and Na_2CrO_4? **[CBSE AIPMT 2015]**

(a) AgI (b) AgCl
(c) AgBr (d) Ag_2CrO_4

Ans. *(d)*

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

Solubility product

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

$K_{sp} = (1.1 \times 10^{-12})$ (given)

$S = \sqrt[3]{\frac{K_{sp}}{4}} = 0.65 \times 10^{-4}$

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

$K_{sp} = S \times S \quad (K_{sp} = 1.8 \times 10^{-10})$

$S = \sqrt{K_{sp}} = 1.34 \times 10^{-5}$

$AgBr \rightleftharpoons Ag^+ + Br^-$

$K_{sp} = S \times S \quad (K_{sp} = 5 \times 10^{-13})$

$S = \sqrt{K_{sp}} = 0.71 \times 10^{-6}$

$AgI \rightleftharpoons Ag^+ + I^-$

$K_{sp} = S \times S \quad (K_{sp} = 8.3 \times 10^{-17})$

$S = \sqrt{K_{sp}} = 0.9 \times 10^{-8}$

$\because$ Solubility of Ag_2CrO_4 is highest.

So, it will precipitate last.

28 H_2S gas when passed through a solution of cations containing HCl precipitates the cations of second group in qualitative analysis but not those belonging to the fourth group. It is because **[CBSE AIPMT 2005]**

(a) presence of HCl decreases the sulphide ion concentration

(b) presence of HCl increases the sulphide ion concentration

(c) solubility product of group II sulphides is more than that of group IV sulphides

(d) sulphides of group IV cations are unstable in HCl

Ans. *(a)*

In qualitative analysis of cations of second group H_2S gas is passed in presence of HCl, therefore due to common ion effect, lower concentration of sulphide ions is obtained which is sufficient for the precipitation of second group cations in the form of their sulphides due to lower value of their solubility product (K_{sp}). Here, fourth group cations are not precipitated because it require more sulphide ions for exceeding their ionic product to their solubility products which is not obtained here due to common ion effect.

29 The solubility product of a sparingly soluble salt AX_2 is 3.2×10^{-11}. Its solubility (in mol/L) is **[CBSE AIPMT 2004]**

(a) 5.6×10^{-6} (b) 3.1×10^{-4}

(c) 2×10^{-4} (d) 4×10^{-4}

Ans. *(c)*

AX_2 is ionised as follows

$$\underset{S\ \text{mol L}^{-1}}{AX_2} \rightleftharpoons \underset{S}{A^{2+}} + \underset{2S}{2X^-}$$

Solubility product of AX_2,

$K_{sp} = [A^{2+}][X^-]^2$

$= S \times (2S)^2 = 4S^3$

$\because \quad K_{sp}$ of $AX_2 = 3.2 \times 10^{-11}$

$\therefore \quad 3.2 \times 10^{-11} = 4S^3$

$S^3 = 0.8 \times 10^{-11}$

$= 8 \times 10^{-12}$

Solubility $= 2 \times 10^{-4}$ mol/L

30 The solubility product of AgI at 25°C is 1.0×10^{-16} mol^2 L^{-2}. The solubility of AgI in 10^{-4} N solution of KI at 25°C is approximately (in mol L^{-1}) **[CBSE AIPMT 2003]**

(a) 1.0×10^{-10}

(b) 1.0×10^{-8}

(c) 1.0×10^{-16}

(d) 1.0×10^{-12}

Ans. *(d)*

$$AgI \rightarrow Ag^+ + I^-$$

For binary electrolyte

$K_{sp} = S^2$

where, S = solubility in mol/L

$1.0 \times 10^{-16} = S^2$

or $\quad S = 1 \times 10^{-8}$ mol/L

Normality of KI solutiuon $= 10^{-4}$ N

Here change is one

$\therefore \quad M = 10^{-4}$ M $\quad [n = 1]$

or S for KI solution $= 10^{-4}$ M

Solubility of AgI in KI solution

$= 1 \times 10^{-8} \times 10^{-4}$

$= 1 \times 10^{-12}$ mol/L

31 Solubility of MX_2 type electrolytes is 0.5×10^{-4} mol/L, then find out K_{sp} of electrolytes. **[CBSE AIPMT 2002]**

(a) 5×10^{-12} (b) 25×10^{-10}

(c) 1×10^{-13} (d) 5×10^{-13}

Ans. *(d)*

$$\underset{\text{Solubility } 0.5 \times 10^{-4}\text{M}}{MX_2} \rightarrow \underset{0.5 \times 10^{-4}\text{M}}{M^{2+}} + \underset{2 \times 0.5 \times 10^{-4}\text{M}}{2X^-}$$

(on 100% ionisation)

$\therefore K_{sp}$ of $MX_2 = [M^{2+}][X^-]^2$

$= (0.5 \times 10^{-4})(1.0 \times 10^{-4})^2$

$= 0.5 \times 10^{-12}$

$= 5 \times 10^{-13} [M]^3$

32 Solubility of a M_2S type salt is 3.5×10^{-6}, then find out its solubility product. **[CBSE AIPMT 2001]**

(a) 1.7×10^{-6} (b) 1.7×10^{-16}

(c) 1.7×10^{-18} (d) 1.7×10^{-12}

Ans. *(b)*

Solubility of M_2S salt is 3.5×10^{-6} M

$$\underset{3.5 \times 10^{-6}\text{M}}{M_2S} \rightleftharpoons \underset{2 \times 3.5 \times 10^{-6}\text{M}}{2M^+} + \underset{3.5 \times 10^{-6}\text{M}}{S^{2-}}$$

(on 100% ionisation)

$\therefore K_{sp}$ (solubility product of M_2S)

$= [M^+]^2 [S^{2-}]$

$= (7.0 \times 10^{-6})^2 (3.5 \times 10^{-6})$

$= 171.5 \times 10^{-18}$

$= 1.71 \times 10^{-16} [M]^3$

33 The solubility of a saturated solution of calcium fluoride is 2×10^{-4} mol/L. Its solubility product is **[CBSE AIPMT 1999]**

(a) 12×10^{-2} (b) 14×10^{-4}

(c) 22×10^{-11} (d) 32×10^{-12}

Ans. *(d)*

$$\underset{2 \times 10^{-4}\text{M}}{CaF_2} \rightleftharpoons \underset{2 \times 10^{-4}\text{M}}{Ca^{2+}} + \underset{2 \times 2 \times 10^{-4}\text{M}}{2F^-}$$

K_{sp} of $CaF_2 = [Ca^{2+}][F^-]^2$

$= [2 \times 10^{-4}][4 \times 10^{-4}]^2$

$= 32 \times 10^{-12}$ (mol/L)^2

34 Which of the following is most soluble? **[CBSE AIPMT 1994]**

(a) Bi_2S_3 ($K_{sp} = 1 \times 10^{-70}$)

(b) MnS ($K_{sp} = 7 \times 10^{-16}$)

(c) CuS ($K_{sp} = 8 \times 10^{-37}$)

(d) Ag_2S ($K_{sp} = 6 \times 10^{-51}$)

Ans. *(b)*

Higher the value of solubility product, higher is its solubility. In all these compounds the MnS is most soluble because its solubility product is maximum.

35 In which of the following the solubility of AgCl will be minimum? **[CBSE AIPMT 1993]**

(a) 0.1 M $NaNO_3$

(b) Water

(c) 0.1 M NaCl

(d) 0.1 M NaBr

Ans. *(c)*

In 0.1 M NaCl, the solubility of AgCl is minimum due to the phenomenon of common ion effect.

TOPIC 4
pH, Buffer and Indicator

36 The pK_b of dimethyl amine and pK_a of acetic acid are 3.27 and 4.77 respectively at T(K). The correct option for the pH of dimethyl ammonium acetate solution is **[NEET 2021]**

(a) 8.50 (b) 5.50 (c) 7.75 (d) 6.25

Ans. *(c)*

Dimethyl ammonium acetate $[CH_3COONH_2(CH_3)_2]$ is a salt of weak acid (CH_3COOH) and weak base $[(CH_3)_2NH]$. pH of dimethyl ammonium acetate salt solution can be calculated using formula :

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

pK_a of acetic acid = 4.77

pK_b of dimethyl amine = 3.27

$$pH = 7 + \frac{1}{2}(4.77 - 3.27)$$

$$pH = 7 + \frac{1}{2} \times 1.50$$

$$\Rightarrow \quad pH = 7 + 0.75$$

$$pH = 7.75$$

37 The pH of 0.01 M NaOH (aq) solution will be **[NEET (Odisha) 2019]**

(a) 7.01 (b) 2

(c) 12 (d) 9

Ans. *(c)*

NaOH is a strong base, thus

$$[OH^-] = 0.01 M = 10^{-2} \text{ M}$$

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

$$= -\log(10^{-2}) = 2$$

We know that, pH + pOH = 14

$\therefore \quad pH = 14 - 2 = 12$

Thus, option (c) is correct.

38 Which will make basic buffer? **[NEET (National) 2019]**

(a) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH

(b) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH_4OH

(c) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH

(d) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH

Ans.

Key idea *A buffer solution having pH more than 7 is known as basic buffer. It is obtained by mixing weak base and its salt with strong acid in a fixed proportion.*

Let us consider all the options,

(a) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

	CH_3COOH	NaOH	CH_3COONa
Initial conc.	100 mL × 0.1 M = 10 mmol	100 mL × 0.1 M = 10 mmol	0 mmol
Final conc.	0	0	10 mmol

It is not basic buffer because hydrolysis of salt takes place and final solution contains salt of weak acid with strong base only.

Hence, option (a) is incorrect.

(b) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH_4OH

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

	HCl	NH_4OH	NH_4Cl
Initial conc.	100 mL × 0.1 M HCl = 10 mmol	200 mL × 0.1 M = 20 mmol	0 mmol
Final conc.	0	10 mmol	10 mmol

It is basic buffer because final solution contains weak base and its salt with strong acid. Hence, option (b) is correct.

(c) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

	HCl	NaOH	NaCl
Initial conc.	100 mL × 0.1 M = 10 mmol	100 mL × 0.1 M = 10 mmol	0 mmol
Final conc.	0	0	10 mmol

It is a neutral solution. Hence, option (c) is incorrect.

(d) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

	CH_3COOH	NaOH	CH_3COONa
Initial conc.	25 mL × 0.1 M = 2.5 mmol	50 mL × 0.1 M = 5 mmol	0 mmol
Final conc.	0	2.5 mol	2.5 mmol

It is basic solution. Hence, option (d) is incorrect.

39 Following solutions were prepared by mixing different volumes of NaOH and HCl of different concentrations :

$$\text{I. } 60 \text{ mL } \frac{M}{10} \text{HCl} + 40 \text{ mL } \frac{M}{10} \text{NaOH}$$

$$\text{II. } 55 \text{ mL } \frac{M}{10} \text{HCl} + 45 \text{ mL } \frac{M}{10} \text{NaOH}$$

$$\text{III. } 75 \text{ mL } \frac{M}{5} \text{HCl} + 25 \text{ mL } \frac{M}{5} \text{NaOH}$$

$$\text{IV. } 100 \text{ mL } \frac{M}{10} \text{HCl} + 100 \text{ mL } \frac{M}{10} \text{NaOH}$$

pH of which one of them will be equal to 1? **[NEET 2018]**

(a) IV (b) I (c) II (d) III

Ans.

$$75 \text{ mL } \frac{M}{5} \text{HCl} + 25 \text{ mL } \frac{M}{5} \text{NaOH}$$

Milliequivalent of HCl

$$= 75 \text{ mL of } \frac{M}{5} \text{HCl} = \frac{1}{5} \times 75 = 15$$

Milliequivalent of NaOH

$$= 25 \text{ mL of } \frac{M}{5} \text{NaOH}$$

$$= \frac{1}{5} \times 25 = 5$$

$\therefore$ Milliequivalent of HCl left unused

$$= 15 - 5 = 10$$

Volume of solution = 100 mL

$\therefore$ Molarity of $[H^+]$ in the resulting mixture

$$= \frac{10}{100} = \frac{1}{10}$$

$$\therefore \quad pH = \log \frac{1}{[H^+]} = \log(10) = 1$$

40 What is the pH of the resulting solution when equal volumes of 0.1 M NaOH and 0.01 M HCl are mixed? **[CBSE AIPMT 2015]**

(a) 12.65 (b) 2.0 (c) 7.0 (d) 1.04

Ans. *(a)*

Key Concept *When equal volumes of acid and base are mixed, then resulting solution become alkaline if concentration of base is taken high.*

Let normality of the solution after mixing 0.1 M NaOH and 0.01 M HCl is N.

$$\therefore \quad N_1V_1 - N_2V_2 = NV$$

$$\text{or} \quad 0.1 \times 1 - 0.01 \times 1 = N \times 2$$

Since, normality of NaOH is more than that of HCl.

Hence, the resulting solution is alkaline.

$$\text{or} \quad [\bar{O}H] = N = \frac{0.09}{2} = 0.045 \text{ N}$$

$$\text{or} \quad pOH = -\log(0.045) = 1.35$$

$$\therefore \quad pH = 14 - pOH = 14 - 1.35 = 12.65$$

41 Which one of the following pairs of solution is not an acidic buffer? **[CBSE AIPMT 2015]**

(a) $HClO_4$ and $NaClO_4$

(b) CH_3COOH and CH_3COONa

(c) H_2CO_3 and Na_2CO_3

(d) H_3PO_4 and Na_3PO_4

Ans. *(a)*

Strong acid with its salt cannot form buffer solution. Hence, $HClO_4$ and $NaClO_4$ is not an acidic buffer.

42 pH of a saturated solution of $Ba(OH)_2$ is 12. The value of solubility product K_{sp} of $Ba(OH)_2$ is **[CBSE AIPMT 2012]**

(a) 3.3×10^{-7} (b) 5.0×10^{-7}
(c) 4.0×10^{-6} (d) 5.0×10^{-6}

Ans. *(b)*

Given, pH of $Ba(OH)_2 = 12$

$\therefore \quad pOH = 14 - pH = 14 - 12 = 2$

We know that,

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

$2 = -\log[OH^-]$

$[OH^-] = \text{antilog}(-2)$

$[OH^-] = 1 \times 10^{-2}$

$Ba(OH)_2$ dissolves in water as

$$\underset{S \text{ mol L}^{-1}}{Ba(OH)_2(s)} \rightleftharpoons \underset{S}{Ba^{2+}} + \underset{2S}{2OH^-}$$

$\therefore \quad [OH^-] = 2S = 1 \times 10^{-2}$

$$S = \frac{[OH^-]}{2} \qquad [Ba^{2+} = S]$$

$$[Ba^{2+}] = \frac{[OH^-]}{2} = \frac{1 \times 10^{-2}}{2}$$

$$K_{sp} = [Ba^{2+}][OH^-]^2 = \left(\frac{1 \times 10^{-2}}{2}\right)(1 \times 10^{-2})^2$$

$$= 0.5 \times 10^{-6} = 5 \times 10^{-7}$$

43 Buffer solutions have constant acidity and alkalinity because **[CBSE AIPMT 2012]**

(a) these give unionised acid or base on reaction with added acid or alkali
(b) acids and alkalies in these solutions are shielded from attack by other ions
(c) they have large excess of H^+ or OH^- ions
(d) they have fixed value of pH

Ans. *(a)*

If small amount of an acid or alkali is added to a buffer solution, it converts them into unionised acid or base. Thus, its pH remains unaffected or in other words its acidity/alkalinity remains constant. e.g.

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

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

If acid is added, it reacts with A^- to form undissociated H A. Similarly, if base/alkali is added, OH^- combines with H A to give H_2O and A^- and thus, maintains the acidity/ alkalinity of buffer solution.

44 A buffer solution is prepared in which the concentration of NH_3 is 0.30 M and the concentration of NH_4^+ is 0.20 M. If the equilibrium constant, K_b for NH_3 equals 1.8×10^{-5}, what is the pH of this solution? ($\log 2.7 = 0.43$) **[CBSE AIPMT 2011]**

(a) 9.43 (b) 11.72 (c) 8.73 (d) 9.08

Ans. *(a)*

$$pOH = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$= -\log K_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$= -\log 1.8 \times 10^{-5} + \log\frac{0.20}{0.30}$$

$$= 5 - 0.25 + (-0.176)$$

$$= 4.75 - 0.176 = 4.57$$

$\therefore \quad pH = 14 - 4.57 = 9.43$

45 What is $[H^+]$ in mol/L of a solution that is 0.20 M in CH_3COONa and 0.10 M in CH_3COOH? (K_a for $CH_3COOH = 1.8 \times 10^{-5}$) **[CBSE AIPMT 2010]**

(a) 3.5×10^{-4} (b) 1.1×10^{-5}
(c) 1.8×10^{-5} (d) 9.0×10^{-6}

Ans. *(d)*

Key Idea CH_3COOH (weak acid) and CH_3COONa (conjugated salt) form acidic buffer and for acidic buffer,

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

and $\quad [H^+] = -\text{antilog pH}$

$$pH = -\log K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$[\because pK_a = -\log K_a]$$

$$= -\log(1.8 \times 10^{-5}) + \log\frac{(0.20)}{(0.10)}$$

$$= 4.74 + \log 2$$

$$= 4.74 + 0.3010 = 5.041$$

Now, $\quad [H^+] = \text{antilog}(-5.045)$

$$= 9.0 \times 10^{-6} \text{ mol/L}$$

46 If pH of a saturated solution of $Ba(OH)_2$ is 12, the value of its K_{sp} is **[CBSE AIPMT 2010]**

(a) 4.00×10^{-6} M^3 (b) 4.00×10^{-7} M^3
(c) 5.00×10^{-7} M^3 (d) 5.00×10^{-6} M^3

Ans. *(d)*

Given, pH of $Ba(OH)_2 = 12$

So, $\quad pOH = 2$

$\therefore \quad [H^+] = [1 \times 10^{-12}]$

$$K_w = (H^+)(OH^-)$$

$$K_w = 1 \times 10^{-14}$$

$$OH^- = \frac{K_\omega}{H^+}$$

and $\quad [OH^-] = \dfrac{1 \times 10^{-14}}{1 \times 10^{-12}}$

$$[\because [H^+][OH^-] = 1 \times 10^{-14}]$$

$$= 1 \times 10^{-2} \text{ mol/L}$$

$$Ba(OH)_2 \longrightarrow \underset{S}{Ba^{2+}} + \underset{2S}{2\,OH^-}$$

$$K_{sp} = [Ba^{2+}][OH^-]^2 = [S][2S]^2$$

$$= \left[\frac{1 \times 10^{-2}}{2}\right](1 \times 10^{-2})^2$$

$$= 0.5 \times 10^{-6} = 5.0 \times 10^{-6} \text{ M}^3$$

47 In a buffer solution containing equal concentration of B^- and HB, the K_b for B^- is 10^{-10}. The pH of buffer solution is **[CBSE AIPMT 2010]**

(a) 10 (b) 7
(c) 6 (d) 4

Ans. *(d)*

Key Idea *(i) For basic buffer,*

$$pOH = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

(ii) pH + pOH = 14

Given, $\quad K_b = 1 \times 10^{-10}$, [salt] = [base]

$$pOH = -\log K_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$\therefore \quad pOH = -\log(1 \times 10^{-10}) + \log 1 = 10$

$pH + pOH = 14$

$[\because$ concentration of $[B^-] = [HB]$

$pH = 14 - 10 = 4$

48 What is the $[OH^-]$ in the final solution prepared by mixing 20.0 mL of 0.050 M HCl with 30.0 mL of 0.10 M $Ba(OH)_2$? **[CBSE AIPMT 2009]**

(a) 0.10 M (b) 0.40 M
(c) 0.0050 M (d) 0.12 M

Ans. *(a)*

Number of milliequivalents of HCl

$= 20 \times 0.050 \times 1 = 1$

Number of milliequivalents of $Ba(OH)_2$

$= 2 \times 30 \times 0.10 = 6$

$[OH^-]$ of final solution

$$= \frac{\text{Milliequivalents of } Ba(OH)_2 - \text{milliequivalents of HCl}}{\text{Total volume}} = \frac{6-1}{50}$$

$= 0.1$ M

49 Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture? **[CBSE AIPMT 2008]**

(a) 1.11×10^{-4} M (b) 3.7×10^{-4} M
(c) 3.7×10^{-3} M (d) 1.11×10^{-3} M

Ans. *(b)*

Let the volume of each acid = V

pH of first, second and third acids = 3, 4 and 5 respectively

$[H^+]$ of first acid $(M_1) = 1 \times 10^{-3}$

$[\because H^+ = 1 \times 10^{-pH}]$

$[H^+]$ of second acid $(M_2) = 1 \times 10^{-4}$

$[H^+]$ of third acid $(M_3) = 1 \times 10^{-5}$

Total $[H^+]$ concentrated of mixture

$$(M) = \frac{M_1V_1 + M_2V_2 + M_3V_3}{V_1 + V_2 + V_3}$$

$$= \frac{1 \times 10^{-3} \times V + 1 \times 10^{-4} \times V + 1 \times 10^{-5} \times V}{V + V + V}$$

$$= \frac{1 \times 10^{-3} \times V(1 + 0.1 + 0.01)}{3V}$$

$$= \frac{1.11 \times 10^{-3}}{3} = 3.7 \times 10^{-4} \text{ M}$$

50 Calculate the pOH of a solution at 25°C that contains 1×10^{-10} M of hydronium ion. **[CBSE AIPMT 2007]**

(a) 7.00 (b) 4.00
(c) 9.00 (d) 1.00

Ans. *(b)*

$[H_3O^+] = [H^+] = 10^{-10}$

$pH + pOH = 14$ ...(i)

and $pH = -\log [H^+]$

$pH = -\log [10^{-10}]$ ...(ii)

$pH = 10$

from eq. (i) and (ii), we get

$pOH + 10 = 14$

$pOH = 14 - 10 = 4$

51 The hydrogen ion concentration of a 10^{-8} M HCl aqueous solution at 298 K $(K_w = 10^{-14})$ is **[CBSE AIPMT 2006]**

(a) 1.0×10^{-6} M (b) 1.0525×10^{-7} M
(c) 9.525×10^{-8} M (d) 1.0×10^{-8} M

Ans. *(b)*

In aqueous solution of 10^{-8} M HCl, $[H^+]$ ion concentration is based upon the concentration of H^+ ion of 10^{-8} M HCl and concentration of H^+ ion of water.

K_w of $H_2O = 10^{-14} = [H^+][OH^-]$

or $[H^+] = 10^{-7}$ M

(due to its neutral behaviour)

So, in aqueous solution of 10^{-8} M HCl,

$[H^+] = [H^+]$ of HCl + $[H^+]$ of water

$= 10^{-8} + 10^{-7}$

$= 11 \times 10^{-8} \text{ M} \approx 1.10 \times 10^{-7}$ M

52 Which of the following pairs constitutes a buffer? **[CBSE AIPMT 2006]**

(a) HNO_2 and $NaNO_2$
(b) NaOH and NaCl
(c) HNO_3 and NH_4NO_3
(d) HCl and KCl

Ans. *(a)*

A pair constituent with HNO_2 and $NaNO_2$ because HNO_2 is weak acid and $NaNO_2$ is a salt of weak acid (HNO_2) with strong base (NaOH). Hence, it is an example of acidic buffer solution.

53 What is the correct relationship between the pH of isomolar solutions of sodium oxide (pH_1), sodium sulphide (pH_2), sodium selenide (pH_3) and sodium telluride (pH_4)? **[CBSE AIPMT 2005]**

(a) $pH_1 > pH_2 \approx pH_3 > pH_4$
(b) $pH_1 < pH_2 < pH_3 < pH_4$
(c) $pH_1 < pH_2 < pH_3 \approx pH_4$
(d) $pH_1 > pH_2 > pH_3 > pH_4$

Ans. *(d)*

The correct order of pH of isomolar solution of sodium oxide (pH_1), sodium sulphide (pH_2), sodium selenide (pH_3) and sodium telluride (pH_4) is

$pH_1 > pH_2 > pH_3 > pH_4$ because in aqueous solution, they are hydrolysed as follows.

$$Na_2O + 2H_2O \longrightarrow \underset{\text{Base}}{2NaOH} + H_2O$$

$$Na_2S + 2H_2O \longrightarrow \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{H_2S}$$

$$Na_2Se + 2H_2O \longrightarrow \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{H_2Se}$$

$$Na_2Te + 2H_2O \longrightarrow \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{H_2Te}$$

On moving down the group acidic character of oxides increases.

Order of acidic strength

$H_2Te > H_2Se > H_2S > H_2O$

Order of neutralisation of NaOH

$H_2Te > H_2Se > H_2S > H_2O$

Hence, their aqueous solutions have the following order of basic character due to neutralisation of NaOH with H_2O, H_2S, H_2Se and H_2Te.

$Na_2O > Na_2S > Na_2Se > Na_2Te$

($\because$ pH of basic solution is higher than acidic or least basic solution)

54 The rapid change of pH near the stoichiometric point of an acid base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base (In^-) forms of the indicator given by the expression **[CBSE AIPMT 2004]**

(a) $\log \frac{[In^-]}{[HIn]} = pK_{In} - pH$
(b) $\log \frac{[HIn]}{[In^-]} = pK_{In} - pH$
(c) $\log \frac{[HIn]}{[In^-]} = pH - pK_{In}$
(d) $\log \frac{[In^-]}{[HIn]} = pH - pK_{In}$

Ans. *(d)*

Acid indicators are generally weak acid. The dissociation of indicator HIn takes place as follows

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

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

or $[H^+] = K_{In} \cdot \frac{[HIn]}{[In^-]}$ ...(i)

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

From eq. (i) and (ii) we get,

$$\therefore \quad pH = -\log\left(K_{In} \cdot \frac{[HIn]}{[In^-]}\right)$$

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

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

or $\log \frac{[In^-]}{[HIn]} = pH - pK_{In}$

55 Solution of 0.1 N NH_4OH and 0.1 N NH_4Cl has pH 9.25, then find out pK_b of NH_4OH. **[CBSE AIPMT 2002]**

(a) 9.25 (b) 4.75
(c) 3.75 (d) 8.25

Ans. *(b)*

Solution of NH_4OH and NH_4Cl acts as a basic buffer solution. For basic buffer solution

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

$pOH = 14 - pH$
$= 14 - 9.25 = 4.75$
$4.75 = pK_b + \log \frac{0.1}{0.1}$
$pK_b = 4.75$

56 The concentration of $[H^+]$ and concentration of $[OH^-]$ of a 0.1 M aqueous solution of 2% ionised weak monobasic acid is **[CBSE AIPMT 1999]**
[ionic product of water $= 1 \times 10^{-14}$]
(a) 0.02×10^{-3} M and 5×10^{-11} M
(b) 1×10^{-3} M and 3×10^{-11} M
(c) 2×10^{-3} M and 5×10^{-12} M
(d) 3×10^{-2} M and 4×10^{-13} M

Ans. *(c)*

$[H^+]$ in monobasic acid
$=$ molarity $\times$ degree of ionisation
$= 0.1 \times \frac{2}{100}$
$= 2 \times 10^{-3}$ M
ionisation constant of water
$K_w = (H^+)(OH^-)$
$[OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14}}{2 \times 10^{-3}}$
$= 5 \times 10^{-12}$ M

57 A physician wishes to prepare a buffer solution at pH = 3.58 that efficiently resist changes in pH yet contains only small concentration of the buffering agents. Which one of the following weak acid together with its sodium salt would be best to use? **[CBSE AIPMT 1997]**
(a) *m*-chlorobenzoic acid ($pK_a = 3.98$)
(b) *p*-chlorocinnamic acid ($pK_a = 4.41$)
(c) 2, 5-dihydroxy benzoic acid ($pK_a = 2.97$)
(d) Acetoacetic acid ($pK_a = 3.58$)

Ans. *(d)*

By the use of Henderson's equation
$$pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$$
When, $[salt] = [acid]$
$\therefore$ $pH = pK_a$
$\because pK_a = 3.58$, thus at this state
$pH = 3.58$
So, acetoacetic acid ($pK_a = 3.58$) is best to use.

58 The pH value of blood does not change appreciably by a small addition of an acid or base, because the blood **[CBSE AIPMT 1995]**
(a) is a body fluid
(b) can be easily coagulated
(c) contains iron as a part of the molecule
(d) contains serum protein that acts as buffer

Ans. *(d)*

Blood is an example of buffer solution, which contains serum protein, so its pH does not change appreciably by adding small amount of an acid or a base to it.

59 The pH value of a 10 M solution of HCl is **[CBSE AIPMT 1995]**
(a) less than 0 (b) equal to 0
(c) equal to 1 (d) equal to 2

Ans. *(a)*

$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$
$[S = \sqrt{K_{sp}}]$
$[HCl] = 10$ M
$\Rightarrow [H^+] = 10$ mol / L
$pH = -\log [H^+] = -\log 10$
$= -1$, so the pH is less than zero.

TOPIC 5
Hydrolysis of Salts

60 Which among the following salt solutions is basic in nature? **[NEET (Oct.) 2020]**
(a) Ammonium chloride
(b) Ammonium sulphate
(c) Ammonium nitrate
(d) Sodium acetate

Ans. *(d)*

Nature of a salt solution depends on the nature of constituent acid and base whether they are strong or weak.
(a) NH_4Cl is made of $[NH_4OH(WB) + HCl(SA)] \rightarrow$ Acidic solution.
(b) $(NH_4)_2SO_4$ is made of $[NH_4OH(WB) + H_2SO_4(SA)] \rightarrow$ Acidic solution.
(c) NH_4NO_3 is made of $[NH_4OH(WB) + CH_3COOH(WA)] \rightarrow$ Basic solution.
(d) CH_3COONa is made of $[NaOH(SB) + CH_3COOH(WA)] \rightarrow$ Basic solution

[Where $\Rightarrow$ WB = Weak base, SB = Strong base WA = Weak acid, SA = Strong acid.]
Hence, option (d) is the correct.

61 Which of the following salts will give highest pH in water? **[CBSE AIPMT 2014]**
(a) KCl (b) NaCl
(c) Na_2CO_3 (d) $CuSO_4$

Ans. *(c)*

The highest pH refers to the basic solution containing OH^- ions. Therefore, the basic salt releasing more OH^- ions on hydrolysis will give highest pH in water.
Only the salt of strong base and weak acid would release more OH^- ion on hydrolysis. Among the given salts, Na_2CO_3 corresponds to the basic salt as it is formed by the neutralisation of NaOH [strong base] and H_2CO_3 [weak acid].
$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

62 Equimolar solutions of the following substances were prepared separately. Which one of these will record the highest pH value? **[CBSE AIPMT 2012]**
(a) $BaCl_2$ (b) $AlCl_3$ (c) LiCl (d) $BeCl_2$

Ans. *(a)*

$BaCl_2$ is a salt of strong acid HCl and strong base $Ba(OH)_2$. So, its aqueous solution is neutral with pH 7. All other salts give acidic solution due to cationic hydrolysis, so their pH is less than 7.
Thus, pH value is highest for the solution of $BaCl_2$

63 The ionisation constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is **[CBSE AIPMT 2009]**
(a) 5.65×10^{-10} (b) 6.50×10^{-12}
(c) 5.65×10^{-13} (d) 5.65×10^{-12}

Ans. *(a)*

Given, K_a $(NH_4OH) = 1.77 \times 10^{-5}$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$K_a = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.77 \times 10^{-5} \quad ...(i)$$
Hydrolysis of NH_4Cl takes place as,
$NH_4Cl + H_2O \longrightarrow NH_4OH + HCl$
or $NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$
Hydrolysis constant,

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

or $$K_h = \frac{[NH_4OH][H^+][OH^-]}{[NH_4^+][OH^-]} \quad ...(iii)$$

From Eqs. (i), (ii) and (iii)

$$K_h = \frac{K_w}{K_a} \quad [\because [H^+][OH^-] = K_w]$$

$$= \frac{10^{-14}}{1.77 \times 10^{-5}}$$

$$= 5.65 \times 10^{-10}$$

64 Which has highest pH? **[CBSE AIPMT 2002]**

(a) $CH_3CO^-OK^+$ (b) Na_2CO_3
(c) NH_4Cl (d) $NaNO_3$

Ans. ***(b)***

$$pH = \log \frac{1}{[H^+]}$$

pH is inversely proportional to hydrogen ion concentration. As concentration of H^+ decreases pH increases and *vice-versa*.

Ammonium chloride (NH_4Cl) is a salt of weak base and strong acid. So, its aqueous solution will be acidic as

$$NH_4Cl + H_2O \longrightarrow \underset{\text{Weak base}}{NH_4OH} + \underset{\text{Strong acid}}{HCl}$$

So, pH of NH_4Cl is less than 7.

Sodium nitrate ($NaNO_3$) is the salt of strong acid and strong base. So, its aqueous solution is neutral as

$$NaNO_3 + H_2O \longrightarrow \underset{\text{Strong base}}{NaOH} + \underset{\text{Strong acid}}{HNO_3}$$

So, pH of $NaNO_3$ is 7.

Potassium acetate (CH_3COOK) is a salt of strong base and weak acid. Its aqueous solution will be basic and pH value will be greater than $7 \approx 8.8$

$$CH_3COO^-K^+ + H_2O \longrightarrow \underset{\text{Weak acid}}{CH_3COOH} + \underset{\text{Strong base}}{KOH}$$

Sodium carbonate (Na_2CO_3) is a salt of strong base and weak acid. Its aqueous solution is also basic and its pH value will be more than 10,

i.e. highest among them.

$$Na_2CO_3 + H_2O \longrightarrow \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{H_2CO_3}$$

65 The compound whose aqueous solution has the highest pH is **[CBSE AIPMT 1988]**

(a) NaCl (b) $NaHCO_3$
(c) Na_2CO_3 (d) NH_4Cl

Ans. ***(c)***

The hydrolysis of NaCl gives neutral solution because it is salt of strong acid and strong base and hence, its pH is 7. NH_4Cl is salt of weak base and strong acid, so its pH is less than 7. $NaHCO_3$ is also acidic whereas Na_2CO_3 is salt of strong base and weak acid, so its pH is more than 7.